Electrostatic levitation studies of supercooled liquids and metastable solid phases

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Electrostatic levitation studies of supercooled liquids and metastable solid phases

by

Gustav Errol Rustan

A dissertation submitted to the graduate faculty
in partial fulfillment of the requirements for the degree of

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Program of Study Committee:
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Iowa State University
Ames, Iowa
2014

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DEDICATION

I would like to dedicate this work to my girlfriend, Ellen, and our families. Thank you all for your support and encouragement throughout the course of my graduate work.
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ABSTRACT

A new laboratory has been developed at Iowa State University (ISU) to be used for the study of high temperature liquids and solids, with particular focus on the supercooling of liquids and their metastable solidification products. This new laboratory employs the electrostatic levitation (ESL) technique, in which a charged sample is suspended between a set of electrodes to achieve non-contact handling. Owing to the elimination of a crucible, high temperature processing of samples can be achieved with reduced levels of contamination and heterogeneous nucleation. Because of the reduction in heterogeneous nucleation, samples can be supercooled well below their equilibrium melting temperature, opening the door to a wide range of measurements on supercooled liquids. Measurements methods have been implemented for the characterization of thermophysical properties such as: volume/density, ratio of specific heat to total hemispherical emissivity, surface tension, viscosity, electrical resistivity, and magnetic susceptibility. For measurements of electrical resistivity and magnetic susceptibility, a new method has been developed at ISU based on the tunnel diode oscillator (TDO) technique. The TDO technique uses the negative differential resistance of a tunnel diode to drive an LC tank circuit into self-sustained oscillation at the resonant LC frequency. The LC tank is inductively coupled to the samples under study, and changes in the electrical resistivity or magnetic susceptibility of the sample are manifested as changes in the resonant frequency. By measuring the frequency shifts of the TDO, insights can be made into changes in the material’s electrical and magnetic properties. This method has been validated by performing resistivity measurements on a sample of high purity Zr, and by performing measurements on the ferromagnetic transition in a low-carbon steel ball bearing. In addition to the development of the laboratory and its supporting instrumentation, an effort has been carried out to study the metastable phase formation in an Fe$_{83}$B$_{17}$ near eutectic alloy. Initial supercooling measurements using the ISU-ESL identified the formation of three metastable phases: a precipitate phase that shows stable coexistence
with the deeply supercooled liquid, and two distinct bulk solidification phases. To identify
the structure of the metastable phases, the Washington University Beamline ESL (WU-BESL)
has been used to perform in-situ high energy x-ray diffraction measurements of the metastable
phases. Based on the x-ray results, the precipitate phase has been identified as bcc-Fe, and
the more commonly occurring bulk solidification product has been found to be a two-phase
mixture of Fe$_{23}$B$_6$ plus fcc-Fe, which appears, upon cooling, to transform into a three phase
mixture of Fe$_{23}$B$_6$, bcc-Fe, and an as-yet unidentified phase, with the transformation occurring
at approximately the expected fcc-to-bcc transformation temperature of pure Fe. To further
characterize the multi-phase metastable alloy, the ISU-ESL has been used to perform measure-
ments of volume thermal expansion via the videographic technique, as well as RF susceptibility
via the TDO technique. The results of the thermal expansion and susceptibility data have
been found to be sensitive indicators of additional structural changes that may be occurring in
the metastable solid at temperatures below 1000 K, and the susceptibility data has revealed
that three distinct ferromagnetic phase transitions take place within the multi-phase mixture.
Based on these results, it has been hypothesized that there may be an additional transforma-
tion taking place that leads to the formation of either bct- or $\alpha$-Fe$_3$B in addition to the Fe$_{23}$B$_6$
phase, although further work is required to test this hypothesis.
CHAPTER 1. INTRODUCTION

1.1 Metastable Materials

Generally speaking, whether or not a material or a mechanical system is able to undergo a change in its properties is determined by the energy of the system. Under equilibrium conditions, for which the properties of a system are not changing, a system will tend towards a state that results in a minimization of its potential energy. A state characterized as having the minimum amount of potential energy possible is referred to as being in stable equilibrium because the system, on its own, will be unable to undergo any further changes in its description. A common example of this involves gravity: the gravitation potential energy of an object near the surface of the Earth is directly proportional to its height above the ground and, therefore, objects will tend fall or otherwise reduce their height in order to reduce their gravitation potential energy. This is why a quarter ($0.25), when placed on the cover of a steeply inclined book, will tend to slide down the cover and fall to whatever surface is below: the quarter is seeking to reduce its gravitation potential energy in order to achieve a state of stable equilibrium. However, if the incline of the book is shallow, it may be found that the quarter does not slide down the cover. What has happened in this situation is that the friction between the quarter and book has resulted in a kinetic barrier to motion and, as a result, the position of the quarter has been locked in a state of high potential energy: the quarter still wants to slide down the book, but the friction is preventing that from happening. In situations such as this, when an object or a system becomes kinetically locked in a state of non-minimal potential energy, it is referred to as being in a state of metastable equilibrium: the system is not undergoing any change in its description, so it is described as being in equilibrium, but it has not fully minimized its potential energy and is therefore only “sort of” stable, or metastable. If a system
in a metastable state is perturbed or agitated, it may become freed from the kinetic barrier, allowing the system to achieve a more stable state. In the case of the quarter, this can be accomplished by tapping on the cover of the book near the quarter: the tapping disrupts the frictional barrier, and the quarter is able to slide down the cover to achieve a state of lower gravitational potential energy. With enough tapping, the quarter will slide all the way down the book, at which point it achieves a state of stable equilibrium and no further motion takes place.

Just like the quarter, the atoms that make up materials tend to arrange themselves in such a way so as to achieve the lowest potential energy possible and, just like the quarter, it is possible for the atoms to become kinetically locked into arrangements of non-minimal potential energy\(^1\). The formation of metastable materials is a common phenomena, with many such materials playing an important role in the modern world: steels, window glass, and diamonds are all examples of commonly encountered materials whose atoms are arranged in a metastable configuration. Within the field of metallurgy, probably the most heavily studied example of metastability is within the iron-carbon (Fe-C) binary system\(^2\), which forms the basis of some of the most widely used steels: Fe-C mixtures with 1.5% or less of the atoms being carbon are referred to as “low carbon” or “mild” steel, while mixtures containing 12–18% carbon are known as cast iron [2]. Under stable equilibrium conditions, Fe-C mixtures do not form any stable compounds (a.k.a. intermetallic phases). At room temperature, any mixture of iron and carbon would prefer separate itself into microscopic regions of pure carbon (graphite) and pure iron, with only a very small amount solubility existing between the different types of atoms [1]. Despite this fact, multiple iron-carbide phases can be found in real-world steel alloys, most notably Fe\(_3\)C (a.k.a. cementite). In addition to the metastable intermetallic phases, iron-carbon mixtures can also be rapidly cooled to produce supersaturated mixtures of carbon dispersed within an iron crystal structure, resulting in a metastable mixture known as

\(^{1}\)To be clear, the relevant energy when discussing atoms is not gravitation in nature. Rather, it is caused by the electric and magnetic interactions of the atoms as governed by quantum mechanics.

\(^{2}\)Due to its incredible industrial relevance, the number of experimental and theoretical investigations on the Fe-C system has been described as “virtually unlimited” [1]. As a result, metastability in the Fe-C system has been heavily studied [1], and this binary alloy system is now used as a model system when describing metastable materials in introductory Materials Science courses [2].
martensite. Being able to develop an understanding of why, how and under what conditions these metastable iron-carbide phases form is crucial for controlling the mechanical properties of steels, such as hardness and tensile strength, which makes them useful as structural materials. And this is only one example; Table 1.1 lists a variety of other metastable materials with modern industrial uses.

The study of metastable materials is not limited to solids. When a liquid is cooled down to its melting point, the action of freezing is usually facilitated by the presence of impurities, such as dust or dirt, or by defects in the surface of the container which holds the liquid. Because these impurities are not intrinsic to the liquid, they are collectively known as heterogeneous sites, and when they initiate the freezing process it is known as heterogeneous nucleation (nucleation being the first step in the process). Provided that the number of heterogeneous sites can be significantly reduced, or if their influence on the liquid can be otherwise suppressed, then liquids can be supercooled to temperatures well below their natural freezing points, in which case they exist as metastable liquids. The ability of liquids to supercool, and to resist freezing for extended periods of time, has been known for hundreds of years. For instance, water was first shown to supercool below its natural freezing point by as much as 8 K in 1724 by Fahrenheit [3]; more recent studies [4] have shown that water can be supercooled by as much as 42 K under ambient pressure before homogeneous (intrinsic) nucleation occurs. In contrast to water, the ability of metallic liquids to supercool is a more recent discovery. The first report on the consistent supercooling of metallic liquids was in 1908 by Mendenhall & Ingersoll [5], who observed the effect in droplets (approximately 0.1 mm diameter) of a variety of elemental late transition metals being melted on the surface of a Nernst glower\(^3\). Supercooling by as much as 370 K was observed for platinum \((T_m = 2041 \text{ K})\) and rhodium \((T_m = 2236 \text{ K})\). The intent of their research was simply to determine the melting points of high temperature elements, and so the observation of supercooling was unexpected and quite remarkable considering the depth of supercooling achieved. The first systematic studies on the supercooling, nucleation and solidification in supercooled metallic liquids were carried out by Turnbull & Cech in 1950 [7].

\(^3\)A now obsolete device. It consisted of a ceramic tube which, when heated to high temperatures, was used as a source of infrared radiation [6]. In this particular reference, the glower was simply being used as a high temperature ceramic substrate.
Table 1.1  Examples of industrially important metastable materials.

<table>
<thead>
<tr>
<th>Common name</th>
<th>Notes</th>
<th>Uses</th>
</tr>
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<tbody>
<tr>
<td>Amorphous Silicon</td>
<td>Vapor deposited silicon with dopants</td>
<td>Low power and/or flexible photovoltaics</td>
</tr>
<tr>
<td>Metglas Electrical Steel</td>
<td>Family of glassy alloys consisting of primarily (Fe, Co, Ni)-(B, Si) with additional additives</td>
<td>Transformer cores with lowest available core losses</td>
</tr>
<tr>
<td>Vitreloy</td>
<td>Family of bulk forming glassy alloys consisting of primarily Zr with Be, Cu, Ti and other alloying agents</td>
<td>High end sporting equipment and consumer electronics casings</td>
</tr>
<tr>
<td>Diamond</td>
<td>High pressure allotrope of pure C</td>
<td>Abrasive for other hard materials such as oxides and carbides; high pressure cells; jewelery</td>
</tr>
<tr>
<td>Silicate glass</td>
<td>Can be pure SiO2 or used with additives such as B, Na, Ca, or Al oxides</td>
<td>Combination of extremely high glass formability, optical transparency, chemical resistance, and low thermal expansion result in several applications.</td>
</tr>
<tr>
<td>Iron Nitride</td>
<td>Crystalline Fe\textsubscript{16}N\textsubscript{2}</td>
<td>Currently being researched as a replacement for rare-earth permanent magnets. Has a theoretical magnetic energy product of twice that for Nd\textsubscript{2}Fe\textsubscript{14}B, with the benefit of no rare-earths being used.</td>
</tr>
<tr>
<td>Fe-Pt</td>
<td>Crystalline, 50-50 Mixture of Fe &amp; Pt</td>
<td>Chemically ordered L\textsubscript{10} FePt has large magnetic anisotropy and is being researched for application as magnetic storage media. Metastable fcc FePt (chemically disordered with low magnetic anisotropy) commonly forms instead and is therefore a hindrance.</td>
</tr>
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using the droplet dispersion method, in which samples are made into collections of droplets whose size range from 10–100 μm. By breaking the samples into many small droplets, a large fraction of the droplets can be made free of heterogeneous nucleants which would otherwise limit the achievable supercooling. With this method, it was shown that supercooling was a very general phenomena, being observed in a wide variety of materials (transition metals, post transition metals, metalloids, and non-metals) with melting points ranging from 493–1828 K; the degree of supercooling achieved was typically 15–20 % of the material’s melting point. Since these early studies, a wide variety of methods have been developed to study supercooled liquids and their solidification products, including advanced fluxing methods as well as non-contact methods such levitation systems; details regarding these methods are discussed in Sec. 2.2.

In the extreme limit of supercooling, the solidification of a liquid via crystallization can be avoided altogether. In this scenario, the material solidifies by experiencing a dramatic increase in its viscosity while maintaining the same general atomic structure as in the liquid state. This phenomena, in which the material’s viscosity exceeds $10^{12}$ Pa·s (compared to 1 Pa·s for water and 1–10 Pa·s for typical liquid metal) is known as the glass transition of the material. While silicate based glasses have been produced for thousands of years, the first metallic glass was only produced in 1960. Klement el al. [8] were able to quench a Au$_{75}$Si$_{25}$ near-eutectic alloy into a glassy phase using an early implementation of the melt spinning technique. In melt spinning, a small liquid droplet (or narrow stream) is propelled against a much larger spinning copper target which is in the shape of a tube or wheel. The very thin (10s of μm) metallic ribbons which are formed this way, combined with the high rate of conductive heat transfer to the copper, results in extremely high cooling rates on the order of $10^6$ K/s or greater. For many materials, these high cooling rates result in the material’s temperature dropping at a rate greater than that at which the constituent atoms can rearrange themselves and, as a result, crystallization becomes kinetically hindered. Over the last 50+ years, glass formation has been observed in several metallic alloys using rapid quenching techniques, and it is generally accepted that all metals can be formed into a glassy phase provided a high enough cooling rate can be achieved$^4$.

$^4$This is true in theory, but in reality the necessary cooling rates can exceed $10^9$ K/s, which is not achievable
Much of the recent interest in metallic glass formation is related to the creation of metallic glasses at substantially lower cooling rates (less than $10^3$ K/s) and greater thicknesses (greater than 1 mm). Materials which exhibit this type of glass forming ability are referred to as bulk metallic glasses (BMGs). Bulk glass forming ability was first demonstrated in 1969 [10] in a variety of Pd-Si based binary and ternary compounds for which the critical cooling rates were $10^2$–$10^3$ K/s with casting thicknesses on the order of 1 mm. A major advancement in bulk metallic glass technology was made in 1993 [11] when researchers at The California Institute of Technology (Caltech) discovered that an alloy with composition Zr$_{41.2}$Ti$_{13.8}$Cu$_{12.5}$Ni$_{10.0}$Be$_{22.5}$ could be made into a glassy alloy with a cooling rate as low as 1.5 K/s and casting thickness as great as 50 mm. Several variations of this material now exist, all based primarily on Zr with three or four additional alloying agents; the family of alloys has been branded as Vitreloy and are available commercially from Liquidmetal Technologies. Following the discovery of the Vitreloy alloys, other alloy families have been discovered which exhibit similarly exceptional glass forming ability. Of particular note are the Pd-P based quaternary alloys, which feature critical cooling rates of less than 0.1 K/s [12]. Many of the BMGs discovered feature desirable properties, such as high strength, high corrosion resistance, high endurance against impact deformation, and (in the case of Fe- or Co-based BMGs) excellent soft magnetic properties [12]. These properties, combined with the outstanding glass forming ability of these materials which makes it possible to use new casting and molding methods for the production of goods, have spurred on a high level of interest in the field.

While the best glass forming ability is found in alloy families with three or more alloying agents, the most attractive glass formers from the standpoint of basic research are binary alloys such as those based on Cu–Zr, Ni–Zr, Ni–Nb, and Pd–Si. The interest in these materials stems from their simplicity, as fewer chemical species results in fewer degrees of freedom, simplifying the analysis and interpretation of experimental data and, perhaps more importantly, enabling the use of computational methods such as classical and \textit{ab-initio} molecular dynamics simulations. Many open questions still exist regarding the glass transition, such as what gives in any practical sense. Of note, no elemental materials have been formed into a purely glassy phase, although small fractions of glassy phases have been detected in splat quenched pure elements such as nickel [9].
rise to the dramatic increase in the viscosity of the supercooled liquid and whether or not the transition is thermodynamic or purely kinetic in nature [13]. To gain insight into the fundamental nature of this transition, information regarding the short range atomic ordering and dynamics is necessary, and, at present, computational methods provide the only means of analyzing the three dimensional atomic behavior of these materials. However, while a variety of computation methods exist and are commonly implemented, these methods make use of a variety of approximation methods in order to carry out the calculations. As such, high quality experimental data is required to verify, at least to some degree, that these computational methods can accurately predict the behavior of the materials. In particular, measurements of density, specific heat, and viscosity are in high demand, as well as experimental structural data such as that obtained by x-ray and neutron scattering techniques.

Closely related to the ideas of glass formation and rapid quenching is the tendency of many materials to exhibit metastable crystallization. This was demonstrated in 1960, just before the discovery of the first metallic glass, by Duwez, Willens, and Klement [14] using the same rapid quenching technique that they had recently developed. In this instance, the silver-copper binary system was shown to display a metastable fcc-solid solution throughout the composition range when rapidly quenched. This is in contrast to the equilibrium phase behavior, which features a single eutectic point with no intermetallics and limited solubility at each end of the phase diagram. The formation of these metastable solid solutions is driven by the kinetic limitations within the melt in much the same way as glass formation, i.e. it is easier for the atoms to form solid solutions than to undergo the phase separation necessary to form the stable eutectic structure. Metastable solid solutions have been found via rapid quenching in other systems as well, such as Fe-B [15] and Zr-Rh [16]. In addition to metastable solid solutions, metastable intermetallic compounds with more complex crystalline structures have been found in systems such as Fe-Si [17] and Al-Ge [18], and metastable intermetallic quasicrystals have been found in systems such as Al-TM (TM = Cr, Mn, Fe) [19]. Furthermore, when rapidly quenched metastable materials are annealed at high temperature, their transformation from metastable to stable is oftentimes found to proceed through the formation of additional transient metastable phases [20–22]. An understanding of the formation of the primary as well as
transient metastable phases is necessary to be able to control phase formation in these systems. In particular, being able to control the phase formation in Fe-based alloys may be crucial to developing new permanent magnet materials.

While rapid quenching is a useful tool for discovering metastable phases, it is not strictly necessary. In many material systems, metastable phases can be formed from the supercooled melt using very slow cooling rates. Two examples of this are Ti$_{39.5}$Zr$_{39.5}$Ni$_{21}$ and Fe$_{83}$B$_{17}$. For the Ti$_{39.5}$Zr$_{39.5}$Ni$_{21}$ alloy, the equilibrium phase at high temperatures, between 843 K and the liquidus temperature of 1093 K, is a crystalline C14 Laves phase. However, when the alloy is allowed to supercool and subsequently solidify under nonequilibrium conditions, an icosahedral quasicrystal is found to be the primary nucleating phase [23]. Because the nucleation barrier is apparently lower for the icosahedral phase as opposed to the crystalline phase, this behavior was interpreted as indicating a high degree of icosahedral short range ordering in the supercooled liquid, verifying a hypothesis originally made several decades earlier by Frank [24]. In the case of Fe$_{83}$B$_{17}$, the equilibrium phase between room temperature and the liquidus temperature of 1448 K is a eutectic mixture of nearly equal parts Fe$_{2}$B and pure Fe. However, when the alloy undergoes solidification from the deeply supercooled liquid it has been found to grow into a Fe$_{23}$B$_{6}$ crystal structure (present work, see chapter 6). In another experiment, where even deeper supercooling is achieved, Fe$_{3}$B is found as the primary phase in the solidified solid. Each of these phases have also been detected as crystallization products during the annealing of rapidly quenched samples, and their formation and subsequent transformation into the stable phase plays an important role in determining the nature of the chemical ordering of the final product [22]. The formation of multiple metastable crystalline phases, as well as the fact that near eutectic Fe-B alloys are relatively good glass formers, have made this an attractive system to study for gaining insight into the nature of competitive nucleation, phase transformations, and glass formation.

Even in cases where glass formation and metastable crystallization do not occur, interesting and novel behavior may occur in the deeply supercooled liquid. Two examples of this are found in pure Si and Co$_{80}$Pd$_{20}$. In the case of pure Si, extensive work has been carried out to determine whether there may be a liquid-liquid phase transition in the deeply supercooled liquid. This
transition was originally proposed based on the extrapolated Gibbs free energies of amorphous and equilibrium liquid silicon, and the observation that these energies do not merge smoothly. Within the range of supercooling which can be achieved experimentally, about 315 K below the melting point of 1687 K, no discontinuities have been observed in any of the thermophysical properties. However, in the last 15 years multiple computational studies have been performed, utilizing classical [25] as well as ab initio [26, 27] molecular dynamics simulations, and these studies indicate that a first order phase transition may occur at some point between 1060 K and 1232 K (depending on the particular study). While these temperatures are outside the range which is accessible experimentally, experimental results still play an important role because they provide a reality check for the computational results over a wide range of temperatures. Interestingly, there is enough variation among all of the computational and experimental results that the question of whether or not the liquid-liquid phase transition exists has not been laid to rest.

In the case of Co$_{80}$Pd$_{20}$ (liquidus temperature 1606 K), electromagnetic levitation studies have shown that it is possible to supercool the alloy to a temperature very close to its Curie temperature (1253 K), prompting the question of whether or not it may be possible to create a ferromagnetic metallic liquid (a thorough review of this topic has been given in Ref. [28]). This was first demonstrated by placing a strong permanent magnet next to the levitation coils and observing a strong attraction of the sample at very deep supercooling. Multiple subsequent studies were carried out to characterize the magnetization and supercooling ability of the alloy, and in all but one case it was found that supercooling the liquid below the Curie temperature was not possible. Further analysis concluded that the enhanced magnetization of the sample as it approached the Curie temperature resulted in an associated reduction in the nucleation barrier which is brought about by magnetic ordering favoring the higher density configuration of the solid phase. However, one possibility that was not ruled out was the possibility of nucleation being triggered by magnetic fields produced by the levitation coils. Very recently, supercooling experiments on Co$_{80}$Pd$_{20}$ which employed the melt fluxing technique [29] showed that it may be possible to supercool samples by as much as 465 K before solidification occurs, which would put the liquid samples well within the ferromagnetic liquid phase. However, there were no
measurements of magnetic susceptibility or of specific heat capacity of the samples during these experiments, so the ferromagnetic liquid could not be verified. It therefore remains an open question whether or not it is possible to create a ferromagnetic liquid metal, as well as what the true impact of magnetic ordering on the nucleation barrier is.

1.2 The Role of Levitation Techniques

A common problem when trying to study the properties of molten metals, particularly in the supercooled liquid state, is the interference caused by the crucible or other contact materials. The container walls, particularly in areas containing defects or debris, will tend to act as heterogeneous nucleation sites which limit the amount of supercooling that can be achieved and possibly prevent supercooling altogether. Furthermore, the metals under investigation will oftentimes react with the container walls, either because of very high temperature (such as the refractory elements) or because the metallic species contains a strong reducing agent (Ti, Zr, and Al, for example). This reactivity can erode the containers, causing chemical contamination of the specimen under study. As a practical matter, the container can obstruct access to the sample, making it difficult to observe the sample and to perform measurements on it. To eliminate the problems associated with reactivity, and to provide a means of stably observing samples in the deeply supercooled liquid phase, a variety of levitation techniques have been developed for performing non-contact experiments on molten metals, semiconductors, and ceramics.

The most successful levitation techniques which have been applied to the study of high temperature liquids are electrostatic levitation (ESL), electromagnetic levitation (EML), and aerodynamic levitation utilizing a conical nozzle (CNL). As will be discussed in more detail in Ch. 2, each of these techniques has their strengths and weaknesses, and each is most well suited to studying a particular subset of materials. To supplement these levitation techniques, methods have been developed to perform a wide variety of thermophysical properties, including density, specific heat, surface tension, viscosity, electrical resistivity, and in some cases radiative emissivity. Methods have also been developed for measuring crystal growth velocities which change as a function of supercooling, and which play a major role in determining
the microstructure of the solidified material. Especially important is the ability to perform measurements of the underlying atomic structure of the supercooled liquid using synchrotron x-ray diffraction and in some cases neutron diffraction from pulsed or continuous sources. The combination of these measurement capabilities, along with the processing environments of the levitation methods, has allowed for a large quantity of thermophysical property data to be obtained which was previously not possible. Perhaps more importantly, the processing capabilities offered by levitation techniques have enabled new insights to be made into the underlying nature of supercooled liquids as well as their nucleation and solidification properties [23,30–45].

1.3 The Scope of this Dissertation

This dissertation describes the development of a new laboratory at Iowa State University (ISU) which employs the Electrostatic Levitation (ESL) technique to perform studies of deeply supercooled liquids and their metastable solidification products.

Along with the contextual background developed in this introduction, Chapter 2 provides an overview of the theoretical and practical aspects associated with the study of deeply supercooled liquids and metastable solids, beginning with a review of the concepts of thermodynamic stability vs. metastability. After the concepts relating to stability have been established, treatments will be given of the concepts of homogeneous and heterogeneous nucleation, of metastable solid phase formation from deeply supercooled liquids, as well as short range ordering in liquids. These concepts are central to the types of experiments that can be carried out with the ESL system. Following the introduction of these foundational concepts, a literature review will be provided regarding the practical aspects of studying supercooled liquids and metastable solids, including the most popular non-levitation and levitation-based methods.

Chapter 3 contains an in-depth description of the ISU-ESL system and all of its associated systems. In addition to the fundamentals of levitation, key insights regarding the levitation system which have been made at ISU will be highlighted. These new insights have resulted in an improved understanding the sample charging mechanisms, as well as improvements to the ultraviolet charging system and enhanced sample stability via improved electrode design and sample position measurement methods. After the fundamentals of levitation have been
established, practical aspects of sample heating, temperature measurement, and thermophysical property measurements will be discussed in detail.

Chapter 4 describes the development of a new approach to performing measurements of electrical resistivity and magnetic susceptibility of ESL processed samples. Focusing on the ability to measure the resistivity of levitated samples, an overview of resistivity measurements methods will be given, covering both contact and noncontact methods for completeness. Then, the implementation of an inductively coupled tunnel diode oscillator (TDO) method into the ISU-ESL will be discussed. This system has been fully built and implemented, and the ability to measure electrical resistivity as well as ferromagnetic transitions has been demonstrated. In addition to the present design, a next generation design will be discussed that should allow for much faster measurements to be performed, opening the door to performing measurements of samples during free cooling experiments as well as performing measurements across phase transitions.

Chapter 5 provides a discussion of key concepts regarding sample impurities, oxidation–reduction reactions and the role of high vacuum with regard to sample processing and supercooling ability. Most of the samples for which ESL processing has been attempted at ISU have been found to be contaminated with oxide impurity phases that are thermodynamically stable at high temperatures and insoluble in the liquid samples. These impurity phases not only act as heterogeneous nucleation sites, limiting the degree of supercooling that can be achieved for the samples, but also interfere with the ability to perform accurate thermophysical property measurements on the samples. To overcome these complications, an understanding of the nature of the contaminant phases and of sample oxidation in general has been developed. As a result of these efforts, methods for purifying most samples have been developed, and a large class of materials that display self-cleaning behavior has been identified and suggested as candidate materials to be studied.

Chapter 6 details the research efforts that have been carried out on the Fe$_{83}$B$_{17}$ near eutectic alloy. One of the most interesting features of this alloy system is the capacity to form metastable crystalline phases from the supercooled melt. In the present work, the Fe$_{83}$B$_{17}$ alloy has been shown to undergo bulk solidification into a metastable solid phase, as well as to form a
metastable precipitate phase that displays stable coexistence with the deeply supercooled liquid. To identify these metastable phases, high energy x-ray diffraction has been applied, revealing that the precipitate phase is bcc-Fe and that the bulk metastable solidification product is a two-phase mixture of Fe$_{23}$B$_6$ plus fcc-Fe. To further characterize the metastable solid, including its temperature evolution during cooling and metastable-to-stable transformation during heating, measurements of volume thermal expansion and temperature dependent RF susceptibility have been carried out. While still in the early stages of analysis, these thermophysical property measurements have shown that there may be additional phase transformations taking place within the sample as it cools below temperatures for which x-ray diffraction measurements were performed.

Finally, Chapter 7 provides a summary of the work done thus far, and provides some thoughts regarding the future of the ISU-ESL project.
CHAPTER 2. THE PHYSICS OF SUPERCOOLING AND APPROACHES TO ACHIEVING IT

In this chapter the key concepts regarding the physics of supercooled liquids will be covered. We will then go on to discuss experimental approaches to supercooling metallic liquids.

2.1 The Physics of Supercooling

A proper treatment of the thermodynamic and kinetic aspects of nucleation theory is important to understanding both the supercooling of liquids and the metastable phase formation phenomena which are studied using the ESL technique. Detailed reviews of these topics, covering several decade’s worth of research, can be found in references [46] and [47]. Here a brief review will be given, focusing on the more fundamental aspects of nucleation theory. While the basic concepts of nucleation can be applied to any first first order phase transition (melting, freezing, solid-solid structural transitions, etc.), here the context will be in terms of the liquid-solid freezing transition.

2.1.1 Thermodynamics Background

A physical system is said to be in a state of thermodynamic equilibrium when there is no driving force for the spontaneous change in the physical properties of the system. Such an equilibrium state is achieved when the first derivative of the free energy of the system with respect to the appropriate phase space variable is zero [47]. This is shown schematically in Fig. 2.1. Multiple forms of equilibrium states exist. The state which is characterized by a global minimum in the free energy is considered the stable equilibrium state, while those states characterized by local (non-global) minima are considered to be metastable. If, for example,
Figure 2.1  Schematic representation of the barrier between metastable and stable equilibrium states.

Thermal fluctuations cause the system to deviate from a local minimum position, the non-zero derivative in the free energy will result in a thermodynamic driving force which subsequently returns the system to equilibrium. A state which is situated at a local maxima is considered unstable for a similar reason, because even the smallest of fluctuations will result in a driving force away from the maxima. Finally, for a system in a metastable state, the difference in energy between the metastable equilibrium and unstable equilibrium positions is termed the activation energy, as this is the minimum energy barrier which must be overcome for the metastable state to transition into the stable state.

For equilibrium systems characterized by constant temperature and pressure, the relevant free energy is the Gibbs free energy $G$:

$$ G(T) = H(T) - TS(T) $$

(2.1)

where $T$ is the temperature, $H$ is the enthalpy, and $S$ is the entropy of the system. The enthalpy is a measure of the heat content of the system, while the entropy is a measure of the disorder within the system. From Eq. 2.1 it can be seen that the value of the entropy largely determines the temperature dependence of the Gibbs free energy. Because liquids are more disordered systems than crystals and thus have greater entropy, the liquid phase is stabilized
at high temperature. When using the Gibbs free energy to determine the relative stability of multiple possible states of a system, it is only necessary to consider the relative Gibbs free energy between the various states. For the liquid-solid freezing transition we can write

$$\Delta G_{LS} (T) = \Delta H_{LS} (T) - T \Delta S_{LS} (T)$$  \hspace{1cm} (2.2)

where the subscripts $LS$ indicate that the difference in the respective quantities is given in terms of liquid minus solid. At temperatures above the melting point of the equilibrium stable phase, $T_{EM}$, the Gibbs free energy of the liquid is lower than that of the stable solid phase and so $\Delta G_{LS}$ is negative, while for temperatures below $T_{EM}$ the opposite is true. When $T = T_{EM}$, the liquid and solid phases are equally stable, thus $\Delta G_{LS} = 0$ and from Eq. 2.2 we find

$$\Delta H_f = T_{EM} \Delta S_f$$  \hspace{1cm} (2.3)

where $\Delta H_f$ is the enthalpy (heat) of fusion and $\Delta S_f$ is the entropy of fusion. The enthalpy of fusion and equilibrium melting point can be accurately measured experimentally (for example via differential scanning calorimetry), and from these measured variables the entropy of fusion can be determined.

As depicted above, and which will be expanded upon below, an energy barrier may be present which prevents the liquid-solid transition from taking place at the equilibrium melting point. In such a case, the liquid will supercool below the equilibrium melting point. The differences in enthalpy and entropy between the metastable liquid and the stable solid phase can be expressed as

$$\Delta H_{LS} (T) = \Delta H_f - \int_T^{T_{EM}} \Delta C_p (T) \, dT$$  \hspace{1cm} (2.4)

$$\Delta S_{LS} (T) = \Delta S_f - \int_T^{T_{EM}} \frac{\Delta C_p (T)}{T} \, dT$$  \hspace{1cm} (2.5)

where $C_p$ is the constant pressure specific heat and $\Delta C_p = C_{p,L} - C_{p,S}$. By substituting Eqs. 2.4 and 2.5 into Eq. 2.2, we arrive at the following expression for the difference in Gibbs free energy between the supercooled liquid and the stable solid phase:

$$\Delta G_{LS} (T) = \frac{\Delta H_f \Delta T}{T_{EM}} - \int_T^{T_{EM}} \Delta C_p (T) \, dT + T \int_T^{T_{EM}} \frac{\Delta C_p (T)}{T} \, dT$$  \hspace{1cm} (2.6)
where $\Delta T = T_{EM} - T$ is the amount of supercooling.

The Gibbs free energy difference between liquid and solid states, $\Delta G_{LS}$, determines the relative stability between the liquid and solid phases of a material. As such, it plays an important role in determining the driving forces for phase transitions from the liquid state and, therefore, being able to quantify $\Delta G_{LS}$ is important for developing a proper understanding of several processes: nucleation, the formation of metastable crystalline and quasicrystalline phases from supercooled liquids, as well as glass formation. Because of the central role of $\Delta G_{LS}$ in these processes, and because calorimetric measurements on supercooled liquids are generally lacking, several attempts have been made to approximate the temperature dependence of $\Delta G_{LS}$ so that its value in the supercooled state may be calculated based solely on measurements of the enthalpy of fusion, $\Delta H_f$, and/or measurements of the specific heat change upon melting, $\Delta C_p(T_{EM})$ [46]. While these approximations can produce adequate results for low levels of supercooling, their accuracy tends to become worse as the degree of supercooling increases. It is therefore important to be able to measure the temperature dependence of the specific heat of the supercooled liquid, which would allow direct calculation of $\Delta G_{LS}$ via Eq. 2.6.

### 2.1.2 Nucleation

Nucleation is the first step in the process of crystallization from the liquid phase. For single component metals of very high purity, the nature of the nucleation will be determined by the intrinsic thermodynamic variables of the system, and is termed homogeneous nucleation. Within the liquid phase the nature of the atomic ordering is not strictly random, but is instead characterized by a short range order which can be thought of (to first order) as a random packing of hard spheres. The extent of the short range ordering quite small, being characterized by a correlation length that typically extends out only a few atoms in diameter, beyond which the arrangements of atoms are no longer correlated. Over time, thermal fluctuations can result in a larger groupings of atoms coming together and forming small solid-like clusters within the liquid. Above the melting point, the Gibbs free energy of these crystalline clusters is greater than that of the liquid, and the clusters will spontaneously decay back into the liquid phase. As the temperature drops below the melting point, the Gibbs free energy becomes lower for
the crystalline phase than the liquid, and thus cluster formation becomes favored from a bulk standpoint. However, the formation of a crystalline cluster, with ordering different than that of the liquid, also implies the formation of an interface. It is the formation of this interface, along with its associated interfacial free energy, which inhibits crystal nucleation and allows for large supercooling to be achieved in liquids.

If the shape of a crystal nucleus is assumed to be spherical, then the Gibbs free energy of formation of such a nucleus is given by

$$\Delta G_n(r) = -\frac{4}{3} \pi r^3 \rho \Delta G_{LS} + 4 \pi r^2 \gamma_{LS}$$

(2.7)

where $r$ is the radius of the crystalline cluster, $\rho$ is the density of the crystalline phase, $M$ is the molar mass, $\Delta G_{LS} = \Delta G_L - \Delta G_S$ is the difference in the molar Gibbs free energy between the liquid and solid phases, and $\gamma_{LS}$ is the interfacial free energy between the two phases. As a liquid is supercooled below its melting point, the crystalline phase becomes favored and therefore acts to reduce $\Delta G_n$, while the formation of the solid-liquid interface is unfavorable and therefore acts to increase $\Delta G_n$. Because the volume and surface terms have different radial dependences, the function $\Delta G_n(r)$ will pass through a maximum, being dominated by the surface term at low $r$ and by the volume term at high $r$. This is shown schematically in Fig. 2.2.

The maximum in the function $\Delta G_n(r)$ corresponds to the activation energy for the formation of crystal nuclei, $\Delta G_n^*$, and the corresponding size of such a nucleus is the critical radius, $r^*$. For crystal nuclei smaller than $r^*$ the thermodynamic driving force will result in nuclei that tend to decay back into the liquid. Only when a nucleus reaches a size of $r^*$ or greater will it experience a thermodynamic driving force which favors continued growth into the fully crystalline phase. However, even for nuclei greater than $r^*$ there is a finite probability that the nucleus will decay back to the liquid phase because $\Delta G_n$ is still positive and the nucleus is therefore unstable. Only when the nucleus reaches a size of $r_0 = 1.5 r^*$ will $\Delta G_n$ become negative, indicating that the nucleus has achieved thermodynamic stability. Expressions for $r^*$ and $\Delta G_n^*$ can be found by differentiating Eq. 2.7 and solving for the values corresponding to
the maximum. This leads to the following expressions:

\[ r^* = \frac{2M\gamma_{LS}}{\rho \Delta G_{LS}} \]  

(2.8)

\[ \Delta G^* = \frac{16\pi M^2\gamma_{LS}^3}{3\rho^2 \Delta G_{LS}^2} \]  

(2.9)

With Eqs. 2.8 & 2.9 it is possible to calculate explicit values of both the critical cluster size and activation energy for homogeneous nucleation. To do so, expressions for the direct calculation of both \( \Delta G_{LS} \) and \( \gamma_{LS} \) must be available. For \( \Delta G_{LS} \), Eq. 2.6 provides a means of direct calculation provided that information regarding the specific heat of the supercooled liquid and high temperature crystal are available. In the absence of such specific heat data, \( \Delta G_{LS} \) can be reasonably estimated by assuming that the difference in specific heats of the the liquid and crystalline phase are sufficiently small that \( \Delta G_{LS} \) is dominated by the enthalpy contribution, leading to the following approximation:

\[ \Delta G_{LS}(T) = \frac{\Delta H_f \Delta T}{T_{EM}} \]  

(2.10)

Unlike \( \Delta G_{LS} \), for which analytical expressions can be easily derived based on measurable thermodynamic quantities, the interfacial free energy is far more complicated to determine.
The value of $\gamma_{LS}$ depends on the nature of the atomic mismatch which occurs at the interface of a well ordered crystalline phase and an essentially disordered liquid phase. While both experimental and computational methods exist for determining the value of the interfacial energy, the discussion of these methods is beyond the scope of this dissertation. For the sake of brevity, we will simply say that for simple systems the value of $\gamma_{LS}$ can be shown to be well estimated based on the negentropic model of the liquid-solid interface:

$$\gamma_{LS} = \alpha \frac{\Delta S_f T_{EM}}{(N_A v_m)^{1/3}} = \alpha \Delta H_f \left(\frac{\rho^2}{M^2 N_A}\right)^{1/3}$$

(2.11)

where $N_A$ is Avogadro’s number, $v_m$ is the molar volume, and $\alpha$ is a constant that depends on the nature of the crystalline phase. For monatomic close-packed crystals such as HCP and FCC $\alpha = 0.85$, while for BCC crystals $\alpha = 0.70$.

As a numerical example, consider the case of pure nickel. For the values of the various physical properties we use $\rho = 7810 \text{ kg/m}^3$, $\Delta H_f = 17.5 \text{ kJ/mol}$, $T_{EM} = 1728 \text{ K}$, and $M = 0.0587 \text{ kg/mol}$. Because nickel freezes into an FCC crystal structure, $\alpha = 0.85$, leading to a value of the interfacial energy of $\gamma_{LS} = 0.46 \text{ J/m}^2$. For a moderate supercooling of only $\Delta T = 10 \text{ K}$, this leads to values of $\Delta G^* = 53 \text{ keV}$ for the activation energy and $r^* = 67 \text{ nm}$ for the critical cluster size, corresponding to $10^8$ atoms in the critical cluster. Compared to the typical thermal energy of $\sim 0.2 \text{ eV}$ and the size of typical ordered liquid clusters of $\sim 30 \text{ atoms}$, it becomes clear that the probability of homogeneous nucleation occurring near the equilibrium freezing point should be quite small. As the degree of supercooling increases, the sizes of the activation energy and the critical cluster will be reduced. At $\Delta T = 300 \text{ K}$, the values become $\Delta G^* = 62 \text{ eV}$ and $r^* = 2.2 \text{ nm}$, corresponding to a much smaller $4000 \text{ atoms}$.

The discussion thus far has focused only on pure liquids for which the driving forces for nucleation depend only on the intrinsic thermodynamic properties of the liquid. However, in practice the nucleation process is not dominated by the intrinsic properties of the liquid, but by a variety of external influences. These influences could be insoluble oxide phases on the liquid surface, defects or dirt on the surface of a container, or even the container wall itself. Nucleation which is dominated by such external influences is termed heterogeneous nucleation.

The most common way in which heterogeneous nucleation is described is in terms of the
wetting which takes place between a crystal nucleus and a substrate, shown schematically in Fig. 2.3. In such a situation, there will be three distinct interfaces which form along with their associated interfacial energies: the liquid-solid interface, $\gamma_{LS}$; the heterogeneous site-solid interface, $\gamma_{HS}$; and the heterogeneous site-liquid interface, $\gamma_{HL}$. The three interfacial energies will work together to exert a net surface tensile force on the crystal nucleus, resulting in the shape of the nucleus becoming distorted from spherical. The shape of the nucleus is characterized by the wetting angle, $\theta$, and the equilibrium shape will be determined when the individual components of surface tension directed parallel to the wetting surface are equal:

$$\gamma_{HL} = \gamma_{HS} + \gamma_{LS} \cos \theta$$

(2.12)

For a crystal nucleus with a given number of atoms, the wetting of the nucleus onto the heterogeneous site results in a reduction of the volume of the nucleus compared to the situation where wetting does not occur. The reduction in the volume can be determined based on the contact angle, and is given by:

$$f (\theta) = \frac{1}{4} (2 - 3 \cos \theta + \cos^3 \theta)$$

(2.13)

where $0 \leq f (\theta) \leq 1$ for $0 \leq \theta \leq 180^\circ$. Along with the reduction in the volume of the nucleus, there is a corresponding reduction in the activation energy for the formation of a critical nucleus:

$$\Delta G_{het}^* = \Delta G_{hom}^* f (\theta)$$

(2.14)
In this picture of heterogeneous nucleation, the extent to which the nucleation barrier will be reduced depends on the relative energies associated with the formation of each of the interfaces, which in turn will be related to the similarities or differences in the structural and chemical characteristics of the liquid, solid nucleus, and heterogeneous site. For instance, if the heterogeneous site is very similar in nature to the nucleating crystal, the interfacial energy \( \gamma_{HS} \) will be minimized, resulting in a small contact angle, a small value for \( f(\theta) \), and a significant reduction in the nucleation barrier. The opposite is also true: if the heterogeneous site is very dissimilar in nature to the nucleating crystal, the interfacial energy \( \gamma_{HS} \) will be large, resulting in a large contact angle, a value for \( f(\theta) \) close to 1, and very little reduction in the nucleation barrier. From this understanding it can be surmised that if a crucible is going to be used to contain a liquid sample, then a crucible made of an amorphous material will likely yield better supercooling results than a crucible made of a crystalline material. Furthermore, the presence of debris or defects in the container, such as cracks or protrusions, will provide additional surfaces on which to wet, which will result in further reduction in both the size of the critical nucleus and the activation energy for its formation.

With regard to the processing of samples in the ESL, for which the samples are not in contact with a container wall, an understanding of heterogeneous nucleation helps to emphasize the need to ensure that samples are free of insoluble oxide impurities. Most of the naturally formed metal oxides that are found in ESL samples are crystalline and they have very textured surfaces on a microscopic level. The combination of these properties makes the oxides nearly ideal heterogeneous nucleation sites, and their presence can strongly reduce the amount of achievable supercooling or even prevent supercooling altogether.

### 2.1.3 Metastable Phase Formation

In the most general sense, for a given ensemble of atoms there exists several different ways in which the atoms can be arranged. These arrangements include a variety of crystalline phases (bcc, fcc, hcp, etc.) with well defined long range ordering, liquid and amorphous phases characterized by short range ordering, and gas phases with nearly random arrangements of the atoms, as well as a large list of other possible configurations (quasicrystals, plasmas, etc.).
In most cases, out of all of the different possible configurations, one particular configuration will have a substantially lower free energy of formation than all of the rest, and therefore that configuration will be considered to be the stable phase for the system. However, in many materials systems, there may be two or more phases with similar free energies of formation. While the phase with the lowest free energy of formation is still considered to be the only stable phase for the system, those additional phases may be considered metastable phases provided that their free energies of formation are within approximately 20 meV/atom (2 kJ/mol) or less than that of the most stable phase [48]. If such additional metastable phases exist, it may be possible, under the appropriate conditions, for a material to experience a variety of different phase transformation pathways as it transforms from one metastable phase to the next before landing at the one true stable phase. Under certain circumstances it may even be possible for a material to undergo transformation into a metastable phase where it remains indefinitely because of kinetic limitations that prevent the atoms from undergoing rearrangement.

Fig. 2.4 shows a schematic of the Gibbs free energies of formation as a function of temperature for a material system that exhibits liquid (L), metastable solid (MS), and stable solid (S) phases. At temperatures above the melting temperature of the stable solid phase, $T_m,S$, the
The number of solid clusters forming within the liquid that exceed the critical cluster size \( r^* \) is termed the steady state nucleation rate, \( I_{ss} \), and its value is determined as:

\[
I_{ss}(T) = K \exp \left( -\frac{\Delta G^*}{k_B T} \right)
\]

(2.15)

where the exponential term is a result from Boltzmann statistics and the prefactor \( K \) takes into account the kinetic effects related to the structural rearrangement of atoms which must occur in order for the solid cluster to form. Qualitatively, the greater the similarity between the short range ordering of the liquid and the ordering of the solid phase, the greater the value of \( K \). As with the solid-liquid interfacial free energy, the precise quantitative nature of \( K \) is quite complicated and a full analytical treatment is beyond the scope of this dissertation. However, for the rather simple cases of elemental metals, solid solutions, and congruently melting line compounds with very simple crystal structures, the value of \( K \) can be shown to be approximately \( K = 10^{36}/\eta(T) \) m\(^{-3}\)s\(^{-1}\), where \( \eta \) is the liquid viscosity in units of Pa·s. Between the kinetic term and the thermodynamic term, there are at least three distinct reasons as to why solidification into a metastable solid phase might be favored over solidification into the stable solid phase.

The first reason is related to the interfacial free energy associated with the formation of the critical clusters. If there is a greater similarity in the local atomic ordering between the metastable solid and liquid phases than there is between the stable solid and liquid phases, then the interfacial free energy associated with the formation of clusters of the metastable solid
will be lower than that for the stable solid. A reduction in the interfacial energy will result in a reduction in the nucleation barrier $\Delta G^*$, and as a consequence the nucleation rate for the metastable solid will be greater than that for the stable solid. Such an influence of the local atomic ordering has been demonstrated experimentally in samples of Ti$_{39.5}$Zr$_{39.5}$Ni$_{21}$ [23]. The stable phase at high temperature for this material is the C14 Laves phase, a hexagonal crystal with polytetrahedral ordering. However, when this material solidifies from the supercooled liquid, the primary solidification phase is an icosahedral quasicrystal. Nucleation of the quasicrystal is favored over nucleation of the crystalline phase because the supercooled liquid also displays local icosahedral ordering, resulting in a lower interfacial energy for the formation of quasicrystalline clusters.

The second reason that nucleation of a metastable phase might be preferred is related to the diffusion of atoms that must occur during crystal growth. This effect can be particularly pronounced in eutectic systems near the eutectic composition, where solidification into the stable solid may require a large degree of chemical partitioning to occur to allow for the cooperative growth of the two stable crystal phases. The most commonly encountered example of such a situation is in the Fe-C binary system. Examination of the stable phase diagram for this system reveals that there are no stable intermetallic phases. However, the system does melt into a fully miscible liquid when heated above the liquidus temperature (1809–1426 K for carbon content between 0–17 at.%, respectively). When the liquid is then cooled, a large degree of chemical partitioning is required for the atoms to fully separate out of the miscible liquid and into distinct regions of Fe and C (graphite). Compared to the formation of Fe + C, the formation of Fe$_3$C (cementite) is less stable by approximately 20 meV/atom [49]. However, the amount of chemical partitioning required for the miscible liquid to separate into regions of Fe + Fe$_3$C is significantly less than that for the separation into Fe + C. As a result, the formation of Fe$_3$C becomes kinetically favorable, and solidification of Fe-C alloys near the eutectic point nearly always results in its formation. In fact, the formation of Fe$_3$C is so dependable that the metastable Fe-C phase diagram is used more commonly than the stable phase diagram within the field of Materials Science and Engineering [2].

The final reason that will be considered for the formation of a metastable solid phase is
related to glass formation. When a glass forming material is cooled into the supercooled liquid state, its viscosity begins to increase more rapidly than would occur for a non-glass forming material. The increase in the liquid viscosity results in a significant reduction in the atomic mobility, which consequently inhibits the ability of the atoms to rearrange themselves into a critical crystal nucleus. In alloys with several components (3–6 alloying agents) this effect will be enhanced by the strong degree of topological and chemical rearrangement which must occur for cluster formation. The greater the liquid viscosity and the more complicated the chemical makeup of the alloy, the lower will be the nucleation rate. If the liquid is able to cool through a temperature for which its viscosity exceeds $10^{12}$ Pa·s, nucleation of the crystalline phase becomes virtually impossible and the liquid will solidify into a metastable glassy solid phase.

### 2.1.4 Short-range Ordering in Liquids

As was mentioned in Sec. 2.1.2, the nature of the atomic structure in liquids is not purely random, but in fact there is a certain degree of short-range ordering (SRO) that exists at very short length scales. The length scale and the character of the ordering that occurs in a material can be described by the pair distribution function (PDF) of a material, $g(r)$. The PDF is a radial probability function that describes atomic ordering in terms of the probability of finding any two atoms at a particular distance apart: if we consider atom $a_1$ as being fixed at the origin, then the probability that an atom $a_2$ will be found at a radial distance of $r_{12}$ is given by $g(r_{12})$. The PDF is normalized based on the average atomic spacing as determined by the number density of the material. Therefore, randomness is characterized by a flat function with constant value equal to 1, while order is characterized by a periodic function that oscillates about 1. This concept is shown schematically in Fig. 2.5 (originally from [50], adapted from [51]) for an ideal gas, a simple liquid, and single crystal; each phase in this example is monatomic. In an ideal gas the atoms do not interact with each other, and so the spatial distribution of atoms is completely random. It then follows that the PDF for an ideal gas is perfectly flat. For a single crystal, atoms are arranged in well defined, highly ordered sites, and this is reflected by the well defined periodic spikes and zeros that extend to large distances in the single crystal PDF. The situation for the simple liquid is somewhere in between that of a crystal
Figure 2.5  Schematic of the characteristic ordering found in gas, liquid, and crystalline materials, along with representative pair distribution functions $g(r)$ and structure factors $S(Q)$.

and a gas. The oscillations in the liquid PDF indicate non-random ordering at short length scales. Compared to the crystalline peaks, the oscillations in the liquid PDF are quite broad, indicating a diffuse ordering for which the nearest-neighbor distances are less well defined for a liquid than they are for a crystal. The oscillations are also heavily damped, indicating that the ordering is characterized by a finite correlation length. At distances greater than about five atomic diameters, corresponding to 1–2 nm, the value of the liquid PDF approaches unity, indicating that the atomic positions are no longer correlated. In all three cases, the value of $g(r)$ is equal to zero for distances below one atomic diameter to account for the fact that atoms cannot overlap. The function $S(Q)$ is called the structure factor (not to be confused with the atomic form factor), and is equal to the Fourier transform of the PDF. The structure factor is closely related to the diffraction patterns that are obtained from x-ray, neutron, and electron scattering experiments. The parameter $Q$ is referred to as the momentum transfer, and is a function of the scattering angle and wavelength.

The structure of liquids is commonly discussed in terms of the atomic coordination shells that are associated with the oscillations in the liquid PDF. The concept of coordination shells is
shown schematically in Fig. 2.6 (originally from [50], adapted from [51]). The number of atoms contained within each coordination shell can be determined through spherical integration of the PDF:

\[ C_s = 4\pi n \int_{r_{s-1}}^{r_s} r^2 g(r) dr \]  \hspace{1cm} (2.16)

where \( C_s \) is the number is the number of atoms in the \( s \) shell, \( n \) is the liquid number density, and \( r_s \) corresponds to the \( s^{th} \) minimum in the PDF. Most often, the integration is only carried out for the atoms contained within the first shell, and the value of \( C_1 \) is referred to as the coordination number. Most liquid metals have been found to have coordination numbers of 11–13, indicating that the SRO is close-packed. For comparison, close-packed crystal structures such as FCC and HCP both have coordination numbers of 12, as do atoms arranged onto the vertices of a regular icosahedron. Liquid silicon, on the other hand, has a coordination number of approximately 6, which has been interpreted as indicating that the atoms in the liquid phase are affected by the same tendency toward tetrahedral ordering that determines the diamond crystal structure of solid silicon [52].

In liquids containing two or more alloying agents, in addition to the overall or total-PDF there will be a subset of partial-PDFs that describe the various interactions among each of the alloying agents. For instance, in a binary alloy with elements \( a \) and \( b \), there will be three partial-PDFs: \( g_{a-a}(r) \), \( g_{a-b}(r) \), and \( g_{b-b}(r) \). The partial-PDFs each represent a particular fraction of the total-PDF, and the sum of the partials will be equal to the total. Analysis of the of the partial-PDFs provides a measure of the extent to which chemical ordering may be occurring in the liquid. For instance, if there is no chemical ordering occurring (analogous to a solid solution), then the placement of the individual atomic species will be chemically random and the partial-PDFs will be determined entirely by the total-PDF and the composition of the alloy. For instance, if \( X_a \) is the concentration of element \( a \) and \( X_b \) is the concentration of element \( b \), then the partial-PDFs in the absence of chemical ordering will simply be:

\[ g_{a-a}(r) = X_a X_a g(r) \]  \hspace{1cm} (2.17a)
\[ g_{a-b}(r) = 2X_a X_b g(r) \]  \hspace{1cm} (2.17b)
\[ g_{b-b}(r) = X_b X_b g(r) \]  \hspace{1cm} (2.17c)
Figure 2.6 The oscillations found in the pair distribution function of a liquid represent the average packing of atoms into coordination shells, providing insight into the SRO ordering that occurs in liquids.

In the presence of chemical ordering, there will be a preference for one atomic species over the other within each of the coordination shells of the of the total-PDF. The preferential placement caused by the chemical ordering will result in the partial-PDFs deviating from what would be predicted in Eqs. 2.17.

The determination of the exact nature of both the topological and chemical SRO in liquid metals continues to be a challenge. While experimental methods exist for the measurement of diffraction patterns which can yield $S(Q)$ and, ultimately, total-PDFs, there are a number of limitations. First, it must be emphasized that the total-PDF is a radial function only, it contains no information about the angular distribution of the atoms. So while total-PDFs can be useful for gaining insight into average coordination numbers, average packing densities, and average length scales for the topological ordering, they provide little additional quantitative information. For instance, it may be possible to determine that the coordination number of a liquid metal is 12, but it cannot be quantitatively determined whether the coordination is
dominated by FCC-like, HCP-like, or icosahedral-like ordering, or perhaps some combination of them\(^1\). Furthermore, when it comes to investigating the chemical ordering in liquids, experimental determination of the partial-PDFs can be extremely challenging. To solve for each of the three partial-PDFs of a binary alloy, three distinct total-PDFs are necessary and they must be acquired using scattering techniques that allow for differentiation of the relative scattering strengths of the elements. This can be done, for instance, by using anomalous x-ray scattering to emphasize the contribution of one of the atomic species by using x-rays tuned to an absorption edge [53]. However, this x-ray technique is not compatible with all sample processing methods. For instance, the x-ray scattering technique preferred by researchers in the ISU-Ames Laboratory-Washington University collaboration uses high energy x-rays in the 100–130 keV range because these energies allows for diffraction measurements to be performed in a transmission geometry (as opposed to reflection geometry). Because the absorption edges for most elements of interest (Pd or lighter) are less than 25 keV, anomalous x-ray scattering is not compatible with high energy x-ray diffraction. Another way to differentiate scattering strengths is to perform neutron diffraction in conjunction with isotopic substitution. Because neutrons scatter off of the atomic nucleus, different isotopes will tend to have different scattering factors, and can therefore be used for chemical differentiation. Unfortunately, isotopically pure metal can be prohibitively expensive. Consider iron, the fourth most prevalent element on the planet after O, Si and Al, and by far the most heavily produced element [54]. The three isotopes to consider would be \(^{54}\text{Fe}, \, ^{56}\text{Fe}, \text{ and } ^{57}\text{Fe}\), which have relative abundances of 5.8%, 91.7%, and 2.2%, and neutron scattering cross sections of 2.2, 12.42, and 1 barn, respectively [55]. The cost of \(^{54}\text{Fe}\) is $4480 per gram, and \(^{57}\text{Fe}\) is $3500 per gram [56], and typically several grams (5 or more) are required to successfully produce an alloy ingot, especially when being alloyed with a light element such as B, C, Al, or Si. By comparison, high purity gold and platinum begin to look quite affordable at at least less than $200 per gram [57].

Because of the difficulties associated with performing experimental investigations of the

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\(^1\)Attempts have been made to fit experimental \(S(Q)\) with calculations based on simulated atomic clusters with different symmetries such as icosahedral, dodecahedral, and cubic (HCP, BCC, etc.) [23, 36]. While this method provides qualitative insights into the nature of the SRO, it does not provide quantitative information regarding the contributions of the various structural motifs that comprise the SRO.
topological and chemical ordering in liquid metals (as well as glassy solid metals), much of the work being done in this area is performed computationally via molecular dynamics simulations. In classical molecular dynamics, the atomic interactions are calculated by using an inter-atomic potential, such as a Lennard-Jones \cite{58} or a Stillinger-Weber \cite{25} potential. In \textit{ab-initio} calculations, the atomic interactions are calculated using first principals quantum mechanical considerations. In both cases, the locations of the atoms within the simulated liquid model can be determined precisely, and so their topological and chemical ordering behavior can be quantitatively analyzed. However, because varying levels of assumptions are being made as to the nature of the atomic interactions, it is absolutely critical to ensure that the results of simulations methods are verifiable via experiment. In addition to measurable structure information such as total-PDFs, the simulations can be used to calculate density, enthalpy, specific heat capacity, diffusion coefficients, viscosity, and electrical resistivity. It is therefore very important to ensure that these thermophysical properties can be accurately measured experimentally, to provide the greatest number of comparisons and constraints possible to ensure that the simulation results are correct.

\subsection{2.2 Methods for Achieving Supercooling}

Here we will discuss some of the more commonly used methods for achieving large degrees of supercooling in high temperature liquids. While the focus of this dissertation is on the use of ESL for performing studies on high temperature liquids and solids, the additional methods presented here are referred to frequently throughout the literature and they can be used for performing similar types of materials investigations as those which will be performed using ESL. A basic awareness and understanding of these techniques is essential to understanding the various processing behavior that materials display when studied using these different methods, as well as for attempting to design ESL experiments based on the results of investigations using these other methods.
2.2.1 Non-Levitation Techniques

2.2.1.1 Rapid Quenching

Rapid quenching refers to the process of projecting a liquid sample onto a thermally conductive heat sink, usually made of copper. In the simplest variation of this method, the heat sink may be a stationary copper block that is chilled, either using water to maintain a constant temperature near room temperature, or using liquid nitrogen to increase the thermal conductivity of the copper as well as to increase the temperature gradient and therefore cooling power upon contact with the liquid. This simple approach to rapid quenching is often referred to as splat quenching. A more sophisticated approach to rapid quenching makes use of a large spinning copper wheel as the heat sink [59] as shown in Fig. 2.7; this approach to rapid quenching is called melt spinning. In the process of melt spinning, a sample is initially contained in a crucible typically made of either graphite or quartz. The crucible is fashioned so that it has a nozzle at the bottom and a gas inlet at the top. The material is then melted using an induction heating coil, and when fully molten a burst of gas is introduced into the crucible to force the liquid out of the nozzle. The liquid flows as a narrow stream until it makes contact with the copper wheel, which is spinning with a typical tangential speed of 10s of m/s. Upon contact with the spinning wheel, the stream of liquid is formed into a thin, continuous ribbon with a typical thickness of 10s of μm. Because of the combination of the thinness of the ribbon and the excellent heat conduction of the copper wheel, melt spinning can achieve cooling rates in excess of $10^6$ K/s. The ability to quench materials at such rapid rates makes melt spinning a very useful tool for the study metallic glasses. In addition to metallic glasses, melt spinning is very useful for studying the formation of metastable crystalline and quasicrystalline materials, which form either as a direct result of the quenching or as transformation products of annealing experiments on the initially formed glass.

The melt spinning method has a long history. It has found frequent use in basic materials science research, and has also been scaled up to industrial levels for the production of commercial goods such as Nd$_2$Fe$_{14}$B permanent magnets and the Metglas line of soft (transformer core) magnets. However, despite its popularity there are certain drawbacks to the method. The
most important and obvious drawback, in the present context, is that there is no opportunity to perform studies directly on the deeply supercooled liquid due to the extremely short amount of time (few ms) that the material exists in the deeply supercooled state. Another drawback is that the ribbons which are formed can be very inhomogeneous, having different microstructures on the wheel side versus the air side of the ribbon. In some cases there can even be a difference in the glass forming ability between the two sides. The inhomogeneities are a result of the different cooling rates experienced by the two sides of the ribbon.

2.2.1.2 Droplet Dispersion

To study liquids in the deeply supercooled state at slow cooling rates, reducing the quantity of heterogeneous nucleation sites is required. One simple way of reducing the effect of heterogeneous nucleation sites is to divide a sample into several small particles. Assuming that the heterogeneous nucleation sites within a material are initially randomly distributed throughout the volume, and the volume of the material is then divided into several smaller particles, then the probability of an individual particle containing $N$ heterogeneous nucleation sites is given by a Poisson distribution:

$$P(N) = \frac{N^N}{N!} \exp(-nV)$$ (2.18)
where \( P \) is the probability, \( n \) is the number density of heterogeneous nucleation sites, and \( V \) is the volume of the individual particle. It then follows that the probability that an individual particle contains zero heterogeneous nucleation sites is given by:

\[
P(0) = \exp (-nV)
\]  

(2.19)

Therefore, if a material is subdivided into a large number of fragments with small volumes (a droplet dispersion), then a significant fraction of the fragments will contain zero heterogeneous nucleation sites. This idea is shown schematically in Fig. 2.8.

The droplet dispersion method was the method used by Turnbull to perform the first studies on the reliable supercooling of several different metals [7, 60] and has also been more recently applied to the studies of supercooling in pure Al [61] and Al-Mn alloys [62], among others. The droplet sizes used in these investigations are typically on the order of 10–100 \( \mu \)m. The types of investigations that can be carried out using this method include maximum supercooling studies for the analysis of the thermodynamic and kinetic aspects of nucleation, calorimetric investigations of phase transformations from the supercooled liquid, and microstructural investigations of the crystal growth that occurs during non-equilibrium solidification. While this method allows for more careful evaluation of materials in the supercooled state, as well as for the study of solidification from the supercooled state as compared to rapid solidification methods, it does not serve well for the careful studies of the thermophysical properties of deeply supercooled liquids such as mass density, surface tension, viscosity, atomic structure (via diffraction methods) or electrical resistivity. Furthermore, while qualitative calorimetric studies can be performed, extending these studies to a more quantitative level requires extreme care to account for the
fact that only a small portion of the mass of the sample is experiencing deep supercooling, while the remaining sample mass is experience little to no supercooling due to heterogeneous nucleation.

### 2.2.1.3 Flux Immersion

In the flux immersion method (or melt fluxing method), the sample under study is immersed in a molten flux for the purpose of deactivating heterogeneous nucleation sites. This method can be used in conjunction with the droplet dispersion method, or it can be applied to process bulk samples on the order of 1–10 mm in diameter or larger. The material most commonly used as the fluxing agent is pure, dehydrated B$_2$O$_3$, but there have also been applications where Pyrex$^2$ has been used [63], as well as other applications where the flux was an inorganic salt of alkali metals, sulfates, or phosphates [61]. The practical application of the method can be said to be more of an art than a science, because the exact mechanism of how fluxing results in the reduction of heterogeneous nucleation sites is largely unknown [63]. Despite uncertainties regarding the underlying mechanism, the fluxing method has been repeatedly shown to produce extremely deep supercooling in a variety of materials: 415 K in pure Ge [64], 460 K in the Fe$_{83}$B$_{17}$ near eutectic alloy [65], and 465 K in Co$_{80}$Pd$_{20}$ [29]. The melt fluxing method is also the only method which has been able to produce a binary bulk metallic glass at cooling rates below 10 K/s: a 6 mm diameter sample of Pd$_{81}$Si$_{19}$ has been prepared into a glassy state with a cooling rate of only 8 K/s [66].

The types of investigations that can be carried out with flux immersion methods are very similar to those which can be carried out using the droplet dispersion method, except that rather than being limited to sample sizes below 100 μm, the nucleation, calorimetry, and microstructural investigations can be performed on bulk samples. The ability to process bulk samples has made this an attractive method for researches studying bulk metallic glasses [66–68]. However, this method also carries with it the same sort of limitations as droplet dispersion with respect to performing thermophysical property measurements, except the cause of the limi-

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$^2$Pyrex is the trade name for Corning 7740 glass, which has a nominal composition of 80.6% SiO$_2$, 13.0% B$_2$O$_3$, 4.0% Na$_2$O, and 2.3% Al$_2$O$_3$
tion is different. While the droplet dispersion method is limited due to the large, non-uniform population of droplets being studied, the flux immersion method is limited due to the difficulties involved in separating the sample contributions and the flux contributions to any of the measured thermophysical properties.

2.2.2 Levitation Techniques

The rapid quenching, droplet dispersion, and flux immersion methods described above allow for a variety of phenomena to be studied, including glass formation, the formation of metastable crystalline and quasicrystalline phases, as well as calorimetry, nucleation, and microstructural studies relating to solidification from the deeply supercooled liquid. However, they are still limited when it comes to performing measurements of a variety of thermophysical properties. To get around these limitations, several types of levitation techniques have been developed. Here we will introduce the electromagnetic, aerodynamic, and electrostatic levitation techniques. The basic ideas behind the various thermophysical property measurements for each of these techniques are largely the same, and their implementation for ESL systems will be explained in detail in Ch. 3. Here we will focus on the basic principles of operation of the three levitation techniques, and discuss their strengths and weaknesses.

2.2.2.1 Electromagnetic Levitation

In electromagnetic levitation (EML), sample levitation is achieved through the mutual magnetic repulsion between a sample and a set of excitation coils. The coils are powered by a high frequency, high current power supply, and the alternating magnetic field generated by the power supply results in eddy currents being induced in the sample. The induced eddy currents produce two effects. First, they produce their own magnetic field which, due to Lenz’s Law, will oppose the externally applied magnetic field. The two opposing magnetic fields result in a force being applied to the sample which, with proper coil design, will result in the sample experiencing an upward force. Provided that the force of the magnetic interaction is equal to or greater than the sample weight, the interaction will result in sample levitation. The second effect is that, through the action of ohmic heating, the eddy currents will produce a
large amount of heat dissipation in the sample which increases the sample temperature. The excitation coils are wound into the shape of a cylinder, either straight or with a slightly conical shape, and typically contain 5–8 primary windings with an additional 1–2 counterwindings at the top of the coil (see Fig. 2.9 (Right)). The alternating current in the coil is generated using an induction heating power supply, with a typical frequency on the order of 0.3–1 MHz and a typical current of 300-500 A. The precise shape of the coil and values of the excitation frequency and current will depend on the properties of the sample, namely the sample size, density, and electrical resistivity.

The functional forms for the levitation force and heater power in EML can be derived analytically [69], resulting in the following:

\[
F_{EML} = -\nabla \left( \frac{B^2}{2\mu_0} \phi G(x) \right)
\]

\[
HP_{EML} = \frac{B^2}{2\mu_0} \omega \phi H(x)
\]

where \(F_{EML}\) is the levitation force, \(HP_{EML}\) is the applied heating power, \(B\) the magnetic field generated by the coils, \(\omega\) is the angular frequency of the applied current, \(\mu_0\) is the permeability of free space, and \(\phi\) is the sample fill factor, i.e. the ratio of the sample volume to the magnetic
field volume. The functions $G$ and $H$ represent the efficiency of the alternating current in terms of producing sample levitation and heating, and are closely related to the real and imaginary components of the sample’s complex susceptibility, respectively. The exact forms of $G$ and $H$ are:

$$G(x) = \frac{3}{4} \left( 1 - \frac{3}{2x} \sinh 2x - \sin 2x \right)$$

$$H(x) = \frac{9}{4x^2} \left( x \frac{\sinh 2x + \sin 2x}{\cosh 2x - \cos 2x} - 1 \right)$$

where $x = a/\delta$, where $a$ is the sample radius and $\delta$ is the classical skin depth. A plot of $G$ and $H$ as a function of $x$ is shown in Fig. 2.9 (Left). In most cases, the amount of heat which is dissipated in the samples is more than enough to heat the samples above their melting temperature and, in fact, attempting to regulate the sample temperature solely through modification of the induction heater current provides only a small amount of variability (the power supply frequency is usually fixed for a given coil). Furthermore, changing the current will result in an associated change in the levitation force, which will cause the sample to move vertically within the levitation coil. To accomplish temperature variability, a stream of cooling gas must be applied to the sample to control the temperature via convection. To reduce the extent to which the cooling gas must be applied, and to ensure that an ample force can be applied to the sample to achieve levitation, it is desirable to have a sample radius to skin depth ratio of 5 or greater. For a power supply operating at 500 kHz, and assuming a sample resistivity of 100 $\mu$Ω·cm, the minimum sample diameter works out to be 5.7 mm. For this reason, most of the samples studied using EML have diameters in the 6–10 mm range.

EML has been used to perform a wide range of thermophysical property measurements on a wide variety of samples: density and thermal expansion coefficients [70], surface tension [34], viscosity [71], electrical resistivity [72], magnetic susceptibility [33], thermal conductivity [73], enthalpy and specific heat [74, 75], spectral emissivity [76], and atomic structure via x-ray and neutron diffraction [77]. In addition to thermophysical properties, EML has also been used to perform studies of nucleation kinetics through the statistical analyses of maximum supercooling [78], and it has also been extensively used to study the solidification velocity and microstructure of metals as a function of the supercooling achieved before solidification. A
rather thorough review of much of the work that has been performed using EML is provided in Ref. [46].

There are a number of benefits to using EML. For one, the levitation system itself is rather simple. The nature of the magnetic interaction between the levitation coils and the sample results in a natural minimum in the interaction potential, and therefore stable levitation can be achieved without the need for a sophisticated feedback system. Another major benefit of EML is actually a result of the cooling gas requirement. First, because the system operates near atmospheric pressure, the evaporation rate of liquid metals is approximately $10^5$–$10^6$ times lower than what would be experienced under conditions of high vacuum [79]. This allows materials that would otherwise be considered too volatile to not only be processed, but to be processed well above their melting temperatures. Second, the cooling gas is typically either He or a He-H$_2$ mixture with a H$_2$ content of 4–20%, and the gas mixture can be purified using a liquid nitrogen cold trap in combination with an silica-gel Oxisorb system to produce very low levels of O$_2$ and H$_2$O impurities. As will be discussed in Ch. 5, such a gas mixture, in combination with high temperature processing, can be used to reduce most metal-oxides that would otherwise be stable and act as heterogeneous nucleation sites. The combination of reduced evaporation, high temperature processing, and the ability to use a high purity reducing gas, results in a system that has the capacity to produce very high purity, oxide free samples in-situ. For these reasons, EML has been used to process a very wide variety of metallic samples, and tends to achieve greater levels of supercooling compared to ESL.

EML does have its drawbacks. Because the levitation force relies on being able to induce eddy currents in the samples, the types of materials which can be studied are limited to metals or materials that have metallic conductivity in the liquid state (e.g. Si and Ge). The levitation coils may also obstruct the view of the sample, adding to the difficulty of performing many of the thermophysical property measurements. Perhaps the most significant drawback is the way in which the levitation force perturbs the sample. The nonuniformity of the levitation force usually results in a distortion of the sample shape: the samples are not only non-spherical, but may not even have axial symmetry. Furthermore, the levitation force results in a strong electromagnetic stirring of the liquid samples, which may result in turbulent fluid flow. The combination of
shape distortion and fluid flow can make it very challenging to perform accurate thermophysical property measurements under terrestrial gravity, and in fact measurements of viscosity are not possible under terrestrial gravity. Most of these problems can be alleviated if the EML processing is carried out under microgravity conditions, such as those that can be achieved via parabolic flight (a.k.a. the vomit comet) as well as on the International Space Station. While such microgravity experiments have been carried out, they have obvious complications in terms of high cost and limited experiment time. One last, comparatively minor, drawback to EML is that a given coil geometry will not work well for every type of sample. Samples with varying ranges of density and electrical conductivity will require slightly different coil geometries to achieve optimal levitation stability and sample positioning. While it may be possible to use numerical simulation to develop new coil designs, most of this effort is carried out through trial and error.

2.2.2.2 Aerodynamic Levitation

In aerodynamic levitation, sample levitation is achieved through a combination of the momentum transfer and the buoyancy that occur when a sample is placed directly above a vertically oriented gas jet. The levitation force which is applied to the sample is described by [80]:

\[
F_{\text{aero}} = \int \left( \frac{1}{2} \rho u^2 + p \right) \, dA
\]

(2.24)

where \(\rho\) is the gas density, \(u\) is the gas flow rate, \(p\) is the gas pressure, and \(A\) is the sample surface area. The first term in the integrand corresponds to the momentum transfer between the gas jet and the sample, and the second term corresponds to the buoyant force caused by a pressure differential in the vertical direction. The relative contribution of these two terms to the total levitation force will depend on the exact shape of the nozzle that is used to direct the gas. A wide variety of nozzle shapes have been explored, from straight (free-jet) nozzles to converging-diverging conical nozzles and a range in between [81,82], some of which are shown in Fig. 2.10. Levitation using free jets takes place primarily via momentum transfer from the gas to the sample, and therefore the first term in the integrand in Eq. 2.24 dominates. Levitation using conical nozzles is due primarily to the buoyant force caused by the pressure differential.
Figure 2.10  (Left) Several different nozzle configurations considered for use in an aerodynamic levitation system. (Right) A metal oxide drop being aerodynamically levitated in a flow of high-purity argon through a conical nozzle at Oak Ridge National Laboratory.

along the sample surface, and therefore the second term dominates. These differences are largely responsible for the more frequent use of conical nozzles over free jets, because the buoyant force can be generated using a lower gas flow rate which results in reduced temperature gradients and lower levels of turbulent flow being induced in the liquid samples. For this reason, aerodynamic levitation is quite frequently referred to as conical nozzle levitation (CNL).

As with EML, the levitation force in CNL contains a natural minimum in the interaction potential, and therefore levitation can be achieved without the need for a sophisticated feedback mechanism. Additionally, because the levitation force does not depend on the electrical properties of the samples, CNL can be used to levitate metals, semiconductors, and insulating materials such as ceramics equally well. That being said, stable levitation using CNL is most easily achieved for materials with a low density, and therefore much of the effort with CNL has been focused on the study of metal-oxide ceramics and, to a lesser extent, other low density elements and alloys. The most common application of CNL has been for the structural investigations of metal-oxide ceramics using x-ray [83] and neutron [84] diffraction.
methods. In addition to the structure measurements, there have also been efforts to implement measurements of thermophysical properties such as mass density [85], surface tension [86], viscosity [87], and electrical resistivity [88]. A relatively recent review of the applications of CNL can be found in Ref. [80].

While CNL has been successfully used to perform groundbreaking structural measurements on metal-oxides at very high temperatures, it does have several drawbacks. The flowing levitation gas, which approaches the sample from the bottom, in combination with the CO$_2$ laser heating from above, can result in temperature gradients in samples on the order of several 10’s of degrees. The levitation gas can also result in turbulent fluid flow and induce sizable oscillations in liquid samples. Furthermore, the nozzles used in CNL obstruct the view to the sample (see Fig. 2.10). The combination of these drawbacks have led to CNL being used far less than EML or ESL for the purpose of thermophysical property measurements on high temperature liquids, in particular liquid metals. As a final comment, while CNL does result in a levitation force with a naturally occurring minimum, the stability of levitated samples will depend on the sample size, mass density, the composition and flow rate of the gas stream, as well as the precise shape of the nozzle. Just as with EML, the best configuration for achieving stable levitation with CNL is determined through trial and error.

### 2.2.2.3 Electrostatic Levitation

In electrostatic levitation (ESL), levitation is accomplished through the electrostatic force experienced by a charged sample when placed in an electric field. The levitation force is given by:

$$F_{esl} = QE = Q \frac{V}{d}$$

where $Q$ is the charge, $E$ the electric field, $V$ the electric potential applied to the active (usually top) electrode, and $d$ is the electrode spacing between the active electrode and a grounded (bottom) electrode. In most cases, the samples are initially charged capacitively through application of the electric field while the sample is in contact with the grounded electrode. When the sample has become sufficiently charged, the electrostatic force will exceed the sample’s weight and the sample will launch. In some cases, where the conductivity of the sample does
not allow for capacitive charging, the samples may be initially charged via thermionic emission by heating the samples to $\sim 1500$ K in the presence of the electric field; this is referred to as a “hot launch”. Once levitated, sample charge is maintained at low temperatures through application of UV illumination to produce photoelectric charging, and at high temperatures the charge is stabilized through thermionic emission. Because a three-dimensional potential minimum does not exist in this situation (Earnshaw’s theorem), a feedback system is necessary to constantly monitor the sample position and to modify applied voltage to maintain stability.

While a 3D potential minimum cannot exist, it is possible to create a 2D potential minimum in the horizontal plane through proper design of the levitation electrodes. In such a situation, it is possible to achieve stable levitation through single axis vertical feedback, although horizontal feedback may be necessary to damp unwanted oscillations. Because the nature of electrostatic fields and forces is quite simple and easy to model, numerical simulation is a powerful tool for designing electrode configurations. Two different styles of ESL electrodes are shown in Fig. 2.11. Typical values for the electrode spacings, levitation voltages, and sample charge are 8–12 mm, 10–30 kV, and 0.5–1.5 nC, respectively. Sample sizes are typically 2–3 mm, although 5–6 mm samples are used for Neutron-ESL studies.
There are many advantages to using ESL. Because sample charging can be accomplished both capacitively and thermionically, levitation can be accomplished for metals, semiconductors, and oxide materials. There are also no restrictions on the density of samples: materials with densities as low as pure silicon (2.33 g/cc) [89] and as high as pure osmium (22.61 g/cc) [90] have been successfully processed in the ESL, including measurements of key thermophysical properties. Essentially, provided that there is a sufficient combination of sample charge and applied voltage, any material can be levitated and processed. When it comes to performing thermophysical property measurements, ESL is particularly advantageous compared to EML or CNL. The nature of the levitation force in ESL is much less perturbing to the sample, and so concerns about induced fluid flow or unwanted sample oscillations are much less significant. ESL processed samples tend to take on a highly spherical shape, and what distortion does occur is generally symmetric about the vertical axis and can be easily accounted for. Finally, the view to the sample is unobstructed over a large range above and below the horizontal plane. These characteristics have made it possible to develop and successfully apply methods for measuring a wide array of thermophysical properties: density and thermal expansion coefficients [91, 92], specific heat [93], surface tension and viscosity [94, 95], electrical resistivity [96] (also the focus of Ch. 4), spectral emissivity [97], mechanical creep resistance [98], and atomic structure via x-ray [99, 100] and neutron [101, 102] diffraction methods. Reviews of the progress with ESL design and thermophysical property measurement can be found in Refs. [103–105], and many of the major findings with ESL are also reported in Refs. [46, 80].

Despite the successes that have been achieved, ESL does have a number of drawbacks. As already mentioned, unlike EML or CNL, the nature of the levitation force in ESL does not contain a three-dimensional minimum in the interaction potential. Therefore a sophisticated feedback system is necessary to constantly monitor the position of the sample and update the high voltage amplifier outputs to maintain sample stability. While such a feedback system is certainly possible to accomplish, it significantly increases both the cost and the complexity of ESL systems. The complexity of the feedback system, in terms of the number of the individual components, their alignment, and their interconnections, makes it particularly challenging to incorporate ESL systems into x-ray and neutron beamlines for the purpose of structural mea-
surements. As far as the processing of samples is concerned, the greatest drawback of ESL is that the samples must be processed under high vacuum conditions for the prevention of dielectric breakdown. Because of the high vacuum, ESL processed samples are highly susceptible to evaporative mass loss. Having to accommodate the vapor pressures of the elements results in limitations with respect to what types of elements and alloys can be studied, and for those materials that can be studied there are upper limits on the accessible temperature ranges as well as the total duration of the experiments. Furthermore, as will be discussed in Ch. 5, most of the samples that have been processed in the ISU-ESL have been found to contain oxide impurities that are insoluble and very stable, and processing under high vacuum conditions within the accessible temperature ranges of the samples is not sufficient to remove these impurities\(^3\). The presence of these oxide impurities has proven to be the single greatest limiting factor in terms of attempting to perform thermophysical property measurements into the deeply supercooled state on ESL processed samples. If ESL processing of samples under a reducing gas mixture of He-H\(_2\) or Ar-H\(_2\) was possible (in a similar manner to EML), then the limitations associated with evaporation and contamination could be largely overcome.

While the most limiting drawbacks of ESL are associated with the high vacuum that is typically required, it should also be mentioned that a hybrid aerodynamic-electrostatic levitation system has been developed [106] that allows for improved ESL studies on ceramic materials. The hybrid system allows samples to be initially levitated via CNL. With the application of laser heating, the sample temperatures are increased until thermionic emission has resulted in sufficient charging of samples, at which point the levitation mechanism is transitioned from CNL to ESL, allowing for high quality thermophysical property measurements on a variety of ceramic materials. As opposed to operating under high vacuum, the hybrid system operates under 3–5 atm of either N\(_2\) or a N\(_2\)-O\(_2\) mixture. While this system demonstrates the possibility of performing ESL processing of ceramics under pressurized conditions, such a system will not work as well for the processing of metals. Metals processed in such an environment would almost certainly form metal-nitrides or metal-oxides. Unfortunately, attempting such

\(^3\)This much can be said based on first hand experience while trying to process samples in the ISU-ESL. However, based on conversations with researchers from Washington University, as well as consistent patterns in the available literature, this type of sample contamination is not an isolated problem.
pressurized ESL processing with a noble gas or noble gas-H₂ mixture is quite challenging, due to the much weaker dielectric strength of noble gases compared to molecular gases. Dielectric breakdown is discussed in more detail in Sec. 3.9.
CHAPTER 3. ELECTROSTATIC LEVITATION

In this chapter aspects of sample levitation and thermophysical property measurement methods using the electrostatic levitation (ESL) technique will be discussed in detail. Particular attention has been paid to many aspects of the levitation process itself. During construction of the ISU-ESL laboratory, several observations were made regarding the behavior of levitated samples for which there existed no clear explanation. An effort has been made to understand those observations, and to improve those aspects of the levitation system.

3.1 Levitation System Overview

A flow chart outlining key components of the levitation control system is shown in Figure 3.1. A spherical sample, typically 2-3 mm in diameter, is positively charged and maintained in a levitated state via the electric field produced between a pair of vertically spaced electrodes. Because the electrostatic force can only generate unstable equilibrium points (Earnshaw’s theorem), a control system with active feedback is necessary to maintain the sample at a fixed position. The first step in the control system is to measure the location of the sample within the electrode gap by projecting a shadow of the sample onto a position sensitive detector (PSD). Two sets of backlights and PSDs are used, arranged orthogonally, allowing the the three-dimensional position of the sample to be determined. The analog signal from the PSDs is then digitized and read by a computer whose sole task is to run the control algorithm. The control algorithm compares the instantaneous sample position data with the position set points, and determines precisely how to adjust the high voltage amplifiers to maintain the sample at a stable position. The control algorithm used in the ISU-ESL was originally developed by researchers at the German Aerospace Center (DLR) [107], and can be thought of as a modified
proportional-integral-derivative (P-I-D) controller whose stability is improved by comparing instantaneous measurements with expected results based on prior measurements and a well-defined physical model of the system. The results from the control algorithm are then sent to the high voltage amplifiers, whose output changes accordingly. In addition to the vertical amplifier, two sets of lateral electrodes are used to maintain horizontal stability. The feedback rate for the system is 500 Hz.

The computer used to run the control algorithm (the Target) is separate from the computer used to develop and monitor the algorithm (the Host). This separation of duties provides a buffer to protect the levitation system. Because the Host computer is used for multiple duties, including video monitoring and control of other peripherals, there is a non-zero possibility of the Host computer crashing during an experiment. By running the control algorithm on a dedicated, independent machine, the levitation system will not face an interruption in the event of a crash from the Host computer.

3.2 Sample Launching & Levitation

3.2.1 Initial Sample Charging

In most cases the sample is initially charged via electrostatic induction. The initial sample charge of the sample can be made to be either positive or negative, depending on the sign of the applied voltage. However, because natural sample charging mechanisms such as the photoelectric effect and thermionic emission result in positive charge accumulation, the initial sample charge is made positive as well. It then follows that the sign of the applied voltage used for levitation is negative, and this should be understood throughout the following discussion.

For simplicity, we consider the case of a spherical sample placed on the bottom (grounded) plate of a parallel plate capacitor (Fig. 3.2a). For a conducting sample of radius $a$ and a capacitor spacing $h$, where $a \ll h$, it can be shown [108] that when a voltage $V$ is applied to the top plate, the induced charge and associated force acting on the sample are:

$$Q_0 = -\alpha 4\pi \varepsilon_0 \frac{V}{h} a^2$$

(3.1)
Figure 3.1 Flow diagram of key components for the levitation control system.

\[ F_E = \beta Q_0 E_0 = \alpha \beta 4 \pi \epsilon_0 \left( \frac{V}{h} \right)^2 a^2 \]  

(3.2)

where \( Q_0 \) is the net charge accumulated by the grounded sample, \( F_E \) is the electrostatic force, \( \epsilon_0 \) is the permittivity of free space, \( \alpha \approx 1.645 \) and \( \beta \approx 0.832 \). The constant \( \alpha \) is representative of the specific geometry of a conducting sphere on a conducting plane, and \( \beta \) represents the contribution of image forces between the sample and the bottom plate.

For the sample to launch successfully, the electrostatic force must overcome the gravitational force acting on the sample. Setting Eq. (3.2) equal to \( F_g = mg \), we can derive the minimum voltage required to launch a sample:

\[ V_{\text{launch}} = -\frac{h}{2a} \sqrt{\frac{mg}{\alpha \beta \pi \epsilon_0}} = h \sqrt{\frac{\alpha \rho g}{3\alpha \beta \epsilon_0}} \]  

(3.3)

where \( m \) is the sample mass, \( \rho \) the sample density, and \( g \) the gravitational acceleration. Just
Figure 3.2  Schematic diagram of a sample during (a) launching and (b) levitation stages. The dotted circles are the relevant image charges which must be considered.

After the electrostatic force overcomes the gravitational force, the sample will launch and the electrical connection between the sample and the grounded electrode will be broken. At this point, the total charge accumulated by the sample can be determined via Eq. (3.1) by setting $V = V_{\text{launch}}$, resulting in an expression for the initial charge of a levitated sample:

$$Q_{s,i} = 4\pi \sqrt{\frac{a^5 \rho g \alpha \epsilon_0}{3\beta}} \quad (3.4)$$

After the sample has launched and is stably levitating at the midpoint between the electrodes, the image charge factor $\beta$ in Eq. (3.2) will no longer be needed, as image forces on the top and bottom plates will cancel. Thus, the voltage required for stable levitation with the sample located precisely at the midpoint of the electrodes will be reduced by a factor of $\beta$ compared to the voltage required for launching:

$$V_{\text{lev},i} = h \sqrt{\frac{a \rho g}{3\alpha \epsilon_0}} = \beta V_{\text{launch}} \quad (3.5)$$

However, if the sample is not located precisely at the midpoint of the electrodes, the image charges will not completely cancel. As a result, the levitation voltage required to stably levitate a sample will be a function of sample’s vertical position within the electrode spacing, and will vary inversely as the sample position (that is to say, levitating a sample above the midpoint will require a voltage smaller than $V_{\text{lev},i}$, and vice versa). Taking into account only the primary images in the top and bottom electrodes (Fig. 3.2b), and assuming each of the charges to be
point charges, the total electrostatic force acting on a levitated sample is approximately

\[ F_{E,\text{lev}} = -Q_s \frac{V}{h} + \frac{Q_s^2}{16\pi\varepsilon_0} \left( \frac{1}{(h-z)^2} - \frac{1}{z^2} \right) \]  

(3.6)

where \( Q_s \) is the total charge on the sample, \( V \) is the voltage applied to the top electrode, and \( z \) is the position of the sample as measured from the bottom electrode to the center of the sample.

To provide some numerical context to the initial charging, launching, and levitation processes, representative values of sample and electrode parameters have been tabulated in Table 3.1. The quantities \( Q_{s,max} \) and \( V_{\text{lev,min}} \) are the maximum steady state charge and minimum steady state levitation voltage for a sample, respectively, both of which are discussed in the following subsection.

Table 3.1 Some typical values of sample properties and levitation parameters relevant to launching and levitating a sample.

<table>
<thead>
<tr>
<th>Sample and Electrode Parameters</th>
<th>Calculated Charges &amp; Voltages</th>
</tr>
</thead>
<tbody>
<tr>
<td>( a ) 1.25 mm</td>
<td>( Q_{s,i} ) 0.47 nC</td>
</tr>
<tr>
<td>( \rho ) 7.85 g/cc</td>
<td>( Q_{s,max} ) 0.57 nC</td>
</tr>
<tr>
<td>( m ) 64.2 mg</td>
<td>( V_{\text{launch}} ) -16.3 kV</td>
</tr>
<tr>
<td>( h ) 1.0 cm</td>
<td>( V_{\text{lev,i}} ) -13.5 kV</td>
</tr>
<tr>
<td></td>
<td>( V_{\text{lev,min}} ) -11.0 kV</td>
</tr>
</tbody>
</table>

**3.2.1.1 Insights: Peculiar Sample Charging Behavior**

The details so far regarding the initial charging and voltage requirements for levitation have been discussed previously in the literature (for example in Ref. [46]). However, details regarding the behavior of the sample charge after launching have not received the same level of analytical treatment, and as such they have been the cause of discussion and some confusion among those working with ESL systems. For instance, what determines the steady-state charge level of a levitated sample? If ultraviolet light is applied to a levitated sample, the levitation voltage can be seen to decrease, indicating an increase in the sample charge; this makes sense. But the voltage reduction is typically only 1–2 kV, at which point the sample charge seems to saturate. How is the saturation charge determined? Furthermore, on numerous occasions it
has been observed that the application of UV light causes the levitation voltage to increase, indicating a reduction in sample charge; at first glance this does not make sense. To provide insight into this behavior, further analytical and numerical analyses have been carried out.

To fully understand the dynamic and steady state charge behavior of levitated samples, consideration must be given to the distribution of the surface charge on the samples. Due to the presence of the electric field, a sample’s charge will not be uniformly distributed over its surface area. Rather, the surface charge will experience polarization, with positive charge accumulating at the top of the sample. The solution to the problem of a conducting sphere in a uniform electric field is fairly straightforward [109], and the result for the surface charge density is:

$$\sigma(\theta) = 3 \varepsilon_0 E \cos \theta + \frac{Q_s}{4\pi a^2}$$  \hspace{1cm} (3.7)

where $\sigma$ is the surface charge density, $\theta$ is the polar angle as measured from the vertical axis to the radial direction (see Fig. 3.3), $E$ is magnitude of the vertically directed electric field, $Q_s$ the total surface charge, and $a$ the sample radius. The crossover angle, at which the surface charge on the sample changes from positive to negative, is found by setting Eq. (3.7) equal to zero and solving for $\theta$:

$$\theta_c = \arccos \left( \frac{Q_s h}{12\pi \varepsilon_0 V a^2} \right)$$  \hspace{1cm} (3.8)

When the crossover angle is $\theta_c = \pi$, the entire surface of the sample will be covered with positive charge. As a consequence, the direction of the electric field at all points on the sample...
surface will be pointing radially outward (for a metal, \( E = (\sigma/\epsilon) n \)). This means that the force exerted on any electron near the sample surface will be directed radially inward, toward the sample; at this point the sample has reached its maximum possible charge. Solving Eq. (3.8) for \( Q_s \) and setting \( \theta_c = \pi \) provides an expression for the sample charge in this situation:

\[
Q_{s,\text{max}} = -12\pi \epsilon_0 \frac{V}{h} a^2
\]  

(3.9)

If \( Q_{s,\text{max}} \) is taken as the charge of the sample and used to satisfy the levitation equation \( F = QE = mg \), explicit expressions for the values of the maximum sample charge and minimum levitation voltage can be determined

\[
Q_{s,\text{max}} = 4\pi \sqrt{a^5 \rho g \epsilon_0} = \sqrt{\frac{3\beta}{\alpha}} Q_{s,i} \simeq 1.23 Q_{s,i}
\]  

(3.10)

\[
V_{\text{lev},\text{min}} = \frac{h}{3} \sqrt{\frac{a \rho g}{\epsilon_0}} = \sqrt{\frac{\alpha}{3\beta}} V_{\text{lev},i} \simeq 0.81 V_{\text{lev},i}
\]  

(3.11)

And thus we find that the maximum charge a sample can hold is indeed greater than the charge initially gained during the launch according to Eq. 3.4.

The proper way to think about \( Q_{s,\text{max}} \) is that it corresponds to the steady-state charge level for a sample under normal processing conditions. The total positive charge on a sample can be reduced by the flow of positive ions from the sample to the top electrode (in the form of positively charged, outgassing atmospheric molecules), or by the flow of electrons from the top electrode to the sample. The total positive charge can be increased by the flow of electrons from the sample to the bottom electrode. Provided that the number of electrons generated at the sample surface is greater than the number of electrons generated at the top electrode (as is the case for thermionic emission and a properly aligned UV source) plus the number of positively charged outgassing atmospheric molecules, then the steady-state flow of charge will be achieved when \( Q_s = Q_{s,\text{max}} \).

Now that an understanding of the steady-state charge level has been established, insight can be gained into why, on occasion, UV illumination of a newly levitated sample causes the levitation voltage to increase rather than decrease as expected. Essentially what happens is that, during the launch, the sample becomes overcharged with respect to \( Q_{s,i} \) as described by Eq. 3.4. In almost every case where this behavior has been observed, a mechanically actuated
post was used to raise the sample above the plain of the bottom electrode before launching. Based on Eq. 3.4 one would not expect this to affect the sample charge, as $Q_{s,i}$ is independent of the gap size $h$. However, by raising the sample above the plain of the electrode, Eq. 3.4 becomes invalid because it was derived under the assumption of a sphere in contact with a plane, which is no longer the case. To investigate the effect of raising a sample on the post, finite element analysis (FEA) was performed to numerically determine the levels of charge and voltage required for launching a sample.

The FEA analysis was carried out using the commercial software package COMSOL, using a 2-dimensional axisymmetric model of the electrodes and sample. The top and bottom electrodes were modeled as 150 mm diameter discs spaced 8-10 mm apart, the sample diameter considered was 2.5 mm, and multiple radii and heights were considered for the post. The finite element mesh was a free triangular style with minimum element size of $2\ \mu$m, maximum element size of $500\ \mu$m, and an element growth rate of 1.05; elements near areas of tight geometry (e.g. where the sample contacts the electrodes) tend to be close to the minimum size, while elements near open or unchanging geometry tend toward the maximum size. The potentials of the bottom electrode, post and sample were fixed at ground, while the top potential was varied until the total electrostatic force on the sample was equal to the sample’s weight (the launch condition). This procedure was carried out for multiple configurations of electrode separation and post height, and the top electrode voltage and sample charge for each configuration were recorded.

Table 3.2 shows the results of the FEA simulations as well as the calculated results based on the analytical expressions derived thus far. The analytical expressions can only be applied to those situations where the post height is zero, but they still serve as a point of comparison to check the accuracy of the FEA results. As can be seen from the tabulated values, the analytical and FEA results for the sample charge and launch voltage when the post height is zero are in very good agreement, differing by less than 0.4% and demonstrating the validity of the FEA method. A number of interesting trends be identified throughout the results. First, as the height of the positioning post is increased, not only does the launch voltage decrease as expected, but the total charge accumulation on the sample increases as well. For a given post height, reducing the width of the post results in a sizable increase in the accumulated
Table 3.2  Comparison of analytical and FEA results for the sample charge and top electrode voltage required to launch a sample in a variety of geometries. Sample parameters were $a = 1.25$ mm and $\rho = 7.85$ g/cc.

<table>
<thead>
<tr>
<th>Launch Geometry</th>
<th>Analytical Results</th>
<th>FEA Results</th>
</tr>
</thead>
<tbody>
<tr>
<td>$h$ (mm)</td>
<td>$z_{post}$ (mm)</td>
<td>$r_{post}$ (mm)</td>
</tr>
<tr>
<td>8</td>
<td>0</td>
<td>1.5</td>
</tr>
<tr>
<td>8</td>
<td>1</td>
<td>1.5</td>
</tr>
<tr>
<td>8</td>
<td>1</td>
<td>0.75</td>
</tr>
<tr>
<td>9</td>
<td>1</td>
<td>1.5</td>
</tr>
<tr>
<td>9</td>
<td>1</td>
<td>0.75</td>
</tr>
<tr>
<td>9</td>
<td>2</td>
<td>1.5</td>
</tr>
<tr>
<td>9</td>
<td>2</td>
<td>0.75</td>
</tr>
<tr>
<td>10</td>
<td>0</td>
<td>1.5</td>
</tr>
<tr>
<td>10</td>
<td>1</td>
<td>1.5</td>
</tr>
<tr>
<td>10</td>
<td>1</td>
<td>0.75</td>
</tr>
<tr>
<td>10</td>
<td>2</td>
<td>1.5</td>
</tr>
<tr>
<td>10</td>
<td>2</td>
<td>0.75</td>
</tr>
<tr>
<td>10</td>
<td>3</td>
<td>1.5</td>
</tr>
<tr>
<td>10</td>
<td>3</td>
<td>0.75</td>
</tr>
</tbody>
</table>

charge, while the change in the launch voltage is very minor. It is also very interesting to note that, for a given sample-to-top electrode distance, the accumulated charge is greater and the launch voltage is lower for geometries with greater electrode spacing. For instance, consider the geometries designated as 8-0-1.5 and 10-2-1.5 as shown in Fig. 3.4. The spacing between the sample and top electrode in each situation is the same, 5.5 mm, but the top-bottom electrode spacing is clearly different. Surprisingly, the geometry with the 10 mm electrode spacing results in a greater charge accumulation and lower launch voltage than the geometry with the 8 mm electrode spacing. These results indicate that the sample charging process is highly dependent on the curvature of the electric field which is caused by the protrusion of the sample and post into the electrode gap.

Finally, the FEA results confirm what was hypothesized earlier regarding the peculiar de-charging of some samples when exposed to UV light: that in certain situations, when a sample is raised above the plane of the bottom electrode before launching, the amount of charge it
Figure 3.4  Equipotential map of the electric potential derived from FEA simulations. The sample diameter is 2.5 mm and the voltage on the top electrode set to the launch voltage. (Left) Gap size 8 mm with sample on bottom electrode. (Right) Gap size 10 mm with sample raised 2 mm above bottom electrode. The equipotential spacing is 1 kV.

accumulates prior to launch exceeds the steady-state maximum charge allowed for a levitated sample. Using Eq. 3.10, the steady-state maximum charge for each of the situations described in Table 3.2 is found to be $Q_{s,max} = 0.57 \text{ nC}$. For three of the launch geometries, namely 9-2-0.75, 10-2-0.75, and 10-3-0.75, the total charge accumulated by the sample prior to launching exceeds the steady-state maximum charge. When the UV illumination is applied in one of these situations, some of the UV light will strike the top electrode (either directly or as reflected), resulting in a flow of electrons from the top electrode to the sample. This results in a reduction of the sample charge and an increase in the levitation voltage, up until the point when the sample charge has been reduced to the steady-state maximum.

3.2.2 Electrode Design

Proper design of the ESL electrodes is important for maximizing the stability of a levitated sample. While the feedback system allows for the active control of the applied voltage, improper design of the electrodes can result in sample instabilities which are difficult to overcome. To ensure that the electrode geometry allows for the best stability possible, FEA simulations have
been carried out to model the electric field produced within the electrode gap. These simulations have guided the redesign of electrodes used in the ISU-ESL as well as the Neutron-ESL system stationed at the Spallation Neutron Source at Oak Ridge National Laboratory.

A schematic of the original electrodes is shown in Fig. 3.5, and is similar to the DLR design shown in Fig. 2.11. The top and bottom electrodes are both cylindrical, with diameters of 20 mm and 7 mm, respectively. The lateral electrodes are comprised of four equal ring segments placed around, and at the same height as, the bottom center electrode. The lateral electrodes have a 8 mm inner radius and 15 mm outer radius, with 7 mm of space between the individual segments. Lateral electrodes opposite each other are paired, one grounded and the other floating at \( \pm 5 \) kV, and are used to provide sample stability in the horizontal plane.

The original electrode design worked reasonably well, as samples could be launched and levitated in a stable manner. However, the chance that a launch would result in a failure was quite high, on the order of 30–40%. The failed launches seemed to be caused by lateral motion in the samples. If the samples were not perfectly centered during the launch, they had a tendency fly out of the side of the electrode spacing, being lost in the process. To gain insight into why these launches failed, the electric field distribution was modeled using FEA in a similar manner to that described in the previous section. A portion of the results are shown in Fig. 3.6, which shows the equipotential lines that arise as a result of the electrode geometries. The electric field in Fig. 3.6 points upward along the vertical axis (at lateral distance = 0), and is directed perpendicularly the equipotential lines. As a result, lines that slope downward while moving away from the axis will result in a laterally outward force on the sample, and

![Figure 3.5 Schematic of the electrodes used in the ISU-ESL: (a) top view of the original bottom electrodes; (b) side view the original electrodes; (c) side view of the improved electrodes. The dimensions are actual-size.](image-url)
lines that slope upward will result in a laterally inward force. Focusing on the lower portion of the plots in Fig. 3.6(Left), the field distribution of the original electrode configuration was such that a slight outward force would be experienced by samples during the launch if they were not perfectly centered on the axis of the electrodes. This matches the observation that launches tended to fail because samples would fly outward from the electrodes. To resolve this problem, the geometry of the electrodes was modified as shown in Fig. 3.5c. By reducing the diameter of the top electrode and increasing the diameter of the bottom center electrode, the modified electric field distribution results in a natural restoring force towards the center of the electrode gap, as shown in Fig. 3.6(right). Based on these results, new electrodes were constructed and tested for levitation and launch stability. The new electrodes provide much more reliable launching and generally better levitation stability, and failed launches are now a very rare occurrence. In fact, the natural lateral restoring force created by the new electrode geometry is so significant that launches are successful and levitation can be achieved even when the lateral amplifiers are not activated. This is direct evidence of the concept of levitation via single-axis feedback. While such single-axis levitation is possible, the samples have been found to exhibit lateral oscillations on the order of 0.1–1 mm in amplitude. These oscillations result from an off-center sample position during the launch in combination with the natural restoring force of the electrodes. Therefore, the lateral amplifiers are still required to damp the lateral oscillations.

3.2.3 Sample Position Measurement

The first step in the active control process is to measure the position of the sample within the electrode gap. This is achieved by back-illuminating the sample with a bright light and projecting the shadow of the sample onto a position sensitive detector (PSD) (Figure 3.7). A PSD is a semiconductor device that consists of a p-n junction sandwiched between two resistive layers. When light is incident on the device, photoelectrons will be generated which then travel through the resistive layers to two orthogonal pairs of electrodes which have been attached to the edges of the resistive layer. Assuming the resistivity of the resistive layer is highly uniform, the current flowing to each of the electrodes will depend simply on the relative distance of
the incident light spot to each of the electrodes in a pair. In this manner, the location of an incident light spot can be determined in two dimensions by measuring the currents at each of the four electrodes:

\[ x_{cen} = \frac{L (I_{x+} - I_{x-})}{2 (I_{x+} + I_{x-})} \]  

(3.12)

where \( x_{cen} \) is the location of the incident light spot, \( L \) is the width of the PSD, and \( I_{x+} \) and \( I_{x-} \) are the currents produced on either side of the PSD; a similar expression follows for the \( y \)-direction. In the practical realization of this measurement, the currents generated by the PSD are amplified and then used to generate a voltage which is used as the input parameter in position measurement. The conversion between the generated voltage and the sample position is simply

\[ x_{cen} = c_v V_x \]  

(3.13)

where \( c_v \) is a constant whose value, for the particular PSDs used in the ISU-ESL lab, has been empirically determined to be 0.45 mm/V.

When using PSDs to measure the location of a levitated sample, it is not the location of an incident spot that we are trying to measure but rather the location of a shadow within

Figure 3.6  Equipotential map of the electric potential derived from FEA simulations for (Left) the original electrode geometry and (Right) the improved electrode geometry. The contour spacing is 500 V.
a broad incident beam. In this scenario, the output from the PSD will be representative of the intensity centroid of the broad incident light, and this output must be converted into the centroid position of the shadow. Assuming that the backlight is well centered on the PSD, the intensity centroid of the broad incident light containing a shadow is given by

$$x_{cen} = \frac{\int x I(x, y) \, dA_{bl} - \int x I(x, y) \, dA_s}{\int I(x, y) \, dA_{bl} - \int I(x, y) \, dA_s}$$  \hspace{1cm} (3.14)$$

where $x_{cen}$ is the position of the intensity centroid, $I(x, y)$ is the intensity distribution of the backlight, $A_{bl}$ is the area of the backlight, and $A_s$ is the area of the sample. If the intensity distribution of the backlight is assumed to be constant (i.e. the distribution is perfectly flat) and the profiles of the backlight and shadow are symmetric in both directions, then this expression simplifies to

$$x_{cen} = \frac{-x_s A_s}{A_{bl} - A_s}$$  \hspace{1cm} (3.15)$$

where $x_s$ is the centroid position of the sample shadow on the PSD. Combining equations (3.13) and (3.15) we arrive at the expression to determine sample position based on the output voltage.
of the PSD:

\[ x_s = -\left( \frac{A_{bl}}{A_s} - 1 \right) c_v V_x \]  

(3.16)

Within the ESL control algorithm, the the voltage to sample position conversion is carried out on the basis that both the sample and the backlight have circular profiles, and the associated control algorithm variable is

\[ cpsd = -\left( \left( \frac{r_{bl}}{r_s} \right)^2 - 1 \right) c_v \]  

(3.17)

where \( r_{bl} \) and \( r_s \) are the radii of the backlight and sample, respectively. The radius \( r_{bl} \) should really be treated as an effective radius for the backlights, as recent upgrades (to be discussed) have resulted in the backlight profile becoming closer to a square with rounded corners. Furthermore, the value of \( cpsd \) can be modified while a sample is levitated, which can have an effect on the levitation properties. It has been found that making the value of \( cpsd \) artificially small can significantly reduce the noise levels in the levitation voltage, with voltage excursions being reduced by an order of magnitude (from thousands to hundreds of volts). One possible reason this works is because the various gain factors within the algorithm are less than ideally determined, resulting in the system being overly responsive, and reducing the value of \( cpsd \) compensates by reducing the apparent fluctuations in sample position.

### 3.2.4 Sample Backlighting

For most ESL labs around the world, including the ISU-ESL lab in the early stages of development, backlighting of the sample is achieved using beam-expanded helium-neon (HeNe) lasers. The nominal beam width of the lasers is 1 mm, which is then expanded by a factor of 20 and subsequently reduced to 8-10 mm using an aperture. The resulting beam of light is highly collimated (divergence less than 0.04 mrad), very intense, and relatively flat in terms of intensity distribution, making the beam ideal for shadow casting over long distances (shown schematically in Figure 3.1). Additionally, the narrow linewidth (632.8 ± 0.002 nm) and the availability of very narrow (< 1 nm) bandpass filters provides for a high level of filtering against the light radiation emitted by samples, and their high level of polarization can be used to prevent cross-talk between the orthogonally arranged positioning beams. Up until recently, the
combination of these features made HeNe lasers ideal backlights for the position measurement of ESL samples. However, when implementing the new technique for measurements of electrical resistivity and magnetic susceptibility, an unfortunate drawback of the HeNe lasers was noticed.

As will be discussed in Ch. 4, measurements of electrical resistivity are carried out by measuring the resonant frequency of an $LC$ oscillator which is inductively coupled to a levitated sample. For the measurements to be carried out successfully, a frequency resolution on the order of a few hertz or less is required. However, when monitoring the oscillator frequency with a levitated sample coupled to the oscillator coil, a slow, nonrandom modulation of approximately 50 Hz was observed. The source of this frequency modulation was determined to be a slow variation in the vertical position of the sample, which was caused by a variation in the HeNe laser output. The data sheet for the HeNe lasers reports a drift of 0.05 mrad for the direction of the emitted light. Projected over a distance of 1 meter, this drift results in a variation of $\pm 50 \mu m$ for the intensity centroid of the beam, resulting in a subsequent variation of $\pm 50 \mu m$ for the vertical position of the samples. The position dependence of the measured frequency is $\approx 1 \text{ Hz/mm}$, resulting in the observed modulation of the frequency. To resolve this problem, the HeNe lasers were replaced in favor of high power, quasi-monochromatic light emitting diodes (LEDs).

Compared to HeNe lasers, LEDs are highly divergent light sources. Even when lenses are used to provide some degree of collimation, the beam divergence is still on the order of a few degrees ($\approx 50 \text{ mrad}$), resulting in a very poor light source for the purpose of shadow casting. To compensate for the poor collimation, additional imaging optics are required to form a 1:1 image of the sample silhouette on the surface of the PSD, as shown in Fig. 3.8. The type of lenses chosen for the system are simple bi-convex spherical singlets, as the various aberrations they introduce (achromatic, spherical, etc.) have little to no impact in this application. The focal lengths and diameters of the lenses were heavily influenced by the dimensions of the ESL vacuum chamber, which set the minimum working distance to the sample at 270 mm with a viewport diameter of 35 mm. The focal length of the collimating lens is 75 mm, and the LED-lens distance was adjusted such that the image of the LED was projected $\approx 10 \text{ mm}$ behind the sample; this was found to give the best compromise between intensity, flatness of field, and
collimation. The focal length of the imaging lens is 150 mm, and it is located midway between between the sample and PSD with working distances of 300 mm to provide 1:1 imaging.

The peak-wavelengths of the LEDs are 455 and 505 nm, with a full width at half maximum of $\approx 25$ nm. Wavelengths on the blue side of the spectrum were chosen to reduce competition with the light radiated by hot samples, and these particular wavelengths were chosen because they coincided with available bandpass filters. The total output power of the LEDs is approximately 800 and 350 milliwatts, respectively, although less than 5% actually makes it to the PSDs.

The drifting of the sample position has been measured using a high resolution videographic method (discussed in section 3.7). Fig. 3.9 shows a plot of the typical drift in sample position when backlighting is provided by lasers versus LEDs. The use of LEDs is clearly an improvement, reducing sample drift from $\pm 50 \mu m$ to a baseline noise level with a standard deviation of less than $3 \mu m$. The drift in the oscillator frequency for performing resistivity measurements is likewise reduced from approximately $\pm 50$ Hz down to a noise level of less than 3 Hz.

### 3.2.5 Charge Maintenance

During the initial stages of sample processing, as the sample is heated from room temperature to approximately 1500 K, the samples have a tendency to slowly lose charge, resulting in a steadily increasing levitation voltage. The mechanism behind this charge loss is outgassing: as the samples are heated, atmospheric gases trapped within the sample surface are released at an increased rate, many of them leaving as charged molecules. Because the amount of voltage that can be applied is limited (the present amplifier maximum is 20 kV) an additional means of charging the levitated samples is required. To achieve this, an ultraviolet (UV) light source
is employed to charge the sample via the photoelectric effect.

The minimum photon energy for efficient charging via the photoelectric effect is determined by the material work function, which is defined as the minimum energy an electron must absorb in order to escape from from a material. For most transition metals and metalloids, the work function lies within the range from 4–6 eV, indicating a minimum photon energy of 6 eV; this corresponds to a wavelength of 207 nm or less. While 6 eV photons will, in theory, be sufficient to charge the levitated samples, the charging efficiency goes up dramatically as the photon energy exceeds the work function. To understand this, consider the particle interaction rate:

$$ W = JN\sigma $$  \hspace{1cm} (3.18)

where $W$ is the interaction rate, $J$ is the flux on incoming particles (photons), $N$ is the number density of target particles (electrons) and $\sigma$ is the interaction cross section. For photon energies below the x-ray level (about 100 eV) the photoelectric cross section does not depend strongly on the photon energy. However, the number density of target electrons actually does depend on the photon energy, and will increase as the photon energy increases beyond the work function (to a limit). This can be understood from the standpoint of free electron theory.

Fig. 3.10 shows a schematic of electron density as a function of energy, based on a free electron model of copper. For photon energies equal to or slightly greater than the work

Figure 3.9  Comparison of the drift in sample position when the backlight is provided by lasers (blue dots) and LEDs (red line). A plot of oscillator frequency would like nearly identical, with a vertical axis of -60 to 60 hertz.
function, only a small number of electrons will be accessible for excitation to the vacuum energy level. However, as the photon energy increases, significantly more electrons can be excited out of the material. This effectively increases the number density of target electrons, and therefore the interaction rate. In this simple model, photons with an energy of twice the work function will result in an interaction rate 63 times greater than photons with energy equal to the work function. While this model no doubt oversimplifies the situation, the general conclusion is in good agreement with available reflectivity data for a variety of transition metals [110]. While variations in the reflectivity of metals in the visible range are generally small, the reflectivity of all metals is reduced rapidly as the photon energy increases beyond the work function, indicating that a greater number of photons are being absorbed by the material.

Previous ESL laboratories at Washington University in St. Louis and the DLR in Germany have used UV lamps based on a deuterium gas arc discharge, which produces a broad spectrum of UV light with a peak near 160 nm, or 7.8 eV. While this photon energy was high enough for a charging effect to be observed, the effect was very weak, resulting in very long initial processing times on the order of 3–5 hours. To improve this aspect of the system, the UV lamp chosen for the ISU ESL is a helium gas discharge lamp with a peak emission line near 60 nm, or 21 eV. The photon flux reaching the sample from each lamp is approximately the same, but the higher energy of the helium lamp improves the charging efficiency enough to reduce the
initial processing time to less than 1 hour consistently, sometimes as little as 10 minutes.

When the sample temperature approaches 1500 K or higher, thermionic emission of electrons becomes the dominant charging mechanism. The rate of thermionic emission is given by Richardson-Dushman equation [111]:

$$j = AT^2 \exp \left( -\frac{\phi}{k_B T} \right)$$

(3.19)

where $j$ is the thermionic emission current density, $\phi$ is the material work function, and $A$ is a material dependent constant whose value is $0.7-1.2 \times 10^6$ A m$^{-2}$ K$^{-2}$. For a typical sample with a diameter of 2.5 mm and work function of 5 eV, the thermionic emission current at 1500 K is approximately 0.7 nA; compared to the nominal sample charge of 0.5 nC, this is a considerable current. Because thermionic emission is so significant at elevated temperatures, the additional charging via UV is no longer necessary.

After samples have reached temperatures in excess of 1500 K for several minutes, they usually become fully degassed and can be processed freely from room temperature to high temperature without the need for UV assistance. However, even under vacuum conditions of $10^{-7}$ Torr it has been observed that some samples, if maintained near room temperature for an extended period of time, can re-adsorb enough gas molecules to require UV assistance during later processing cycles.

3.2.6 High Voltage Amplifiers

As was mentioned in the previous section, when samples are processed in the ESL system there is a possibility for the charge on the sample to change due to outgassing or evaporation. Usually the charge loss is slow and can be compensated by UV illumination or thermionic emission, but occasionally the loss is very sudden. To compensate for this rapid charge loss, the high voltage amplifiers used in the ESL system must be capable of rapidly changing their output voltage. The minimum slew rate of an amplifier which is necessary for stable levitation can be estimated easily.

Consider that the maximum acceleration that can be experienced by a sample, in the event of total loss of charge, is that provided by gravity, $a_g = 9.8 \text{ m/s}^2$. Then, the amount of time it
takes for a sample to fall a distance $\Delta z$ is given by:

$$t = \sqrt{\frac{2 \Delta z}{a_g}}$$

(3.20)

If an acceptable fall distance is taken to be 0.1 mm, then the fall time is 4.5 ms. If the maximum swing in voltage is taken to be 20 kV, then the required slew rate of the amplifier is found to be 4.4 kV/ms. The vertical amplifier used in the ISU-ESL system has a slew rate of 450 kV/ms, making it more than fast enough for the job.

Of course, in determining the slew rate requirements, all that was considered was how quickly the amplifier can reach its maximum output voltage. Whether the sample will regain stability or continue to fall depends on the extent of the charge loss, and how quickly the sample can be recharged. If a sample is in free-fall, it will only take 32 ms to fall 5 mm, at which point it will contact the electrodes. In that amount of time, with a sample temperature of 1500 K, only 0.02 nC of thermionic charging will occur, which is quite small compared to the 0.5 nC typically required for stable levitation. In other words, if the sudden charge loss is large enough, sample dropping may be inevitable. Many samples have been lost due to situations such as this.

### 3.3 Control of Sample Temperature and Axial Rotation

#### 3.3.1 Control of Sample Temperature

The levitated samples are heated using a fiber-coupled diode laser which operates in the near infrared. This type of laser was chosen rather than a CO$_2$ laser primarily for two reasons. First, the absorptivity of metals is generally greater at common diode wavelengths near 1 $\mu$m than at the CO$_2$ emission wavelength of 10.6 $\mu$m, which provides for more efficient heating of the samples. Second, the fiber-coupling of the diode laser allows for more flexibility in terms of light delivery. CO$_2$ lasers are large tube lasers which tend to be quite bulky, and if they cannot be setup near the chamber with the output beam pointing directly at the sample, a system of mirrors becomes necessary to direct the beam to the sample. The fiber-coupled output of the diode laser allows the laser itself to be located anywhere in the lab, and focusing optics are
easily constructed to allow variable spot sizes. The output power of a diode laser is also easily controlled by varying the DC current applied to the lasing diode.

Several diode laser wavelengths are available near 1 μm; the ISU-ESL heating laser system operates at a wavelength of 980 nm. Originally, the laser system featured a single fiber output with four different sets of focusing optics to produce spot sizes at the sample of 1, 2, 3, and 4 mm. To achieve the smallest spot sizes, the fiber diameter chosen for the system was 100 μm. The focusing optics connect to the fiber via a standard SMA-905 threaded connection. However, a number of problems were encountered with this system as it was originally supplied by the manufacturer.

The first problem encountered was that the focusing optics (which were purchased from the laser manufacturer) were poorly designed. It was eventually discovered that the fiber-to-lens distance had been poorly set, resulting in spot sizes at the sample position of 10–20 mm instead of the desired sizes of 1–4 mm. To remedy this problem, a custom optical mount was constructed to allow the largest focusing lens to be used with the fiber without being fixed by the SMA connection. This allowed the fiber-to-lens distance to be variable, allowing for 1–4 mm spot sizes with a single focusing element.

The second problem encountered with the original system was caused by the single fiber output. To perform free cooling experiments on a sample the laser power must be abruptly set to zero. It was noticed on numerous occasions that when the laser power was cut, the sample would display recoil motion in the horizontal direction. This recoil was being caused by the photon pressure from the incident light. As the samples were slowly heated, the voltage on the lateral amplifiers would increase to compensate for the photon pressure. When the laser power was suddenly removed, the excess lateral voltage pushed the sample back, and 1–2 s were required for the lateral motion to be damped. In addition to the problem of recoil during free cooling experiments, it was realized that the temperature gradients on the samples with single-beam heating may be higher than originally thought [112].

The final problem encountered was that the in-house cooling water supply was not sufficient to properly cool the diode during standard operation. This proved to be detrimental to the health of the laser system. The excess heat and large temperature variations experienced by
the diode during regular use ultimately lead to the optical fibers becoming misaligned from the
diode. At this point the laser system was sent back to the manufacturer for a tune-up. While
the laser system was with the manufacturer, the decision was made to have the laser output
split into two different fibers. This would allow for multi-beam heating on opposite sides of the
samples, significantly reducing the problems detailed in the previous paragraph. To prevent
overheating of the laser diode in the future, a dedicated water cooling and recirculating unit was
purchased to ensure adequate cooling. Finally, two new sets of focusing optics were designed
and constructed in-house to ensure high quality light delivery.

The in-house optics were designed on the following basis: using a single 25.4 mm diameter
lens, the minimum achievable spot size on the sample should be 1 mm or smaller, and the
effort required to vary the spot size should be minimal. This problem is best treated as an
imaging problem, with the fiber acting as the object and the spot being the image. With a fiber
diameter of 100 μm, a spot size of 1 mm or less is achieved with image-object distance ratio of
\( s_i/s_o > 10 \). The minimum image distance is determined by the vacuum chamber geometry to
be approximately 350 mm, indicating a minimum focal length 32 mm for the focusing lens. The
upper limit on the focal length is set by the numerical aperture of the fiber (NA = 0.22), which
determines the size of the emitted cone of light. To ensure that all emitted light is captured by
the lens, the diameter of the cone is limited to 80% of the lens diameter, yielding a maximum
object distance of 45.4 mm, and ultimately a maximum focal length of 40.2 mm for the lens. On
this basis the parameters of the optical system were chosen to be \( f = 40 \) mm, \( s_o = 45 \) mm and
\( s_i = 360 \) mm, yielding a magnification factor of 8 and a minimum spot size of 0.8 mm. Because
aspherical lenses matching these specifications are not readily available, a 40 mm achromatic
doublet was chosen as the focusing lens (achromatic doublets are still far superior to spherical
singlets in terms of spherical and other aberrations). Because the desired specifications were
determined on the basis of the thin-lens approximation, and a doublet is decidedly not thin,
numerical ray tracing software [113] was used to ensure that all specifications were indeed met.
Construction of the lens assembly was done using optomechanics available from Thorlabs Inc.
The fiber-lens distance \( s_o \) is easily adjustable by rotating a threaded lens tube (designed for
5 mm travel), and this allows for the spot size at the sample location to be varied by defocusing.
the beam. The lens tube plus SMA fiber connector are integrated into a kinematic mount which provides for fine adjustment of tilt in the vertical (pitch) and horizontal (yaw) planes.

Two methods are available for controlling the output power of the laser, namely manual and automated. Manual control is used when fixed rates of heating or cooling are not necessary, usually during the initial heating stage, through the first several heating-cooling cycles, and during free cooling experiments. If fixed rate ramps or repetitive step-holds are required, a modified P-I-D controller has been developed in-house to provide more precise control over sample temperature. The output power of the laser under automated control is given by

\[ P_\ell = \alpha_\ell T_{\text{set}}^4 + p (T_{\text{set}} - T) + i \sum (T_{\text{set}} - T) \]  

(3.21)

where \( P_\ell \) is the laser power, \( T_{\text{set}} \) is the temperature setpoint, \( T \) is the instantaneous sample temperature, \( p \) is the proportional error constant, \( i \) is the integral error constant, and \( \alpha_\ell \) is constant derived from blackbody theory which encompasses several other properties of the sample such as surface area, total hemispherical emissivity, spectral emissivity at 980 nm, as well as the Stefan-Boltzmann constant \( \sigma \). To use the automated controller, values of \( \alpha_\ell \), \( p \) and \( i \) must be determined, and usually in that order. The constant \( \alpha_\ell \) is determined by manually heating the sample to a temperature roughly in the middle of the temperature range of interest, at which point it can be determined directly as \( \alpha_\ell = P_{\ell,\text{cal}} / T_{\text{cal}}^4 \). As the sample temperature is changed from the calibration temperature, the true temperature will begin to deviate from the setpoint temperature because of variations in the sample’s properties. To reduce the variation, the proportional error constant \( p \) is set to a value between 0.01 and 0.05. As the value of \( p \) increases the amount of noise added to the temperature controller also increases, so choosing the exact value of \( p \) is becomes a compromise between reducing the temperature deviation and reducing the noise. In most cases, the model+p controller performs well enough that the integral error constant is set to \( i = 0 \). If \( i \) is to be non-zero, the value is usually on the order of \( 10^{-5} \). However, the integral portion of the controller has a tendency to cause unwanted oscillation in the sample temperature during ramps as well as when approaching the temperature setpoint during step-holds, so it is usually left out in favor of stability and a slight temperature deviation.
3.3.2 Control of Axial Rotation

In addition to controlling the temperature of the sample, the heating laser can also be used to control sample rotation about the vertical axis. This is accomplished via the photon pressure of the incident light if the laser beams are aligned off center of the sample. A photon of wavelength $\lambda$ carries a momentum given by $p_\lambda = h / \lambda$, where $h$ is Planck’s constant. When a photon is incident on a surface, the momentum imparted will depend on whether the photon is absorbed or reflected. At a given wavelength the absorptivity and emissivity of a surface are identical, and for an opaque material the reflectivity can be represented by $r_\lambda = 1 - \varepsilon_\lambda$. It then follows that the momentum imparted onto a surface by a photon is:

$$\Delta p_{ph} = \Delta p_{abs} + \Delta p_{ref} = p_\lambda \varepsilon_\lambda + 2 p_\lambda (1 - \varepsilon_\lambda) = \frac{h}{\lambda} (2 - \varepsilon_\lambda) \quad (3.22)$$

The total number of photons impinging on the surface of the sample is determined from the laser power. A photon of wavelength $\lambda$ carries an energy given by $E_\lambda = hc / \lambda$, where $c$ is the speed of light. From this it follows that the total number of photons emitted at a laser output power $P_\ell$ is given by:

$$N_{ph} = \frac{P_\ell}{E_\lambda} = \frac{P_\ell \lambda}{hc} \quad (3.23)$$

and by combining Eqs. 3.22 and 3.23 we find the total momentum imparted to a surface by the heating laser to be:

$$\Delta p_\ell = N_{ph} \Delta p_{ph} = \frac{P_\ell}{c} (2 - \varepsilon_\lambda) \quad (3.24)$$

When the laser beam strikes the sample, a torque will be experienced by the sample given by $\tau = r_\tau \Delta p_\ell$, where $r_\tau$ is the effective distance from the vertical axis to the laser beam center. The phrase “effective distance” is used because this variable accounts for the fact that the spot size of the beam is a considerable fraction of the sample size (0.8 mm vs. 2.5 mm typical), as well as the fact that the momentum imparted will be reduced from that given in Eq. 3.24 due to the increasing angle of incidence for distances further from the vertical axis. For the purpose of estimating the angular acceleration of the sample, $r_\tau$ is taken to be half the radius of the sample, $r_\tau = a/2$. The angular acceleration can then be calculated as $\alpha_\ell = \tau/I$, where
\( I \) is the moment of inertia of a solid sphere, which leads to the following expression:

\[
\alpha_{\ell} = \frac{5P_{\ell}}{4amc} (2 - \varepsilon_{\lambda})
\]  

(3.25)

For typical values of \( P_{\ell} = 5 \text{ W}, a = 1.25 \text{ mm}, m = 60 \text{ mg}, \) and \( \varepsilon_{\lambda} = 0.25, \) the angular acceleration is \( \alpha_{\ell} \approx 0.08 \text{ rev/s}^2. \) With this level of acceleration, a sample with no initial angular speed could be brought to a rotation rate of 5 rev/s in approximately one minute. Of course, this assumes optimal beam size and alignment on the sample. A more typical timescale experienced in the lab is a few minutes to go from rest to 5 rev/s.

The rotational speed of the sample can be measured using a visualization camera with high spatial resolution (pixel density) along with a long focal length lens to provide high quality video imaging of the sample (see next section). If the frame rate of the camera is reduced from a value much higher than the rotation rate of the sample, then as the frame rate approaches the sample rotation rate the sample will appear to be slowing down. The frame rate at which the sample appears to have stopped completely is equal to the rotation rate of the sample. It is important to note that the rotation rate of the sample is equal to the highest frame rate of the camera for which the sample appears motionless, because the same effect will be observed for any frame rate which is an integer fraction of the sample rotation rate. With this stroboscopic method, the rotation rate can be measured to an accuracy of 0.5 rev/s or better.

### 3.4 Sample Visualization

In addition to being used for the determination of sample rotation rates as just described, the visualization camera plays an integral role in determining the quality of the surface condition of levitated liquid samples. To function well in this regard, the visualization system must be capable of capturing high resolution color video, with high magnification, at a frame rate of approximately 30 Hz. The video system developed for the ISU-ESL makes use of a high quality CMOS color camera with a sensor resolution of 1280x1024. The camera can operate at 25 Hz for full frame acquisition, and higher frame rates are possible with reduced areas of interest. To accomplish the high magnification, a standard 75 mm focal length, C-mount camera lens is used in combination with magnification rings of 1.5x and 2.0x, resulting in a pseudo-telephoto
lens with an effective focal length of 225 mm. The large effective focal length is necessary to ensure a narrow field of view at long working distances, thus ensuring a high magnification factor. When the video captured with this system is subsequently displayed on a standard computer monitor with 96 dpi resolution, the resulting video system magnification factor is approximately 45x. In other words, a 2.5 mm diameter sample has a viewing size of more than 10 cm when viewed at full resolution on a standard monitor. The spatial resolution of this system is limited by the pixel size of the sensor, and based on the the observed system magnification and viewing resolution, the spatial resolution is approximately 10 μm. The high resolution and good video quality of this system makes it possible to assess the surface quality of samples during ESL processing, including the detection of very small insoluble impurities such as that shown in Fig. 3.11.

3.5 Measurement of Temperature

The basis of non-contact temperature measurement lies within blackbody radiation theory. However, blackbody theory applies strictly to idealized, perfect radiators. In applying blackbody theory to measure the temperature of real objects, certain assumptions must be made about the emissive characteristics of those objects. Because a proper understanding of sample emissivity is crucial to not only pyrometric temperature measurement, but also to the
measurement of sample specific heat via ESL experiments, a detailed treatment of the subject will be given here.

3.5.1 Single Color Pyrometry

The modified Planck formula for thermal radiation of non-blackbody objects is given as:

\[ P_\lambda(T) = \varepsilon_\lambda \frac{2\pi hc^2}{\lambda^5} \frac{1}{\exp\left(\frac{hc}{\lambda k_B T}\right) - 1} \delta \lambda \]  

(3.26)

where \( P_\lambda \) is the power emitted per unit area of the emitting surface; \( \lambda \) and \( \delta \lambda \) are the center wavelength and spectral width under consideration, respectively, with \( \delta \lambda \ll \lambda \); \( \varepsilon_\lambda \) is the spectral emissivity at the center wavelength \( \lambda \); \( h \) is Planck’s constant; \( k_B \) is Boltzmann’s constant; \( c \) is the speed of light; and \( T \) is the temperature of the emitting surface. While Eq. 3.26 is exactly solvable for temperature, it is usually sufficient, for the temperatures of interest here, to use the Wien approximation, wherein \( hc \gg \lambda kT \), and Eq. 3.26 simplifies to

\[ W_\lambda(T) = \varepsilon_\lambda \frac{2\pi hc^2}{\lambda^5} \exp\left(\frac{-hc}{\lambda k_B T}\right) \delta \lambda \]  

(3.27)

and solving Eq. 3.27 for \( T \) we get

\[ T = \frac{hc}{\lambda k_B \ln\left(\frac{2\pi hc^2}{W_\lambda \lambda^5 \varepsilon_\lambda \delta \lambda}\right)^{-1}} \]  

(3.28)

Eq. 3.28 forms the mathematical basis of what is known as single color pyrometry: a photosensitive device is used to measure the power radiated by an object within a single narrow spectral band, which is then used to determine the temperature of the object. For Eq. 3.28 to yield an accurate result, it is necessary to know the value of the spectral emissivity of the object under study. Manufacturers of pyrometers will often include lookup tables with approximate values of emissivities for various materials under a variety of conditions, but oftentimes these values are inadequate for analytical purposes, or unavailable altogether. A better way to determine the spectral emissivity of a material is to use known critical temperatures as reference points, such as solid-solid or melting transitions, and to adjust the value of the pyrometer emissivity setting such that the critical temperatures are accurately reproduced by the pyrometer. The formalism for performing this step is straightforward: an initial (educated) guess is made
as to the value of the sample emissivity $\varepsilon_{\lambda}$, the sample temperature is then cycled through the
critical temperature and, using the known value of the critical temperature, the true spectral
emissivity and measured temperatures can be recalculated as:

$$\varepsilon'_{\lambda} = \varepsilon_{\lambda} \exp \left( \frac{hc}{\lambda k_B} \left( \frac{1}{T'} - \frac{1}{T_c} \right) \right)$$  \hspace{1cm} (3.29)$$

and

$$T' = \left( \frac{1}{T} + \frac{k\lambda}{ch} \ln \left( \frac{\varepsilon'_{\lambda}}{\varepsilon_{\lambda}} \right) \right)^{-1}$$ \hspace{1cm} (3.30)$$

where $T_c$ is the known critical temperature, the unprimed variables represent values used or
observed during the measurement, and the primed variables represent the corrected values.

One of the assumptions made thus far is that the spectral emissivity $\varepsilon_{\lambda}$ can be determined
at a single calibration point and subsequently used to measure temperatures over a wide range
(several hundred degrees). However, material emissivities are known to be temperature depen-
dent quantities. While a single calibration point will allow accurate temperature measurement
near the calibration temperature, as the temperature deviates from the calibration point the
potential error in the measurement will likewise increase. Eq. 3.30 can be used to estimate the
extent of the error induced in a temperature measurement based on an assumed error in the
emissivity value for a material. For instance, suppose that the actual emissivity of a sample has
changed by 5% from the calibration point. For measurements near 1000, 1500, and 2000 K, a
5% error in the value of the emissivity corresponds to errors in the temperature measurements
of 5, 12, and 21 K, respectively. If those temperatures correspond to a maximum supercooling
of $\Delta T = 0.2 T_m$, then the corresponding errors in the measurement of supercooling depth are
approximately 2, 3, and 4%, respectively. Furthermore, emissivities have been known to change
substantially at phase transitions, both solid-solid structural and melting/freezing, hindering
the accuracy of the single color method for measuring temperatures across such transitions. To
reduce the impact of the spectral emissivity’s temperature dependence on performing accurate
temperature measurement, two color pyrometry can be utilized.
3.5.2 Two Color Pyrometry

The two color ratio method of pyrometry is based on the assumption that, while the emissivity at a specific wavelength or waveband may be temperature dependent, the ratio of emissivities for two closely separated wavelengths will remain constant. Going back to Eq. 3.27, we can solve \( \frac{w_1}{w_2} = \frac{W_{\lambda_1}(T)}{W_{\lambda_2}(T)} \) for the temperature based on the ratio of intensities at two different wavelengths:

\[
T = \frac{hc}{k_B} \frac{\lambda_1 - \lambda_2}{\lambda_1 \lambda_2} \ln \left( \frac{w_1 \lambda_1^5 \varepsilon_1}{w_2 \lambda_2^5 \varepsilon_2} \right)^{-1}
\]  

(3.31)

While the two color ratio method is generally assumed to be more accurate than single color pyrometry, care must also be taken when performing ratio temperature measurements, particularly across phase transitions. It has been observed in the lab that the spectral emissivity function can experience a significant change in the wavelength dependence when crossing through a phase transition. As a result, the ratio of the emissivities used for pyrometry is constantly changing through the transition. The changing ratio has led to odd looking temperature curves, such as the apparent temperature dropping significantly during the melting process, or a solidification temperature that steadily rises instead of plateaus.

Because of the uncertainties associated with both single color and two color ratio temperature measurements, the best approach to pyrometric temperature measurements is to use both methods, and to compare, contrast, and carefully scrutinize the results to ensure that the most accurate and sensible temperature determination is being made.

3.5.3 Multi-Wavelength Pyrometry and Emissivity Measurements

Multi-wavelength pyrometers that make use of more than two sensing wavelengths also exist. The basis of their operation is essentially an extension of the two-color ratio method, with added redundancy to improve the accuracy of measurements. Such a multi-wavelength pyrometer has been purchased for the ISU-ESL lab. This multi-wavelength pyrometer uses a spectrometer to measure light intensity over a wavelength distribution of 1050–1650 nm with 2.5 nm resolution. Then, using the ratio method and a proprietary algorithm to perform the redundancy check, a self consistent temperature is determined. In conjunction with the
determined temperature, blackbody theory, and the measured spectral intensity, the spectral emissivity of the sample can be determined. Supposedly this multi-wavelength pyrometer can be used to perform self-corrected temperature measurements with errors no greater than 0.75%. However, several problems have been encountered during the testing of this pyrometer which have resulted in limited use, so it will not be discussed in detail in this section. Details of the pyrometer, benchmarking tests, and attempts at using the raw spectral intensity data for performing two-color ratio pyrometry and in-house emissivity determination can be found in Appendix A.

3.6 Measurement of Specific Heat

The specific heat is an important quantity in experimental and computation physics as well as applied physics and engineering. In the experimental characterization of materials, measurements of the specific heat can be used to identify first and second order phase transitions. Additionally, knowledge of the specific heat in conjunction with enthalpies of fusion is necessary for quantitatively understanding nucleation and metastable phase formation. Computationally, measurements of specific heat are important for validating interaction potentials used in atomistic simulations. In applied physics and engineering, knowledge of a material’s specific heat is necessary to understand and properly model heat flow.

The first description of measurements of the specific heat for electrostatically levitated samples was given by Rulison & Rhim [93]. For a sphere which is levitated under the conditions of high vacuum, the heat flow equation is:

$$\alpha_\ell P_\ell - \varepsilon A\sigma T^4 = mc_p \frac{dT}{dt}$$

(3.32)

where $\alpha_\ell$ is the laser absorption coefficient (accounting for spot size and absorptivity), $P_\ell$ is the applied laser power, $\varepsilon$ is the total hemispherical emissivity\(^1\), $A$ is the sample surface area, $\sigma$ is the Stefan-Boltzmann constant, $m$ the sample mass, $c_p$ the constant pressure specific heat, and $T$ the sample temperature. If the sample is brought to high temperature and then the laser

\(^1\)The terms “total hemispherical” imply that the emissivity function of the sample has been integrated over all wavelengths and emission angles between ±90 degrees.
power is turned off, allowing the sample to experience a free radiative cooling (a free cool), Eq. 3.32 can be solved for the ratio of specific heat to total hemispherical emissivity:

\[
\frac{c_p}{\varepsilon} (T) = -\frac{4\pi\sigma r^2 T^4}{m} \left( \frac{dT}{dt} \right)^{-1}
\]

(3.33)

where \( r \) is the sample radius. Thus, if free cooling measurements are performed and the cooling rate at each temperature can be accurately determined, along with simultaneous measurements of the sample radius, then the ratio of specific heat to total hemispherical emissivity can be determined. It should be emphasized that, strictly speaking, what can be measured during free cooling measurements is not purely the temperature dependence of the sample specific heat, but the temperature dependence of the ratio of specific heat to total hemispherical emissivity. Just as the spectral emissivity of a sample can be a temperature dependent quantity, the total hemispherical emissivity can also depend on temperature. Without information regarding the temperature dependence of the total hemispherical emissivity, measurements purely of the specific heat are not possible.

If the changes in a sample’s radius, specific heat, and total hemispherical emissivity are relatively small, then Eq. 3.33 can be solved to provide insight into the maximum available cooling rates of ESL processed samples. In doing so we find:

\[
\frac{dT}{dt} = -\frac{4\pi\sigma r^2}{mc_p} T^4
\]

(3.34)

Using values of \( \varepsilon = 0.2, \ r = 1.25 \text{ mm}, \ m = 50 \text{ mg}, \) and \( c_p = 400 \text{ J/(kg K)}, \) the maximum cooling rates that can be achieved during free cools at temperatures of 1000, 1500, and 2000 K are 11, 56, and 178 K/s, respectively. Generally speaking, the maximum cooling rates should have very little effect on the outcome of an experiment. The one counter-example would be for those experiments where in-situ glass formation of the sample is being attempted. The low cooling rates that can be achieved below 1000 K would seem to indicate that the study of bulk metallic glass formers, at least in terms of being able to observe the vitrification, will be limited to those materials with critical cooling rates below 10 K/s.
3.7 Measurements of Volume and Mass Density

Like the specific heat, a material’s mass density plays a crucial role in experimental, computational, and applied physics. It can serve as a sensitive probe for phase transitions, is used to verify the results of atomistic simulations, and is an important parameter to consider in engineering endeavors.

Measurements of the mass density of electrostatically levitated samples were first described by Chung et al. [91] and later improved upon by Bradshaw et al. [92]. The quantity which is actually measured during the course of an experiment is the sample’s volume expansion, which is performed with a videographic method. The density is then determined using the measured volume data along with the sample’s mass, which must be accurately determined before and after an experiment to ensure that mass loss over the course of the experiment was minimal.

The videographic measurement of sample volume is done by back-lighting the sample with an intense light source and then recording a video of the sample’s silhouette. In the ISU-ESL implementation, the back light is a moderately collimated high power LED. The LED is quasi-monochromatic, with center wavelength of 405 nm. This wavelength was chosen so that a high level of contrast could be achieved against the higher wavelength thermal radiation produced by the samples. Additionally, a band-pass filter with a closely matched transmission band is used on the camera side of the setup, further enhancing the contrast and providing a very clean image of the silhouette. The backlighting system for volume/density measurements is nearly identical to the system that was developed for the purpose of sample position determination, which was described in Sec. 3.2.4.

On the camera side, a high resolution monochrome video camera (Pixelink PL-B741) coupled with a telephoto lens (Infinity K2) allows high quality video of the sample to be recorded. The Infinity K2 is often referred to as a “long-distance microscope” because it allows for very small fields of view over long distances. The camera-lens combination for volume/density measurements is actually similar to that which is used for sample visualization, except much higher quality components have been used to ensure best accuracy and precision possible. At a typical working distance of 300 mm from lens to sample, the field of view is $9 \times 8$ mm with standard
Figure 3.12  Example of a sample silhouette used for volume/density determination. The red box indicates the video acquisition mode used for acquiring surface tension and viscosity data.

optics, and $4.5 \times 4$ mm using a $2\times$ doubler tube. An example of the type of image that is acquired for a volume/density measurement is shown in Fig. 3.12.

To determine the volume of the sample from the acquired video data, the profile of the sample must be determined using image analysis methods. The first step in the process is to determine the location of the pixels that correspond to the edge of the sample. The edge detection is performed in two steps, first by identifying the high contrast areas of the image, and then by fitting a cubic polynomial to the edge transition to achieve sub-pixel edge detection. After determining the coordinates of the edge pixels, the center coordinates of the sample can be determined from the arithmetic mean of the edge coordinates. Having obtained the coordinates of the sample center and edges, there are two possible methods of calculating the volume. The first method uses a least squares technique to fit the edge coordinates of the sample to a sixth order Legendre polynomial, which accounts for deviations in the sample shape from that of a perfect sphere:

$$r(\theta) = \sum_{i=0}^{6} a_i P_i(\cos \theta)$$  \hspace{1cm} (3.35)

where $r(\theta)$ is the angular dependence of the sample radius, $P_i(\cos \theta)$ is the $i^{th}$-order Legendre
polynomial, and $a_i$ are the respective Legendre coefficients. Once the sample’s profile has been fit to Eq. 3.35, the volume can determined through the following integration:

$$V = \frac{2\pi}{3} \int_0^{\pi} r(\theta)^3 \sin \theta \, d\theta$$

(3.36)

For an individual video data set, the units for the sample radius and volume are “pixels” and “pixels cubed”, respectively. To convert these units into actual lengths and volumes, calibrations tests must be performed using precision spheres. The sphericity, or roundness, of a calibration sphere is indicated by its grade, which is a standard defined by the American Bearing Manufacturers Association. The number of the ball grade corresponds to the diameter tolerance in millionths of an inch for an individual ball of that grade, however the basic diameter variation from one ball to another of the same grade is greater by a factor of 4–10. For instance, the best calibration spheres that can be produced are grade 3, indicating a diameter tolerance for an individual ball of 76 nm $(3 \times 10^{-6} \text{ in.})$ and a ball-to-ball diameter variation of at most 760 nm. The highest grade of readily available ball (e.g. from industrial retailer McMaster-Carr) is grade 24, indicating an individual ball diameter tolerance of 610 nm and a maximum ball-to-ball diameter variation of 2.5 μm [114]. With the available diameter tolerances, the accuracy of a volume calibration can be determined by:

$$\frac{\Delta V}{V} = 3 \frac{\Delta d}{d}$$

(3.37)

If the calibration sphere is grade 3 with 2.5 mm diameter, then the uncertainty in the volume calibration is approximately 0.09%; using a grade 24 ball, the uncertainty is 0.3%. The precision of the technique, based on benchmarking tests and derived from the standard deviation in measurements performed on a variety of samples, is better than 0.04%.

It should also be noted that the calibration spheres should be made of mechanically hard materials. The mechanical hardness is necessary to prevent deformation of the precision spheres through handling. Tungsten carbide is the preferred material, but stainless steel will also suffice. Materials such as aluminum, brass, and copper should be avoided.

While the method of volume determination through the fitting of Legendre polynomials has been proven to be very effective, it has also proven to be computationally intensive, resulting in
data processing times on the order of an hour to process one minute’s worth of data. To speed up the computation process, an alternate method of volume determination has been developed that avoids the need for least squares fitting [115]. In this method, the edge detection process is used to determine the diameter of the sample cross section as a function of distance along the vertical axis of the sample, \( D(y) \). Then, the volume of the sample can be determined through numerical integration according to:

\[
V = \frac{\pi}{4} \int_0^{h_s} D(y)^2 \, dy
\]  

(3.38)

where \( h_s \) is the vertical length of the sample. Based on benchmarking tests, the precision of this method of volume determination is approximately 0.1%. While this is slightly less precise than the least squares fitting of Legendre polynomials, it is still quite small, especially when compared to the calibration accuracy that can be achieved using a grade 24 calibration ball. Furthermore, the computational speed of this method is approximately 10 times faster than the Legendre polynomial method.

Additional details regarding the volume determination algorithms and their implementation, including corrections for sample tilt and gradients in the background light, can be found in Ref. [115].

### 3.8 Surface Tension and Viscosity

Measurements of surface tension and viscosity are based on the oscillating sample method, and the implementation of this method for measurements of electrostatically levitated samples was first demonstrated by Rhim et al. [94]. In the oscillating sample method, measurements of surface tension and viscosity are coupled together. An axisymmetric oscillation is induced in the sample, resulting in the expansion and contraction of the sample shape in the vertical direction. Measurement of the frequency of the oscillation ultimately yields the surface tension of the sample, and measurement of the decay rate of the oscillation amplitude (after excitation is removed) yields the viscosity.

For a free floating droplet in the limit of weak damping, if an axisymmetric excitation is applied and then removed the droplet will experience axisymmetric oscillations. During this
time, the modulation of the drop shape $r(t)$ is described by

$$r(t) = r_0 + r_2 \cos(\omega_2 t) P_2(\cos \theta) e^{-t/\tau_2}$$  \hspace{1cm} (3.39)

where $r_0$ is the spherical radius of the drop, $r_2$ is the amplitude of oscillation, $\omega_2$ is the angular frequency of the oscillation, $P_2$ denotes the second order Legendre polynomial, $\theta$ is the angle measured from the vertical axis to the radial direction, and $\tau_2$ is the decay time of the oscillation. The subscript “2” in these variables is representative of the fact that Eq. 3.39 describes the $n = 2$ mode of oscillation. For a charged drop in a uniform electric field, the characteristic oscillation frequency is determined as

$$\omega_2^2 = \frac{8\sigma}{\rho r_0^3} C_1(\sigma, q) C_2(\sigma, q, e)$$  \hspace{1cm} (3.40)

where $\rho$ is the mass density of the sample and $\sigma$ is the surface tension. The functions $C_1$ and $C_2$ are corrections which describe modifications to the classical characteristic oscillation frequency. Function $C_1$ accounts for the fact that the sample carries a net surface charge, and function $C_2$ accounts for the effect of the uniform electric field in which the sample resides. These functions can be shown to be [94]:

$$C_1(\sigma, q) = 1 - \frac{q^2}{4r_0\sigma}$$  \hspace{1cm} (3.41)

and

$$C_2(\sigma, q, e) = 1 - \frac{(243.31\sigma^2 - 63.14q^2\sigma + 1.54q^4)e^2}{176\sigma^3 - 120q^2\sigma^2 + 27q^4 - 2q^6}$$  \hspace{1cm} (3.42)

where $\sigma$ is the surface tension and $q$ and $e$ are defined by

$$q^2 = \frac{Q_s^2}{16\pi^2 r_0^2 \epsilon_0}$$  \hspace{1cm} (3.43)

and

$$e^2 = E^2 r_0 \epsilon_0$$  \hspace{1cm} (3.44)

where $Q_s$ is the sample charge, $E$ is the applied electric field, and $\epsilon_0$ is the permittivity of free space. The spherical radius $r_0$ can be determined using the videographic method described in the previous section. The sample charge $Q_s$ can be estimated from the levitation requirement $mg = Q_s E$, however, as described in Sec. 3.2, care must be taken to ensure that the sample is well centered in the electrode gap to reduce the effect of image charges on the levitation force.
To set the sample into oscillation, an AC modulation is added to the DC output voltage of the vertical high voltage amplifier. The AC modulation is accomplished via the control algorithm, and therefore the maximum frequency is limited by the speed of the digital-to-analog converter, which is 500 Hz. However, in most instances the natural oscillation frequency should be less than 250 Hz, and so this method should be sufficient. For the amplitude of the AC modulation, a value of 1–2.5 kV has been found to be sufficient. While it may seem as though such a modulation to the levitation voltage could result in gross movement of the sample, the mass inertia of the sample prevents such motion from occurring at high driving frequencies. For example, while a slow modulation on the order of 1–2 Hz can result in modulation of the sample position, it has been found that for driving frequencies greater than 10 Hz, the gross movement of the sample is barely detectable. Finally, it should be mentioned that the driving frequency of the oscillation needs to be within approximately 10% of the natural oscillation frequency of the sample. Frequencies outside this range will be heavily damped to the point of being undetectable. Also, while induced oscillations are possible within approximately ±10% of the natural frequency, the amplitude of the induced oscillation will be maximized by matching the driving and natural frequencies as closely as possible.

The oscillation amplitude, frequency, and decay time are measured using a videographic method similar to that used for density measurements, and in fact the same physical setup is used for both. However, rather than capture video of the entire sample, only a narrow strip along the vertical axis is recorded: video is typically recorded at 16 × 512 pixels, corresponding to a width of ~0.1 mm; this is shown in Fig. 3.12. The narrow video format emphasizes the distortion of the sample along the vertical axis, as well as allowing for reasonably fast frame rates: 1500+ frames per second (fps) can be achieved at standard resolution, and 3000+ fps is possible using a pixel decimation factor of 2. Since typical sample oscillation frequencies are ~250 Hz or less, and the Nyquist sampling frequency is only twice the measured frequency, the available video rates are adequate for oscillation frequency determination. To extract the oscillation parameters from the acquired video data, each frame is analyzed to determine the average illumination level. As the vertical axis of the sample expands and contracts, the average illumination of a frame will be reduced or increased accordingly. The mean illumination
value vs. time can then be fit using Eq. 3.39 (with illumination amplitude substituted for radius) and the oscillation frequency and decay time constant can be determined.

Measurement capabilities for surface tension and viscosity have only recently been implemented for the ISU-ESL. Due to the short amount of time since implementation, as well as issues with sample purity (see Ch. 5), detailed analysis of surface tension and viscosity measurements have not yet been carried out. However, the capabilities for inducing sample oscillations, as well as for determining the characteristic oscillation frequencies and decay times via image analysis, have been carried out on samples of Fe$_{83}$B$_{17}$ and pure Al. Representative data for a decaying oscillation is shown in Fig. 3.13.

![Oscillation decay](image)

**Figure 3.13** Oscillation decay used for measurements of surface tension and viscosity of an Fe$_{83}$B$_{17}$ sample. In this instance, the oscillation frequency was 179.5 Hz and the decay time constant was 78.9 ms.

### 3.9 Sample Environment

The sample environment for ESL processing is largely determined by the need to prevent electrical arcing, which is caused by the dielectric breakdown of processing gases in the presence of high voltage. For this purpose, the environment must be either be either high vacuum ($< 10^{-5}$ Torr) or high pressure (∼3 atm or higher). Pressure levels in between, particularly
from a few millitorr up to ambient pressure, are unusable for ESL processing because gases are particularly susceptible to dielectric breakdown in these pressure ranges. The strength of a gaseous environment against such breakdown is described by Paschen’s Law.

Paschen’s Law describes the breakdown of a gas as a function of the product of gas pressure and electrode spacing:

\[ V_b = \frac{a \cdot pd}{\ln(pd) + b} \]  

(3.45)

where \( V_b \) is the breakdown voltage, \( p \) is the pressure, \( d \) the electrode spacing, and \( a \) and \( b \) are empirically determined constants. A plot of Eq. 3.45 for a variety of gasses is shown in Fig. 3.14 (adapted from Ref. [116]). From the plots it is evident that there is a critical value of the product \( pd \) for which the breakdown voltage is minimized. For values of \( pd \) greater than the critical value, the possibility of arcing can be reduced by increasing either the gas pressure or the electrode spacing, while for values of \( pd \) less than the critical value the possibility of arcing is reduced by decreasing the gas pressure or the electrode spacing; arcing will actually become less likely to occur under vacuum conditions if the electrodes are brought closer together. This may seem counterintuitive at first, and has been the topic of some conversation in the ISU-ESL lab, but this behavior can be understood by considering the role of the mean free path in the breakdown process.

Dielectric breakdown occurs when free electrons and ions in a gas are accelerated by an external electric field to the point where their kinetic energy becomes significantly greater than the ionization energy of the gas molecules. On the side of the Paschen curve corresponding to high values of \( pd \), increasing the electrode spacing reduces the electric field strength and therefore also reduces the acceleration experienced by the electrons, while increasing the gas pressure reduces the mean free path of the electrons/ions and therefore also reduces the time between collisions. In each case the effect is the same: the amount of kinetic energy an electron/ion is able to obtain between collisions is reduced, which reduces the likelihood of breakdown at a given voltage. On the side of the Paschen curve corresponding to low values of \( pd \), reducing either the electrode spacing or the gas pressure results in the mean free path

---

2Strictly speaking, the threshold kinetic energy for ionization of a gas molecule is equal to the ionization energy of the target molecule. However, the ionization cross section is nearly zero at this energy, and does not become substantial until kinetic energies reach roughly ten times the threshold value.
of the electrons/ions becoming comparable to or greater than the electrode spacing. As the mean free path exceeds the electrode spacing, the probability of free electrons or ions colliding with a gas molecule decreases, which therefore reduces the likelihood of breakdown occurring. For values of \( pd \) in the middle, the possibility of breakdown occurring is optimized because the mean free path is large enough for the electrons/ions to obtain an appreciable kinetic energy, while still being sufficiently small compared to the electrode spacing so as to ensure a high probability of collisions among the gas molecules.

For air at 1 atm pressure, the dielectric strength is 30 kV/cm [110]. Consider an electrode gap of 10 mm, with a 2.5 mm sample on the bottom electrode, and the breakdown voltage would be 22.5 kV. While this is less than the maximum output voltage of the high voltage amplifier, it leaves very little room for error. Furthermore, the dielectric strength of a material is usually determined for DC voltages, and can be significantly lower when attempting to insulate against rapid transients. For this reason, attempts at performing ESL processing of samples under a gaseous environment are usually performed at pressures of 4–5 atm [106].

The pressure dependence of the dielectric strength of gases is determined primarily from the mean free path of the gases, and therefore processing under 4 atm pressure would increase the
dielectric strength of air to approximately 120 kV/cm. Whether the gas mixture is pure N\textsubscript{2} or a N\textsubscript{2}-O\textsubscript{2} mixture makes very little difference because these gases have very similar dielectric breakdown strengths.

While processing under 4–5 atm of N\textsubscript{2} or a N\textsubscript{2}-O\textsubscript{2} mixture may suitable for studying nitride or oxide ceramic materials, it is unsuitable for the processing of pure metals because it will inevitably lead to sample contamination through the formation of unwanted nitrides or oxides. It would therefore be preferable to perform high pressure ESL processing under an inert gas atmosphere such as pure Ar. Unfortunately, pure Ar is a very weak dielectric material compared to N\textsubscript{2} or O\textsubscript{2}. Table 3.3 (data from Ref. [110]) shows a comparison of the relative dielectric strengths for a variety of gases compared to that for air. As can be seen, the dielectric strength of pure Ar is only 0.19 times that for air, or approximately 5.7 kV/cm at 1 atm of pressure. Even under 5 atm of pressure, the dielectric strength of Ar would only be approximately 28 kV/cm. The situation is actually somewhat worse for pure He. Because of the extremely weak dielectric strengths of the noble gases, there have been no reports of ESL processing under noble gas environments.

Table 3.3  Relative dielectric strengths of various gases at 1 atm pressure compared to air.

<table>
<thead>
<tr>
<th>Gas</th>
<th>Relative dielectric strength</th>
</tr>
</thead>
<tbody>
<tr>
<td>N\textsubscript{2}</td>
<td>1.03</td>
</tr>
<tr>
<td>O\textsubscript{2}</td>
<td>0.95</td>
</tr>
<tr>
<td>H\textsubscript{2}</td>
<td>0.52</td>
</tr>
<tr>
<td>He</td>
<td>0.15</td>
</tr>
<tr>
<td>Ar</td>
<td>0.19</td>
</tr>
<tr>
<td>SF\textsubscript{6}</td>
<td>2.58</td>
</tr>
<tr>
<td>CO</td>
<td>1.06</td>
</tr>
<tr>
<td>CO\textsubscript{2}</td>
<td>0.87</td>
</tr>
</tbody>
</table>

Because a suitable gas does not exist for the purpose of processing metals under a pressurized ESL atmosphere, high vacuum is the desired sample environment. To prevent dielectric breakdown under conditions of low gas pressure, the mean free path of the gas molecules should be significantly larger than the relevant electrode gap. The relevant electrode gap in this case is not the ESL electrode gap, but rather the largest distance possible between the high voltage electrode and a part of the grounded metal vacuum chamber. In the ISU-ESL system,
this distance is approximately 50 cm, therefore the mean free path should be 5 m or greater, corresponding to a pressure of $10^{-5}$ Torr or lower [117].

### 3.10 Summary

A new laboratory for the purpose of performing ESL processing of high temperature liquids and solids has been developed and brought to a functional level. In its current state, the system is capable of noncontact processing of a variety of metallic and semiconducting samples at high temperatures in a high vacuum environment. A variety of thermophysical properties can be measured with the new system, including mass density and thermal expansion coefficients, ratio of specific heat to total hemispherical emissivity, surface tension, and viscosity. New measurement methods are currently being developed for the measurement of electrical resistivity and ferromagnetic transitions (see Ch. 4), as well as measurements of spectral emissivity (see Appendix. A). In addition to getting the new ESL lab operational, several key aspects of the system have been greatly improved. These aspects include: an improved understanding ESL sample charging behavior, including both the initial capacitive charging as well as the steady-state charge behavior; improved photoelectric charging of levitated samples through the use of a UV arc lamp with increased photon energy; more reliable sample launching capabilities using redesigned electrodes; improved mechanical stability of levitated samples through both the redesigned electrodes as well as by converting the positioning system from laser to LED backlighting; improved characterization of the sample surface quality using a high magnification visualization system; and improved mechanical stability and temperature uniformity of levitated samples through the use of two-beam laser heating.
CHAPTER 4. MEASUREMENTS OF ELECTRICAL RESISTIVITY AND MAGNETIC SUSCEPTIBILITY

One of the primary goals in developing the new electrostatic levitation system at Iowa State was to implement a method of performing measurements of electrical resistivity and magnetic susceptibility. Compared to measurements of other material properties (density, surface tension, viscosity, specific heat, and atomic structure) measurements of electrical resistivity and magnetic susceptibility have lagged considerably. This is true for each of the major levitation techniques: ESL, EML, and CNL. The lack of data is not for lack of effort: methods of performing these measurements have been developed for each of the levitation techniques. However, each of the methods developed thus far have suffered drawbacks which limit their use.

In this chapter we will discuss in detail the measurements of electrical resistivity, and to a lesser extent magnetic susceptibility. We will start by providing the motivation behind performing these measurements, followed by a literature review of the previous attempts at combing these measurements with levitation techniques, and then move on to discuss the current implementation of these measurements in the Iowa State University Electrostatic Levitation system.

4.1 Motivation

Knowledge of a material’s electrical resistivity, particularly its temperature dependence, is of great interest in both experimental and applied physics. Among experimental condensed matter physicists, measurements of electrical resistivity are often used as a probe of changes in a materials electronic and/or atomic structure. The Drude model provides a simple but effective way of understanding a material’s electrical resistivity, and within this model the
The electrical resistivity of a metal can be shown to be [118]:

\[ \rho_e = \frac{1}{n_e e \mu_e} \]  \hspace{1cm} (4.1)

where \( \rho_e \) is the electrical resistivity, \( n_e \) is the electron number density, \( e \) the electron charge, and \( \mu_e \) the electron mobility. The number density is related to the nature of the chemical bonding in a material (e.g. valence states), and the mobility is related to electron scattering, whether by the lattice, defects, or magnetic interactions. Thus, measurements of the temperature dependence of the electrical resistivity can provide indirect hints about the electronic, magnetic, and structural changes that may be occurring in a material.

Another way of understanding the electrical resistivity comes from the description via the Kubo formula [119]:

\[ \frac{1}{\rho_e} = \frac{e^2}{12\pi^3 \hbar} \int \lambda_e dS_f \]  \hspace{1cm} (4.2)

which describes the electrical resistivity as an integral of the electron mean free path, \( \lambda_e \), over the Fermi surface, \( S_f \). Within this description, the electrical resistivity can be used as an indicator of the nature of a material’s electronic structure. This can be used to provide insight into the nature of phase transitions involving different classes of material conductivity, such as the metallic, semimetallic, and semiconductor classifications of materials. In addition to being able to provide such insight into materials based on experimental investigations, this understanding of electrical resistivity has another major advantage: the electrical resistivity of a material can be calculated based on the results of molecular dynamics simulations. Such computational calculations have been performed, for instance, on liquid silicon to demonstrate a metal-to-semimetal transition in deeply supercooled liquid silicon which is modeled using a Stillinger-Weber potential [120]. Therefore, it may be possible to use experimental measurements of electrical resistivity to validate the 3D atomic structures that are generated computationally via ab-initio and classical molecular dynamic simulations. As these computational methods are currently the only means of determining the 3D atomic structure of metallic liquids, their verification is important.

In addition to electronic and structural insights, the electrical resistivity can also provide insight into other properties of metals, such as thermal conductivity and radiative emissivity.
The connection between electrical resistivity and thermal conductivity is provided by the Wiedermann-Franz law, which can be shown to be [118]:

\[ k_t \rho_e = LT \]  

where \( k_t \) is the thermal conductivity, \( T \) the temperature, and \( L \) the Lorenz number. In theory the Lorenz number has a constant value of \( 2.45 \times 10^{-8} \) W·Ω·K\(^{-2} \), though experimentally it has been found to vary weakly with composition and temperature. Knowledge of the thermal conductivity is important in both laboratory and computation settings as it allows heat transfer rates to be determined, provides insight into temperature gradients which may be forming in materials, and also provides insights into the convective fluid flow that can occur in liquids as a result of temperature gradients in the liquid (i.e. Marangoni flow).

There are several theories that describe the relationships between the electrical resistivity and the total normal, total hemispherical, and normal spectral radiative emissivities of metals, and these theories have been applied with varying levels of success [121,122]. One such relationship between the electrical resistivity and the normal spectral emissivity of metals, which has been successfully applied to a number of liquid metals [76,123,124], is found by applying the Drude free electron model in relation to a material’s optical constants. Within this framework, the optical constants of a metal can be shown to be [76]:

\[ n^2 - k^2 = 1 - \frac{\omega_p^2\tau^2}{1 + \omega^2\tau^2} \]  

\[ 2nk = \frac{\omega^2\tau}{\omega(1 + \omega^2\tau^2)} \]  

where \( n \) is the index of refraction, \( k \) is the extinction coefficient, \( \omega \) is the frequency of the electric field, \( \omega_p \) is the plasma frequency of the metal, and \( \tau \) is the relaxation time of the conduction electrons. The plasma frequency and relaxation time can be determined from:

\[ \omega_p^2 = \frac{Ne^2}{m_e\epsilon_0} \]  

\[ \tau = \frac{m_e}{Ne^2\rho_e} \]  

where \( N \) is the free electron density, \( e \) the electron charge, \( m_e \) is the electron mass, \( \epsilon_0 \) the permittivity of free space, and \( \rho_e \) is the electrical resistivity. Therefore, if values of the electrical
The standard method of measuring the electrical resistivity of solid materials is the four-probe method, shown schematically in Fig. 4.1. In this method, electrical contact is made at four locations along the length of a sample. The two outer connections deliver a DC excitation current that generates a potential along the length of the sample. The two inner connections, using a significantly smaller sense current, measure the electrical potential along the sample.
generated by the excitation current. A Keithley 2001 digital multimeter, for instance, uses an excitation current of approximately 10 mA and a sensing current of less than 100 pA. This allows the voltage generated across the sample to be significantly larger than the voltage generated along the sensing lead wires. Then, if the dimensions of the sample are well characterized, the resistivity is determined as:

$$\rho_e = \frac{V_s}{I_{ex}} \frac{A}{\ell}$$  \hspace{1cm} (4.9)

where $V_s$ is the measured sense voltage, $I_{ex}$ is the excitation current, $A$ is the cross sectional area of the sample, and $\ell$ the distance between the sense voltage contacts. When measured this way, the sense voltage provides a much more accurate indicator of the potential over the sample versus a two-probe method, for which the potential along the probe wires can be substantial and lead to erroneous resistivity values.

The four-probe method has been applied to the study of liquid metals (see for instance Refs. [126, 127]). However, extreme care must be taken which choosing the crucible and probe contact materials. Many metals, such as Al, Zr, and Ti are quite reactive and can react with both the crucible and the measurement contacts. Even if the crucible and contacts are not critically damaged, the reaction will cause significant contamination of the sample under study. This is evident in the discussion in Refs. [126, 127], in which the resistivity of liquid silicon was measured and the choice of crucible material (boron-nitride, aluminum oxide, or graphite in this case) is carefully scrutinized with regards to reactivity and contamination.
Furthermore, the physical contact required with this method extremely limits, if not outright prevents, supercooling of the liquid.

### 4.2.1.2 Pulse-Heating Method

In the pulse heating method, the sample to be studied is made into the form of a thin wire which is connected to a high voltage, high capacity capacitor bank, and via discharge of the capacitor the sample is rapidly heated. Heating rates achievable in this manner can be as high as $10^8$ K/s. Because of such rapid heating, the sample can be brought from room temperature, through the melting point, and up to the boiling point without the use of crucible, as there is insufficient time for the sample to deform under gravity. The electrical resistivity of the sample is measured essentially using the four-probe method, by measuring the discharge current of the capacitor and the voltage drop across the length of the sample using knife-edge contacts. This method has been successfully applied to measure the electrical resistivity of a variety of pure transition metals [128, 129] and binary alloys of Ni-Cu and Ni-Cr [130, 131] in the high temperature solid and equilibrium liquid phases. In addition to the electrical resistivity, the pulse heating method can be used to measure enthalpy, specific heat, and thermal expansion.

One potential drawback of this method is that ultra-high heating rates employed can result in a deviation of the measured properties from their true equilibrium values. Based on comparisons with data from other techniques, this does not seem to have been a problem for the materials measured thus far. The more serious drawback, with regard to studying supercooled liquids, is that the samples are destroyed during the measurement and thus there is no opportunity to study the supercooled liquid. This also eliminates the possibility for any post-measurement analysis on the samples.

### 4.2.2 Non-contact Techniques for Levitation Systems

#### 4.2.2.1 ESL

Rhim et. al [96] developed a variation of the rotating magnetic field technique to be used with ESL. A rotating magnetic field was generated by four wire coils wound around iron cores,
arranged uniformly around the top electrode and pointing at a downward angle toward the sample. By applying an appropriate cyclical current through the coils, a rotating magnetic field was generated at the sample position which resulted in a torque being applied to the sample. Because the levitation force is axisymmetric and the experiment takes place under high vacuum conditions, there are no additional drag forces being applied to the sample and the torque results in a steady angular acceleration of the sample about the vertical axis. By measuring the rates of angular acceleration or deceleration experience by the sample, the magnitude of the applied torque can be determined and, from that, ultimately the resistivity of the sample can be obtained.

This technique was applied to samples of pure aluminum and pure germanium with good success, but no other results have been published based on this technique. The major difficulty associated with the technique was in measuring the angular velocity of the sample. A metallic liquid which is pure and has an axisymmetric shape will appear isotropic during axial rotation. As such, strictly speaking, it is not possible to measure the angular velocity of a pure metal. For the technique to work, there must be distinguishable surface features on the sample. In the case of aluminum, those features were provided by the insoluble aluminum oxide patches that form as a result of exposure to atmospheric oxygen. There was likely a stable oxide impurity present in the case of germanium as well; this assumption is based on the limited supercooling achieved, as well as from personal experience in attempting to study germanium in the ISU-ESL.

4.2.2.2 CNL and EML

Methods for the measurement of electrical resistivity have been incorporated into both CNL [88] and EML [72]. In each case, the resistivity measurements are performed through the inductive coupling of the levitated samples to a sensing coil. The inductive coupling results a change of the AC impedance characteristics of the coil as a function of the electrical resistivity of the sample (this is similar to the technique developed for the ISU-ESL, and the mathematical formalism describing this behavior is described in the next section). To measure the electrical resistivity of the levitated samples, an AC-bridge method is used in combination with frequency scanning to perform measurements of the inductance and AC resistance of the coil. Changes
in the coil inductance are related to the real component of the complex susceptibility of the sample, while changes in the AC resistance of the coil are related to the imaginary component of the complex susceptibility of the sample. After characterization of the complex susceptibility of the sample, the electrical resistivity of the sample can be determined through analysis of the skin effect behavior.

While these techniques have been developed, they have also suffered drawbacks that have limited their use. In the case of the CNL implementation, the most significant drawback has been found to be the temperature stability of the sensing coil. During the course of experiments, the drifting temperature of the sensing coil has resulted in observed changes in the coil impedance characteristics that are not representative of changes in the sample’s electrical resistivity, but rather that are due to the coil’s own temperature dependent AC impedance. For this reason, the CNL electrical resistivity technique has only been applied to the measurement of the approximate liquid phase resistivities of materials that exhibit abrupt changes in the nature of their electrical resistivity upon melting, such as pure Ge [88], Si [88,132], B [133], and Al$_2$O$_3$ [88,134]. Because each of these materials are non-conducting in the solid phase, they are essentially invisible from an impedance standpoint and therefore the abrupt change in resistivity that occurs during solidification allows the liquid phase electrical resistivity to be determined. However, by and large no results have been published regarding the temperature dependent resistivities of these materials. Furthermore, while attempting to measure the temperature dependence of the electrical resistivity of liquid Al$_2$O$_3$, it was observed that the measured value of the resistivity varied depending on the type of gas that was used to achieve levitation [134].

In the case of the EML implementation of electrical resistivity measurements, a somewhat larger degree of success has been realized, although the number of results is still quite limited. Measurements have been performed on the temperature dependence of the electrical resistivity of high temperature solid and supercooled liquid Co$_{80}$Pd$_{20}$ [135], as well as a series of Cu$_{100-x}$Ni$_x$ ($x = 0, 20, 40, 60, 80, 100$) alloys [136]. The primary difficulty associated with EML measurements appears to be associated with the deformation of the sample shape, which is caused by the nature of the levitation forces. When the shape of the sample becomes sufficiently distorted from spherical, the assumptions that are made as part of the mathemat-
ical formalism relating the coil’s AC impedance to the sample’s electrical resistivity become invalid. While it has not been explicitly stated, it would not be surprising if the EML implementation also suffers from thermal instability of the sensing coil, based on similarities of the technique with the CNL implementation as well as the temperature instabilities encountered in the present work. Finally, more recent electrical resistivity measurements on the Cu-Ni alloys have been performed by a different research group who were also using EML, and the measured temperature dependences have been found to be different than the earlier measurements [137]. Beyond these reports, no other application of the EML implementation of electrical resistivity resistivity measurements on supercooled liquids could be found.

4.3 Mathematical Formalism for Inductively Coupled Measurements

The measurement technique employed in the ISU-ESL is similar to those techniques employed in CNL and EML, in that it is also an inductively coupled measurement technique. However, rather than performing direct measurements of the AC impedance of a coil through bridge-based measurements of inductance and AC resistance, the current technique relies upon frequency measurements of a self sustaining oscillator circuit to infer changes in coil inductance. Compared to bridge based AC impedance measurements, measurements of frequency can be performed to a very high degree of precision and accuracy in a very short amount of time. This is advantageous when measurements over wide temperature ranges are to be performed on the time scale of minutes as opposed to hours. The trade-off is that converting from units of frequency to units of electrical resistivity or magnetic susceptibility can be difficult, and usually require calibration with very well characterized materials with physical dimensions matching those of the sample under study. However, even when such calibration cannot be practically carried out, the measured frequency data can still be used to acquire relative measurements of resistivity and susceptibility. This allows the temperature dependent behavior of the electrical resistivity or magnetic susceptibility to be determined on a relative basis compared values obtained at a fixed temperature, such as room temperature or a materials melting point.

Oscillator techniques are based on the concept of $LC$ harmonic oscillators, whose resonant
frequencies are given by the well known equation:

$$f_0 = \frac{1}{2\pi \sqrt{LC}} \quad (4.10)$$

For the case of an inductively coupled oscillator, small perturbations in the inductance of the circuit will shift the resonant frequency by:

$$\frac{\Delta f}{f_0} = -\frac{1}{2} \frac{\Delta L}{L_0} \quad (4.11)$$

To understand how a sample’s proximity to a coil can change the coil’s inductance, we must consider the AC impedance of the coil. As part of an AC circuit, an inductor features a complex impedance given by:

$$Z = R_0 + i \omega L_0 \quad (4.12)$$

When a material with complex susceptibility $\chi_c = \chi' + i \chi''$ is placed inside of the inductor, the impedance characteristics of the inductor will be modified as follows:

$$Z = R_0 + i \omega (1 + \varphi \chi_c) L_0 = (R_0 - \omega \varphi \chi'' L_0) + i \omega (1 + \varphi \chi') L_0 \quad (4.13)$$

which yields the following two equations commonly found in the literature for relating the impedance characteristics of a coil to the susceptibility of a sample:

$$\frac{\Delta L}{L_0} = \varphi \chi' \quad (4.14)$$

$$\frac{\Delta R}{R_0} = -\frac{\omega L_0}{R_0} \varphi \chi'' \quad (4.15)$$

In these equations, $\varphi$ is the sample filling factor, a dimensionless quantity that describes the fraction of magnetic field energy stored within the volume of space occupied by the sample. In the case of an ideal solenoid, this would simply be the ratio of sample to solenoid volumes. In practice, because the magnetic fields generated by laboratory coils are not uniform, $\varphi$ must be determined via calibration with a well characterized sample.

Prados et al. [138] derived expressions for the complex susceptibility of a magnetic conducting sphere in an AC magnetic field. If the oscillator frequency is sufficiently high, such that the skin depth $\delta$ is much smaller than the radius $a$ of the sphere, then the complex susceptibility can be approximated as

$$\chi' = -\frac{3}{2} + \frac{9\delta}{4a} (1 + \chi) \quad (4.16)$$
\[
\chi'' = \frac{9\delta}{4a} (1 + \chi)
\] (4.17)

where \( \delta = \sqrt{2\rho/\mu\omega} \) is the classical skin depth, \( \rho \) is the sample resistivity, and \( \mu = \mu_0 (1 + \chi) \) is the permeability of a sample with DC magnetic susceptibility \( \chi \). Typical oscillator frequencies and skin depths encountered in the current application are \(~10\) MHz and \(~100\) \( \mu \text{m} \), respectively.

Combining Eqs. 4.11, 4.14, and 4.16, we arrive at an expression that relates the shift in oscillator frequency to the properties of the sample:

\[
\frac{\Delta f}{f_0} = \frac{3}{4} \varphi \left(1 - \frac{3}{2a} \sqrt{\frac{\rho}{\pi f_0\mu_0}} \sqrt{1 + \chi}\right)
\] (4.18)

It should be noted in Eq. 4.18 that any shift in oscillator frequency is caused by a combination of changes in sample resistivity and magnetic susceptibility. However, in general for a conducting sphere, the oscillator frequency will be much more sensitive to changes in resistivity than magnetic susceptibility. This is made clear by noting that \( \Delta f \propto \sqrt{\rho (1 + \chi)} \); because \( \chi < 10^{-2} \) for most materials [110], the magnetic contribution can usually be ignored. One obvious exception to this is any material which undergoes a paramagnetic-ferromagnetic transition, for which transitions from \( \chi < 1 \) to \( \chi > 1 \) are typical.

Table 4.1 lists some computed values of skin depth and oscillator frequency shifts for different resistivities, assuming a sample diameter of 2.5 mm, an oscillator frequency of 10 MHz, a filling factor of \( 5 \times 10^{-4} \), and zero magnetic susceptibility. Of note, while the total shift of frequency decreases as resistivity increases, the measurement sensitivity increases. The information in table 4.1 will be useful when considering the frequency stability of the oscillator circuit and pickup coil used in the practical implementation of this technique.

Table 4.1  Frequency shifts for some representative materials

<table>
<thead>
<tr>
<th>Material</th>
<th>( \rho ) (( \mu \Omega \cdot \text{cm} ))</th>
<th>( \Delta f ) (Hz)</th>
<th>( \Delta (\Delta f) ) (Hz) for ( \Delta \rho ) of 1%</th>
</tr>
</thead>
<tbody>
<tr>
<td>Perfect conductor</td>
<td>0</td>
<td>3750</td>
<td>0</td>
</tr>
<tr>
<td>Pure liquid Cu at melting point</td>
<td>21.0</td>
<td>3420</td>
<td>1.6</td>
</tr>
<tr>
<td>Typical liquid pure transition metal</td>
<td>100</td>
<td>3030</td>
<td>3.6</td>
</tr>
<tr>
<td>Typical bulk metallic glass</td>
<td>200</td>
<td>2740</td>
<td>5</td>
</tr>
</tbody>
</table>
4.4 Implementation of Inductively Coupled Oscillator

4.4.1 Tunnel Diode Oscillator

Generally speaking, there are several different types of $LC$ oscillator circuits that are capable of providing self-sustaining sinusoidal signals. Examples include the Hartley and Colpitts oscillator circuits commonly found in amateur radio systems. The particular oscillator circuit which has been used in the current implementation is the Tunnel Diode Oscillator (TDO), which has been used with good success in low temperature physics for several decades. The widespread use of the TDO stems from its ability to provide an exceptionally high level of frequency stability for the RF signal used in measurements, with stability on the order of $1-10$ parts per billion being commonly achievable [139]. Previously, the TDO has been used to perform measurements of magnetic susceptibility [140, 141], London penetration depth [142], and normal state resistivity of materials at cryogenic temperatures [143]. Compared to these previous implementations of the TDO, the current implementation is unique in that it has been adapted to perform measurements on solids and liquids at temperatures well above $1000$ K. As will be described below, this high temperature application introduces a new set of challenges regarding the temperature stability of the circuit which can limit the accuracy of physical property measurements.

A schematic of the TDO circuit is shown in Fig. 4.2. The basic operating principle of the circuit lies within the current-voltage ($I$-$V$) characteristics of the tunnel diode. When properly biased in the forward operating direction, the tunnel diode features a region of negative differential resistance in its I-V curve. This negative resistance effectively cancels the real (positive) resistance in the rest of the circuit, and allows for spontaneous oscillation at the resonant frequency of the $LC$-tank circuit. The resistors $R_1$, $R_2$, and $R_3$ work together to provide the proper DC-bias for the tunnel diode. Resistor $R_1$ serves to provide a high level of isolation for the circuit from rack mounted instrumentation. Resistor $R_3$ serves to suppress the amplitude of the oscillations such that the peak-peak voltage is within the most linear region of negative differential resistance of the tunnel diode; oscillation amplitudes beyond this region results in non-linear excitation of the $LC$-tank, resulting in harmonic generation and distortion.
Figure 4.2 Schematic of the TDO circuit.

of the signal. Capacitor C1 presents a high impedance to the RF signal, while capacitor C2 presents a low impedance. This configuration allows the RF voltage to be measured while drawing an insignificant amount of RF current, allowing the RF current to flow in an essentially closed loop consisting of the LC-tank, the tunnel diode, and R3. The TDO circuit is located within close proximity to the pickup coil to prevent the electrical connection between them from becoming too long and contributing significantly to the resonant frequency, and the RF signal travels up to the rack-mounted measurement electronics along the same coaxial cable that provides the DC supply voltage. A recipe for determining the values for each of these components can be found in Ref. [139].

When the RF signal reaches the electronics rack, it is first amplified and then mixed with a sinusoidal signal from a high stability local oscillator (LO), whose frequency is chosen to be 5-20 kHz higher than the fundamental frequency of the TDO. Mixing of the TDO and LO signals results in a new signal which contains frequencies $f_{\text{mix}} = f_{LO} \pm f_{TDO}$. The mixed signal is then bandpass filtered to reduce noise and eliminate any higher harmonics, allowing variations in the fundamental frequency of the TDO to be cleanly measured. The bandpass filtered signal is then amplified once more before being sent to a frequency counter for frequency determination. More detailed information regarding the specifications of the measurement electronics, as well as the DC power supply for the TDO, can be found in Ref. [144].
4.4.2 Temperature Sensitivity of the Pickup Coil

One aspect of the TDO that was not fully appreciated before work began on the project, is just how sensitive the TDO frequency is to the temperature of the pickup coil, and to a lesser extend the temperature of the TDO circuit as a whole. The temperature sensitivity of the coil was first noticed when the measured frequency was observed to shift by tens of Hz when the backlights for the ESL positioning or density systems were shone on the coil. As it turned out, the tens of milliwatts of power landing on the coil was enough to raise the coil temperature by a few tenths of a Kelvin, resulting in the observed frequency shift. Measurements of the actual temperature dependence were performed shortly after, with a coil mounted to a ceramic block and a temperature sensor mounted alongside. The results indicated that the temperature dependence was approximately 250-300 Hz/K. Considering the information in Table 4.1, this level of temperature sensitivity is quite problematic, as it indicates that the temperature of the coil needs to be stable to within 10 mK to perform accurate resistivity measurements. Accomplishing this level of stability is far from trivial when the coil is to be placed within close proximity to a sample which is radiating several watts of power and undergoing rapid temperature variations.

One of the major differences between the present implementation of the TDO technique with previous implementations is the ambient temperature at which the coil resides. As previously mentioned, almost all previous applications of the TDO have been for performing materials property measurements at cryogenic temperatures. In these applications, not only is the sample under study at cryogenic temperatures, but the TDO circuit and pickup coil are as well. In the low temperature physics labs at Iowa State, for instance, the TDO circuit and coil are both maintained at a temperature of 5 K [144]. To understand why the operating temperature of the TDO can make such a difference, we will discuss what gives rise to the temperature dependence in the first place.

The formula for the self-inductance of an empty circular loop with \( n \) turns is [145]:

\[
L_{\text{loop}} = \mu_0 n^2 r \left( \ln \left( \frac{8r}{a} \right) - 2 + F \left( \frac{\delta}{a} \right) \right)
\]

(4.19)

where \( \mu_0 \) is the vacuum permeability, \( r \) is the radius of the loop, \( a \) is the radius of the wire,
and \( \delta \) is the skin depth. The function \( F \) depends on the frequency of operation, and tends to a value of 0.25 when \( \delta \gg a \) and a value of 0 when \( \delta \ll a \). For small variations in temperature, the temperature dependence of the inductance, taking into account thermal expansion of the wire as well as the changes in skin depth caused by resistivity variations, is determined by

\[
\frac{\Delta L}{L_0} = \left( \alpha + \mu_0 n^2 r_0 \frac{F'(T_0)}{L_0} \right) \Delta T
\]  

(4.20)

While the functional form of \( F \) is difficult to derive analytically, it can be understood that its temperature dependence is driven primarily by changes in the resistivity of the wire forming the loop. This can be shown by considering the temperature dependence of the ratio of \( \delta/a \):

\[
rat = \frac{\delta}{a} = \frac{1}{a_0} \left( \frac{\rho_0 (1 + \beta \Delta T)}{\pi f_0 \mu_0} \right)^{\frac{1}{2}}
\]

(4.21a)

\[
\implies \frac{\Delta rat}{rat} = \frac{\beta - 2\alpha}{2} \Delta T
\]

(4.21b)

where \( \alpha \) and \( \beta \) are the temperature coefficients of thermal expansion and resistivity, respectively. For copper near room temperature, \( \alpha = 16.6 \times 10^{-6} \text{ K}^{-1} \) and \( \beta = 4.0 \times 10^{-3} \text{ K}^{-1} \), indicating that the temperature dependence of \( \delta/a \) is indeed due to changes in resistivity, not thermal expansion. We can then rewrite Eq. 4.20 as

\[
\frac{\Delta L}{L_0} = (\alpha + \beta B) \Delta T
\]

(4.22)

where \( B \) is a constant determined by the geometry of the particular coil. For the coils used in the ESL implementation of the TDO, the value of \( B \) has been determined empirically to be approximately 0.01; this value has been confirmed computationally via numerical simulation.

By combining Eqs. 4.11 and 4.22, we arrive at an expression for the change in TDO frequency caused by variations in coil temperature:

\[
\frac{\Delta f}{\Delta T} = -f_0 \frac{(\alpha + \beta B)}{2}
\]

(4.23)

Table 4.2 contains calculated values of \( \Delta f \) at a few select temperatures as well as experimental values for the thermal expansion and resistivity coefficients [146, 147]. As can be seen, the TDO frequency is most susceptible to temperature variation at temperatures in the region of
77 K. This is primarily due to the increase in the temperature coefficient of resistivity upon cooling towards low temperature. However, by the time the coil reaches a temperature of 5 K, the copper wire has entered the regime of impurity scattering and the temperature coefficient of resistivity approaches zero. Additionally, the temperature coefficient of thermal expansion decreases steadily as the temperature is reduced, with a particularly rapid reduction as the temperature drops below about 20 K. Taken altogether, we find that the TDO frequency is more than 10 thousand times more stable at 5 K than it is near room temperature. Furthermore, the properties of the circuit as a whole will become less temperature dependent as the various additional components (resistors, capacitors, tunnel diode, interconnects) are all operating in a regime where temperature fluctuations have very little effect on their electrical and mechanical properties.

<table>
<thead>
<tr>
<th>Temperature (K)</th>
<th>$\alpha$ ($10^{-6}K^{-1}$)</th>
<th>$\beta$ ($10^{-3}K^{-1}$)</th>
<th>$\Delta f$ (Hz/K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>293</td>
<td>17</td>
<td>3.9</td>
<td>285</td>
</tr>
<tr>
<td>77</td>
<td>8.0</td>
<td>31</td>
<td>1590</td>
</tr>
<tr>
<td>5</td>
<td>0.0046</td>
<td>0</td>
<td>0.023</td>
</tr>
</tbody>
</table>

The last thing that should be mentioned on this topic is that, in addition to the significantly reduced temperature sensitivity of the TDO frequency at 5 K vs. room temperature, the pickup coil also experiences essentially zero heat load. Because the coil and sample are not in contact and are mounted on different fixtures, and because radiation is so inefficient at cryogenic temperatures, there is no substantial heat being transferred to the coil over the course of a measurement and temperature stability of 1 mK is rather easily achieved. In fact, in some cases the opposite problem has been observed: eddy currents induced in the sample by the RF magnetic field of the coil can cause the sample temperature to fluctuate. This is a very different scenario than the one faced when trying to integrate the TDO into the ESL.
4.4.3 Integration of TDO Coil into ESL Electrodes

When incorporating the TDO coil into the ESL system, consideration must be given to several key points:

1. Maximizing the sample filling factor. As per Eq. 4.18, the magnitude of the frequency shift caused by a sample is directly proportional to the sample filling factor. Therefore, the coil should be brought as close to the sample as is reasonably possible, and the coil geometry should allow the sample to occupy a large fraction of the magnetic field produced by the coil.

2. Maintaining a clear optical path in the plane of the electrode gap. Many aspects of the ESL system rely on having an unobstructed view of the sample for operation. As such, any attempt at placing the coil within the plane of the electrode gap will likely interfere with one of the several ESL subsystems. For this reason, configurations where the coil is mounted on a horizontal linear translator and brought within close proximity to the sample have been avoided. A more favorable approach is one where the coil is built into the electrodes themselves, providing a close proximity while avoiding optical interference.

3. Electrical isolation of the coil from the high voltage electrodes, particularly the top electrode. Because the system makes use of high voltages with rapid transients, electrical isolation can be challenging. For instance, a ceramic spacer was designed for use with the top electrode with a DC breakdown strength of 200 kV. While this spacer could withstand 20 kV DC as well as a 0-20 kV step (using a bench-top power supply to control the amplifier output), the spacer broke down during the attempted launch of a sample. During sample launch, the high voltage amplifier output can go from 0 to 20 kV in approximately 2 ms (the time constant of the digital-analog controller), and such a rapid transient is difficult to insulate against. Attempts to integrate a coil into the top electrode should therefore be avoided, while integration into the bottom center electrode is most favorable.

4. Coupling of the RF magnetic field to the electrodes. The basic principle which allows
the coil to couple to the sample will also result in the coil becoming coupled to the levitation electrodes. Because the electrodes are quite large compared to the samples under investigation, the TDO frequency will be quite sensitive to changes in their temperature. Furthermore, due to the skin effect the electrodes play an important role in determining the shape of magnetic field distribution, and under certain circumstances may even block or absorb the field in such a way as to nearly eliminate the sample filling factor. Adequate spacing must be provided between the coil and all metallic components. There is a trade-off between the levitation requirements and the susceptibility measurement requirements, and so a compromise must be made between the two.

5. The thermal stability of the coil. As outlined in the previous section, the TDO frequency is very sensitive to the coil temperature. Therefore, there must be a means of either: shielding the coil from the sample’s thermal radiation to prevent significant heat transfer; intentionally heating and cooling the coil to provide a means of temperature control; or accurately, precisely, and quickly measuring the coil temperature, and developing a background model to allow the temperature induced drifting to be subtracted from the measurement. In practice, shielding the coil from thermal radiation has proven to be challenging, as the best thermal radiation shields tend to be films of metal such as gold, copper, or aluminum, and such films will strongly interfere with the RF magnetic field. Therefore, the last two options have been more heavily explored.

Taking into account each of these considerations, the coil integration scheme which was ultimately developed is displayed in Fig. 4.3. In this new electrode design, the bottom center electrode is replaced with a pedestal made of boron nitride ceramic. This pedestal forms the structure onto which the TDO coil and the temperature control components are mounted. Boron nitride was chosen because it has the best combination of engineering properties for this particular task: it is electrically insulating and nonmagnetic, so it is essentially invisible to the RF magnetic field; it has a high range of operating temperatures, up to 800 K; its thermal conductivity ranges from 33–59 W/m·K\textsuperscript{1}, significantly better than most ceramics; it is easily

\textsuperscript{1}Boron nitride ceramic is a cemented and pressed material, and the thermal conductivity depends on the pressing direction. For rods, the thermal conductivity is 33 W/m·K in the radial direction, and 59 W/m·K in
machined using standard tooling, enabling rapid prototyping; and finally, it is compatible with high vacuum. The pickup coil is made of 30 AWG copper wire (0.25 mm thickness) with polyimide insulation. The shape of the coil is that of a loop, approximately 9 mm in diameter with 10 turns in total (5 vertical, 2 radial). The coil is wound into a groove near the top of the pedestal and is potted in two steps: in the first step, a low viscosity cyanoacrylate adhesive is used to bond the wire to the ceramic, fill the gaps in the wire turns, and to provide structural rigidity; in the second step, the bonded wire is encapsulated using a high vacuum compatible two part epoxy. To measure the temperature of the coil, a platinum resistance thermometer (RTD) is epoxied onto the pedestal adjacent to the coil. To control the temperature of the coil, nichrome heating wire is wound onto the pedestal 1.5 cm below the TDO coil; the heating wire is potted in a similar manner to the TDO coil. The pedestal is attached to a large copper block, which stabilizes the pedestal temperature by providing heat capacity as well as assisting in heat transfer to the vacuum chamber. Prior to beginning a measurement, the coil temperature is raised well above room temperature (≈350 K) and maintained within a few Kelvin by reducing power to the nichrome wire as the samples temperature is increased.

While this design effectively stabilizes the coil temperature, it does not completely eliminate temperature changes of the coil over the course of an experiment. As previously mentioned, the TDO frequency is extremely sensitive to changes in the coil temperature, and so fluctuations on the order of hundredths of a Kelvin must be accounted for. Fortunately, this temperature dependence has been found to be very repeatable over a wide range of temperatures, and can be treated as a removable background provided a suitable model and measurable parameters exist. The platinum RTD allows for a temperature resolution of 1 mK, and therefore allows very small changes in the temperature of the coil to be measured. However, during the course of an experiment an offset develops between the temperature measured by the RTD and the true temperature of the coil. This offset is caused by the different locations of the two heat sources in play. As a sample’s temperature is increased, it begins to radiantly heat the pedestal from above, and the power of the nichrome heater is reduced accordingly. To dissipate the power from the sample, a temperature gradient will form along the length of the pedestal. Due to the axial direction
Figure 4.3  Electrode assembly incorporating the TDO coil and temperature regulating components: [Tan] Copper or stainless steel electrodes ((a) 0 to 20 kV; (b) fixed to ground; (c)+/−5 kV); [Light grey, (d)] Boron nitride mounting pedestal; [Green, (e)] Region where TDO coil is wound and potted; [Blue, (f)] Platinum resistance thermometer; [Red, (g)] Region where nichrome heating wire is wound and potted. A 3 mm hole drilled along the axis of the pedestal allows a stainless steel or copper rod to translate up and down, providing support for sample positioning and charging before initiating levitation. Top and bottom cylinders are 12 mm in diameter.

orientation and extent of the platinum RTD, a temperature gradient will form along its length as well and, as a result, the average temperature measured via the RTD will be lower than the actual temperature of the coil. This offset can be corrected because the magnitude of the temperature gradient is proportional to the amount of radiant power being dissipated, which itself is proportional to the amount by which the nichrome heater power must be reduced. Therefore, by monitoring the changes in the nichrome heater power the temperature offset can be compensated for. The exact scale factor between the nichrome heater power and the offset, as well as the dependence of the TDO frequency on the coil temperature, have been determined by performing empty-coil measurements. In these empty-coil measurements, a laser was used
to heat the top end of the boron nitride pedestal to simulate radiative heating from a sample and, by observing the change in TDO frequency as a function of coil temperature and heater power, a suitable background model can be obtained. The arrangement used to determine the background model is shown in Fig. 4.4.

![Schematic of the laser heating method](image)

Figure 4.4 Schematic of the laser heating method which was used to simulate the radiative heating from a sample and obtain the background thermal response of the TDO coil.

One consequence of the current design is that, due to a sample’s location above the plane of the TDO coil, the sample resides in a fringing magnetic field. As a result, the filling factor of any sample will depend on its position along the vertical axis of the electrode gap and, for a given position, the filling factor will not scale exactly as volume of the sample. As a result, calibration of the system becomes complicated because determination of the filling factor would require a standard sample to have the exact same size and position as the sample under investigation. Furthermore, the size and vertical position of the sample must be measured simultaneous to the TDO frequency during an experiment to allow the effects of thermal expansion and positional drifting to be accounted for. While the size and position of a sample can be accurately measured using the video imaging method described in Sec. 3.7, additional modeling is required to determine the exact functional dependence of the filling factor on these variables. Examples of such modeling can be found in Appendix B, however the full implemen-
tation of these corrections has not yet been carried out. For the extent to which this system has been used thus far, the effects of thermal expansion and positional drifting of the sample are sufficiently small so as to be ignored. However, to achieve the highest level of sensitivity and accuracy, such as would be required to perform reliable measurements of the temperature coefficient of resistivity in liquid metals (which can be quite small), these corrections must be carried out.

4.5 Validation of the Technique

4.5.1 Resistivity Measurements on Zirconium

To validate the technique for measurements of electrical resistivity, measurements were made on a 60 mg sample of pure zirconium. Zirconium was chosen for a number of reasons: (i) it is nonmagnetic, ensuring clear interpretation of the data; (ii) it has a well defined solid state resistivity over a wide temperature range (293–1973 K), including an anomaly at the structural transition from hexagonal close packed (HCP) to body centered cubic (BCC); (iii) the latent heat associated with the HCP-BCC phase transition at 1136 K provides a calibration point for pyrometric temperature measurements. Zr is also commonly used for testing other aspects of the ESL, due to its favorable properties of low vapor pressure, ability to reduce oxide impurities, and large oxygen solubility. The sample was prepared by arc melting a 60 mg piece of Zr on a water-cooled copper hearth, forming a small bead \( \sim 2.6 \text{ mm} \) in diameter which was suitable for levitation. Subsequent melting and solidification in the ESL resulted in the sample taking on a spheroidal shape with sufficient sphericity for the subsequent measurements. A high level of sphericity is important not only to ensure proper interpretation of the data via equation (4), but to reduce the scatter in the frequency data caused by sample rotation which tends to occur during heating. For molten samples this is less of a concern, because the surface tension forms the melt into a highly spherical shape.

Measurements were made over the temperature range from 640–1973 K. The sample was initially raised from room temperature to 640 K and maintained at that temperature for several minutes to allow the boron nitride post and all components mounted on it to achieve a steady
state of thermal transport which resulted in stable temperature measurement. The sample
temperature was then ramped at approximately 2 K/s to a maximum temperature of 1973 K.
During the ramp the TDO frequency, coil temperature, and heater power were all recorded at
a rate of 1 Hz. The measured frequency data were corrected for thermal drifting of the coil by:

\[
\Delta f' = \Delta f - A \Delta T_{Coil} + B \Delta P_{Coil}
\]  

(4.24)

where \(\Delta T_{Coil}\) is the change in coil temperature, \(\Delta P_{Coil}\) is the change in heater power, and the
factors \(A\) and \(B\) are determined prior to the experiment (as described in the previous section)
and found to be 205 Hz/K and 45.2 Hz/W, respectively. The raw data and the corrected
frequency data are shown in Fig. 4.5. Comparison of the raw and corrected frequency data
makes clear the need to monitor and control the TDO coil temperature, as the raw frequency
data have drifted by a factor of four compared to the corrected data. Frequency data for
sample temperatures above 1770 K have not been included because the heating of the levitation
electrodes by the sample radiation (which scales as \(T^4\)) caused an additional drifting of the
TDO frequency beyond that point. This problem can likely be overcome by redesigning the
electrode mounts to provide a more efficient means of dissipating the power absorbed from
radiation by the sample. Planned future modifications include replacing the current mounting
material, made of the low thermal conductivity steatite and MACOR ceramics, with the much
more thermally conductive boron nitride ceramic.

To convert the measured frequency data to an absolute value for the resistivity using
Eq. 4.18, two additional unmeasured quantities are required: the filling factor, \(\phi\), and the
extraction frequency. Nevertheless, the frequency data are still representative of the relative
temperature dependence of the resistivity, and to show this the frequency data have been plotted
along with the square root of the resistivity based on published data [148], and the results
are shown in Fig. 4.6. The measured frequencies can be seen to reproduce the published data
very well, capturing the temperature dependent trends above and below the structural transition,
as well as the anomaly which occurs at the transition. A comparison of these data has
also been used to determine the value of the filling factor during this experiment, which was
found to be \(6.8 \times 10^{-4}\).
To estimate the uncertainty in the measurement, we begin by noting the level of scatter in the data during an isothermal hold. During the 90 s hold at 640 K, the standard deviation, $\sigma$, of the measured frequency is 3.0 Hz. All data during the hold lie within $3\sigma$ of the mean, and so a conservative estimate of the uncertainty associated with a single data point would be $\delta f = 9.0$ Hz. At the HCP-BCC transition, there is a frequency shift of 70 Hz associated with a change in resistivity of 20 $\mu\Omega \cdot \text{cm}$, giving an approximate conversion of 3.5 Hz/$\mu\Omega \cdot \text{cm}$. From this, the uncertainty associated with a measured change in the resistivity is 2.6 $\mu\Omega \cdot \text{cm}$, and given that $\rho \approx 120$ $\mu\Omega \cdot \text{cm}$ at the transition, the relative uncertainty in the frequency
measurements is approximately 2.2%.

4.5.2 Paramagnetic-Ferromagnetic Transition in Steel

To demonstrate the measurement of a ferromagnetic transition with the current technique, measurements were performed on a commonly available low-carbon steel ball bearing (McMaster-Carr part # 96455K49) with a diameter of 3.2 mm. This type of steel is composed of at minimum 98 at.% iron, with the balance made up of roughly equal amounts carbon and manganese. The Curie temperature of this alloy is approximately the same as that for pure iron, 1043 K. Closely associated with the Curie temperature is a structural transition, from a low temperature phase of mainly BCC iron with small amounts of Fe$_3$C, to a high temperature phase of face centered cubic (FCC) iron.

The steel ball was brought to a temperature of 715 K and held at that temperature for several minutes until the boron-nitride post achieved a steady state of thermal transport. The sample temperature was then ramped at 1 K/s to a maximum of 1340 K, where it was held for one minute before cooling at the same rate back down to 715 K. After another one minute hold,
the heating-cooling cycle was repeated three additional times. While the sample temperature was being cycled, the TDO frequency and coil temperature were recorded at a rate of 0.5 Hz. At the time that these measurements were made, the heater power was not recorded; however, as will be evident, the corrections are not necessary for the purpose of simply observing the ferromagnetic transition. The pyrometer was calibrated such that the ferromagnetic-paramagnetic transition occurred at the anticipated temperature.

Figure 4.7  TDO frequency shift (blue dots) and temperature (red line) for a 3.2 mm, 130 mg low-carbon steel ball bearing processed in the ESL. The insets show the temperature plateau during heating and recalescence during cooling, and indicate that the ferromagnetic-paramagnetic transition occurs simultaneously with the BCC-FCC structural transition.

Fig. 4.7 shows the sample temperature and TDO frequency as a function of time for the second heating-cooling cycle. The small plateau in the sample temperature, near 450 s, indicates the location of the BCC-FCC transition, which appears to occur simultaneously with the magnetic transition at 1043 K (within 2 K). The transition from a ferromagnetic state to a paramagnetic state is indicated by a sudden drop in TDO frequency of 3370 Hz. During cooling, the transformation from the FCC to BCC structures does not occur at the same temperature as on heating, but rather is reduced by 95 K. Such supercooling has also been observed for the
BCC/HCP transition in pure Zr, and is possible due to the first order nature of the transitions. The release of the latent heat of transformation results in the sample temperature rise from 948–971 K near 1330 s in Fig. 4.7, as well as the back-bending in the $\Delta f$ vs. $T$ cooling data in Fig. 4.8. The supercooling of the FCC phase results in an associated reduction in the onset temperature for ferromagnetism, as only the BCC phase of iron is known to be ferromagnetic. The third and fourth heating-cooling cycles (not shown) produced results identical to the second, while a slight difference is observed for the first cycle. The different behavior is likely due to a difference in the thermal history of the sample for the first cycle compared to the second through fourth cycles.

![Figure 4.8 TDO frequency shift vs. temperature during heating (red closed circle) and cooling (blue open circle) for the 3.2 mm steel ball bearing.](image)

A better understanding of the behavior of the TDO frequency in this example can be realized by again noting that $\Delta f \propto \sqrt{\rho (1 + \chi)}$, along with a comparison of the results from pure Zr. At the HCP-BCC transition in Zr, a 17% change in the resistivity produced a change in the TDO frequency of 70 Hz. At the transition temperature for steel, the 3370 Hz transition would correspond to an approximately 10-fold increase in the product of the resistivity and the relative permeability. This increase is due entirely to the magnetic term, and corresponds to
a volume magnetic susceptibility of $\chi \sim 10$ (SI) below the transition temperature (assuming $\chi \ll 1$ above the transition temperature). This order of magnitude estimate seems reasonable given the low excitation field of the TDO coil, and is comparable to a value obtained for nickel using a similar technique [149]. The increase in the slope of $\Delta f$ vs. $T$ below the transition is caused by a combination of the greater value of the susceptibility as well as the greater temperature coefficient of resistivity [150, 151], and in general the behavior of the frequency below the transition is due to a mixture of the electrical and magnetic properties of the sample.

### 4.6 Outlook: Next Generation Design

After the initial validation the TDO method for performing relative measurements of electrical resistivity and ferromagnetic transitions, attempts were made to perform resistivity measurements on a sample of molten Cu$_{50}$Zr$_{50}$. However, due to the poor quality of the sample (see Ch. 5), it was difficult to obtain reliably good supercooling. In an effort to improve the supercooling, a significant overheating was performed on the sample which resulted in approximately 3 mg of Cu evaporating from the sample. Based on the amount of mass that was lost, as well as the distance from the sample to the boron nitride pedestal, the resulting layer of Cu that was deposited on the pedestal was estimated to be 0.5–1.0 $\mu$m thick. Following the deposition, the sensitivity of the TDO measurements was found to have dropped by roughly a factor of 50, rendering them essentially unusable. For a 10 MHz field, the skin effect of copper near room temperature is 21 $\mu$m, and so at first the diminished sensitivity may seem surprising. However, it is important to recognize that the deposited copper creates a highly conducting layer whose surface is perpendicular to the magnetic field generated by the TDO coil, while the classically defined skin depth is only valid for time-varying fields directed parallel to a surface. For a time-varying magnetic field directed perpendicularly to a conducting plane with adequate conductivity, the magnitude of the field approaches zero [109]. This would seem to indicate that the tolerance for sample evaporation, from the standpoint of performing RF susceptibility measurements, is extremely low. From these experimental results a 1 $\mu$m layer of copper deposition has been shown to be enough to inhibit the transmission of the RF magnetic field, but even layers on the order of 100 nm or less are likely to interfere with measurements provided
that they have a high enough conductivity. These findings indicate that present TDO method should only be used to study materials with extremely low vapor pressures.

To make matters worse, it has been found that even non-conducting deposition layers can affect the measurement performance of this technique. However, rather than influencing the magnetic field distribution, the non-conducting layers strongly influence the thermal behavior of the boron nitride pedestal, and as a result they influence the validity of the thermal background characterization as described by Fig. 4.4 and Eq. 4.24. This effect was first noticed when the boron nitride was cleaned to remove the aforementioned Cu deposition. After removing the deposition, another round of validation measurements were performed using a pure Zr sample to ensure that all was well with the system. The thermal behavior of the coil was modeled for these measurements using the same model and coefficients as discussed in Sec. 4.5.1. However, the results of these validation measurements were erratic and inconsistent with the previous results. In light of these findings, the laser heating method shown in Fig. 4.4 was reapplied to redetermine the thermal background coefficients. The results of the background determination were confusing. The heater power coefficient, $B$, which characterizes the temperature gradient along the length of the platinum RTD, had changed from a well defined value of positive 45 Hz/W to a less well defined value of approximately -16 Hz/W (negative!!). A negative value for this coefficient would indicate that hot end of the platinum RTD was away from the sample, instead of towards the sample as would be expected. These results were difficult to understand when first encountered, however, a physical explanation has been developed to explain them.

Boron nitride has an extremely low absorptivity towards electromagnetic radiation in the visible and infrared portions of the electromagnetic spectrum. This is what leads to boron nitride ceramics (as well as alumina ceramics, among others) appearing to be white in color. This property also means that when light is incident on piece of boron nitride, a large fraction of the light will be diffusely reflected away, while the remaining fraction will experience diffuse transmission into the material. If the particular workpiece is sufficiently thick, the portion of light which is diffusely transmitted will eventually become absorbed by the material. This results in light absorption taking place at penetration depths on the order of several mm inside
the boron nitride. However, if the boron nitride is coated with a material that is strongly absorbing in the visible and infrared portions of the spectrum, then transmission into the boron nitride will be limited and light will either be diffusely reflected or absorbed at the surface of the workpiece. This is the physical explanation for the strange observations made regarding the thermal behavior of the boron nitride pedestal.

At the time the background model was originally determined using the method described by Fig. 4.4 and Eq. 4.24, the boron nitride had been coated with a layer of pure Ge while attempting to measure the semiconductor-metal transition that occurs in Ge upon melting. After the Ge deposition had occurred, no attempt was made to remove it from the boron nitride because it was thought that the Ge deposition, being a thin semiconducting layer, would have no impact on the magnetic field. While this was true, the Ge had strongly changed the thermal behavior of the pedestal by changing the pedestal’s light absorbing characteristics. With the Ge deposition, light absorption occurred at the surface of the pedestal, resulting in the pedestal becoming hottest at its top end. When the pedestal was cleaned to remove all deposition, the majority of the light absorption occurred at several mm thickness into the pedestal. This is why the heater/gradient coefficient changed from a positive value to a negative value. Upon realizing this, a sample of Ge was processed in order to recreate the deposition layer. After deposition, the thermal characteristics of the coil were qualitatively restored to their initially measured state, but their exact quantitative value was still different. Further attempts to study Ge as well as Si resulted in additional deposition which further shifted the value of the heater/gradient coefficient, indicating that the exact value of the coefficient was very sensitive to the thickness of the deposition layer, and was therefore likely to be changing in a continuous manner during the course of any measurements on samples with any level of measurable evaporation.

One way to mitigate the effects of evaporation is to modify the coil system so that the susceptibility measurements can be performed at a much higher rate, on the order of 10 Hz as opposed to the rather slow 1 Hz that the current system is capable of. The reason why measurements with the current system must be performed slowly is because of the rather long thermal response time of the temperature measurement. Modifying the design to use a temperature
sensor with a shorter thermal response time would allow for faster measurements. However, it
has been difficult to identify a temperature sensor that has the requisite properties necessary
for the job: temperature measurement with precision and reproducibility better than 10 mK, a
very short thermal response time, a very small form factor (to avoid the temperature gradient
problems), and an operating temperature range above 300 K. Because of the lack of commercial
availability of such a sensor, another option has been explored: using the TDO coil itself to
determine its own temperature. This could be accomplished by performing measurements of
the DC resistance of the coil simultaneously to the measurements of the TDO frequency. In this
way, the coil would serve as a temperature probe in precisely the same manner as a platinum
RTD. With the coil serving as its own temperature probe, the conditions of thermal response
time and form factor are all ideally met, and the temperature range (for polyimide insulated
wire) extends up to 473 K.

To function as its own temperature probe, the remaining qualifications which the coil must
meet are the precision and reproducibility of the resistance measurement. This is where the
design considerations much be very carefully considered. For the coil to act as a precision RTD,
it must have a sufficiently high absolute resistance. The reason for this is that the temperature
resolution of the RTD is determined by the following:

$$\Delta T = \frac{\Delta R}{\alpha R_0}$$  \hspace{1cm} (4.25)

where $\Delta T$ is the temperature resolution, $\Delta R$ is the resolution of the resistance measurement,
$R_0$ is the absolute resistance of the RTD, and $\alpha$ is the resistivity temperature coefficient for the
metal from which the RTD is made. By increasing the magnitude of the absolute resistance
of the RTD, smaller changes in the temperature can be resolved. Lake Shore Cryotonics,
producers of some of the most commonly used temperature control hardware, tend to discuss
temperature measurement resolution in terms of the sensitivity, $S_T$, of a device:

$$S_T = \frac{\Delta R}{\Delta T} = \alpha R_0$$  \hspace{1cm} (4.26)

For instance, Lake Shore recommends the use of platinum RTDs over the temperature range
from 30–873 K [152], and throughout that temperature range the sensitivity of the platinum
RTDs varies between 0.191–0.423 $\Omega$/K [153]. Using the lower value of 0.191 $\Omega$/K along with a value of 0.0039 K$^{-1}$ for copper’s resistivity temperature coefficient near room temperature, the resistance of the TDO coil would need to be 49 $\Omega$ to match the low end of the performance of a platinum RTD while using Lakeshore’s electronics. For comparison, a typical TDO coil made of 28 AWG copper with 10 turns and a 4.5 mm radius has an absolute resistance of only 60 m$\Omega$. While it is possible to increase the resistance of the TDO coil by using a copper wire with a smaller radius as well as by increasing the number of turns, there are limits to the extent that this can be done before the performance of the RF circuit becomes compromised.

The three primary characteristics of the circuit that will be affected by increasing the resistance of the coil are: the impedance characteristics of the circuit, the quality factor the the coil, and the resonant frequency of the $LC$ tank. Referring back to Fig. 4.2, the values of the resistors R2 and R3 are typically on the order of 300 $\Omega$. If the DC resistance of the coil, LT, were to be increased from 60 m$\Omega$ to 49 $\Omega$, the voltage distribution throughout the circuit would be entirely changed, requiring an extensive effort to re-tune the circuit. Furthermore, even if the circuit could be tuned in such a way as to maintain self-sustaining oscillations, the quality factor of the coil would go down dramatically. The quality factor of an AC circuit element is determined by the ratio of energy stored vs. the amount of energy dissipated per cycle. Because capacitors tend to have very high quality factors, for a typical $LC$ tank circuit the quality factor will be determined by the inductor. For an inductor with a non-magnetic core the quality factor can be shown to be [154]:

$$Q = \frac{2\pi f_0 L}{R_L} = \frac{f_0}{2 \delta f}$$

(4.27)

where $Q$ is the quality factor, $f_0$ is the resonant frequency, $L$ is the inductance, $R_L$ is the DC resistance of the inductor, and $\delta f$ is the bandwidth of the $LC$ tank. Increasing the value of the coil’s DC resistance will result in an increase in the bandwidth of the $LC$ tank, which will effectively increase the noise level when attempting to perform measurements of the resonant frequency of the circuit. Lastly, increasing the inductance will result in a reduction of the resonant frequency of the tank circuit via Eq. 4.10, and consequently an increase in the magnetic skin depth. To ensure that Eq. 4.18 remains valid, the skin depth experienced by
a sample should be less than \(1/3\) of the sample’s radius (see Appendix B). While the value of the tank capacitor can be reduced to compensate for this effect, doing so will result in the resonant frequency becoming more susceptible to stray capacitances, and therefore care must be taken to minimize these effects.

Based on these considerations, parameters for a new coil can be suggested. The new coil should have the same size as the existing coil, approximately 4.5 mm radius, but it should be wound using 40 AWG copper wire with a total of 20 turns. The resulting coil will have an absolute resistance of approximately 2.0 Ω. Using a high precision digital multimeter (e.g. Keithley 2001) and a four-probe arrangement, a resistance resolution of 10 μΩ should be readily achievable. Such a combination of absolute resistance and measurement resolution will lead to an effective temperature resolution of 1.1 mK, which is comparable to the resolution achieved using a platinum RTD along with Lake Shore’s electronics. The inductance of the resulting coil will be approximately 11 μH, considerably greater than the 2 μH of the existing coil. The value of the tank capacitor should be chosen as the largest value possible which will result in a resonant frequency of 4 MHz. At this frequency, the condition that \(3δ \leq a\) will be satisfied for any sample with radius \(a \geq 1.1\) mm and resistivity \(ρ \leq 200 \mu Ω \cdot cm\), which should cover most samples of interest.

One other point that should be considered when determining the new coil design, is that the 40 AWG lead wires extending from the coil should be maintained as short as possible and should be connected to the rest of the circuit using a heavier gauge wire. This will ensure that the resistance which is being measured is dominated by the coil windings. This is important because any additional resistance contributed by the lead wires may result in errors in the characterization of the coil temperature, and these errors may be as large as the ratio of the length of the lead wires to the coil windings, per degree difference in their respective temperatures. For example, the proposed coil will be wound using 580 mm of wire; if each of the two lead wires are 10 mm long, and the coil wire and lead wires are at different temperatures, then the error in the temperature characterization of the coil may be as high as 3.4% per degree difference. To minimize this error, the lead wires should either be made shorter, or they should be heat sunk in such a way that their temperature is stabilized and the only change in
resistance that occurs is for the coil wire.

Another aspect of this idea that must be considered is that to perform DC resistance measurements on the coil while it is part of the TDO circuit, the resistance measurement probes and instrumentation will all become coupled to the RF circuit. This will result in the resonant frequency of the circuit becoming very sensitive to the stray capacitances and inductances of the resistance measurement probe wires and instrumentation. One way to mitigate this effect would be to connect inductors in series with the hot end of the probe wires as shown in Fig. 4.9. There are several characteristics that these inductors should have in order to allow the system to work as closely to ideal as possible. The inductance value of the blocking inductors should be much greater than that of the tank inductor, because the three inductors will form a parallel circuit. A value of $L_B \geq 200 L_T$ will limit the contribution of the blocking inductors to the total TDO inductance to less than 1%. The inductor core should have a magnetic permeability with a large real component and small imaginary component to ensure that the blocking inductors are not lossy. The blocking inductors should also have a low DC resistance. Strictly speaking, the resistance of the lead wires (including blocking inductors) should not impact the measured resistance when using a four-probe method. However, Keithley recommends that the total lead plus measured resistance not exceed $21 \Omega$ in order for the multimeter to achieve maximum accuracy. The inductors should also either be shielded or have a closed magnetic field distribution to prevent them from coupling to adjacent materials. And finally, it should be possible to thermally stabilize the inductors so that their values of inductance and DC resistance do not drift significantly over time.

As it turns out, inductors that meet each of the specifications just stated are very difficult to obtain commercially. However, it should be possible to construct a custom inductor that comes close to meeting the ideal specifications. The style of the inductor should be that of a toroid, because the magnetic field of a toroid will be contained within the highly permeable core and therefore create a closed (intrinsically shielded) magnetic field. A number of different toroidal ferrite cores are available, for instance from Fair-Rite Products Corp, with various sizes and magnetic properties. As an example, we consider a toroidal inductor made using Fair-Rite part no. 5952020601, which is a ferrite ring with 22.7 mm O.D., 13.5 mm I.D., and
6.35 mm height. At 4 MHz, the relative permeability of this ring is $\mu_r = 250 + 10 \, i$, so the core losses will be minimal. Using 32 AWG wire (0.2 mm diameter) and allowing for single diameter spacing along the ring interior, it should be possible to get $n = 105$ turns around the core. The inductance factor for this ring is $151 \, \text{nH} \, n^{-2}$, giving a total inductance of 1.66 mH, a factor of 150 greater than the TDO coil. The resistance per unit length for 32 AWG is 538 m$\Omega$/m, and so the total DC resistance of this inductor would be 1.2–1.5 $\Omega$, depending on the tightness of the windings. Finally, thermal stability could be achieved by placing the wound toroid into a small container and encapsulating it with an impregnating potting compound. This would increase the thermal mass of the inductor as well as help to minimize heat transfer to or from the surroundings. Ohmic heating of the inductor should be minimal.

The last topic to be considered as part of the redesign is the thermal stability of the electrodes and their mounting structures. At present, the structure onto which all of the electrodes are ultimately mounted (referred to as the electrode stage) is made of stainless steel. The standoffs on which the top, floating lateral, and grounded lateral electrodes are all mounted are made of Macor, steatite, and 304 stainless steel, respectively. Each of these materials has a low thermal conductivity (1.5, 3, 16 W m$^{-1}$K$^{-1}$, respectively), and as a result the temperature of the electrodes will tend to slowly and continually rise during the course of an experiment. This situation is made worse by the lack of thermal compound at the mounting interfaces, which results in very poor heat transfer between the individual components. Because the
electrodes are coupled to the RF field of the TDO, a drift in the temperature of the electrodes will result in a drift in the background level of the TDO frequency. To mitigate this effect, the electrode stage and standoffs should all be rebuilt using more thermally conductive materials. The electrode stage can be constructed out of aluminum, whose thermal conductivity (170 W m\(^{-1}\)K\(^{-1}\)) is much greater than that of stainless steel. The mounting structure for the top electrode can be constructed using a pressed boron nitride rod, whose axial thermal conductivity (55 W m\(^{-1}\)K\(^{-1}\)) is far better than that of Macor. The length of the boron nitride standoff must be great enough to prevent electrical breakdown during the rapid high voltage transients which occur during sample processing (particularly during the launch). It has been experimentally found that a 4 mm length (200 kV DC strength) is not sufficient to withstand the 0–20 kV transient that occurs during a sample launch, therefore a 40 mm length would be suggested. The lateral electrodes and the boron nitride post onto which the coil is would should be mounted onto a large copper block to provide passive heat sinking. The floating lateral electrodes can be insulated from the copper heat sink using a 1.5 mm thick layer of boron nitride ceramic; the lateral electrodes do not experience the same rapid transients as the top electrode, and therefore the DC dielectric strength of 75 kV should be plenty. Finally, if possible, thermal epoxy should be used to permanently bond the electrodes and their respective standoff materials to ensure the best interfacial thermal conductance possible. For the rest of the electrode state, where the use of thermal epoxy is not feasible, a non-bonding thermal adhesive should be used along with standard machine screws to ensure adequate thermal conductivity across the various interfaces.

4.7 Conclusions

A new method for performing measurements of the electrical resistivity and magnetic susceptibility of electrostatically levitated materials has been successfully implemented in the ISU-ESL. The new method makes use of a tunnel diode oscillator (TDO) circuit in combination with inductive coupling to the samples. Through measurements of the oscillator frequency, relative measurements of the electrical resistivity can be performed, as well as the detection of paramagnetic-ferromagnetic transitions. The ability to perform relative electrical resistivity measurements was demonstrated by measuring the change in the TDO frequency while a sam-
ple of pure Zr was heated from 640–1770 K. The measured frequency data were found to be in excellent agreement with literature values for the electrical resistivity of pure Zr, capturing both the temperature dependent behavior as well as the resistivity anomaly that occurs at the HCP-BCC solid state transition. The ability to detect paramagnetic-ferromagnetic transitions was demonstrated on a commercially available low carbon steel ball bearing. The change in the TDO frequency that occurs at the magnetic transition is on the order of thousands of Hz, and is therefore easily detectable. Furthermore, the ability to supercool the high temperature phase of steel, and therefore suppress the onset of the ferromagnetic transition, has been demonstrated.

While the current system has been shown to suffer from unwanted thermal drifting of the coil temperature, as well as from interference caused by vapor deposition on the boron nitride pedestal on which the coil is mounted, it should still be possible to use the system in its present state to perform measurements on several materials of interest. A wide range of materials exist that have both low melting temperatures (below 1500 K) and low vapor pressures (showing no deposition). Examples of materials for which there is a known scientific interest include: several Zr binary alloys in systems such as Zr-Ni, Zr-Pt, Zr-Pd; the Vitreloy family of Zr-based bulk metallic glasses; Ti_{39.5}Zr_{39.5}Ni_{21}; Ni-Nb alloys near the eutectic Ni_{62}Nb_{38}; Pd-Si alloys with concentrations near Pd_{80}Si_{20}; and quite likely several others. The system is also presently capable of detecting ferromagnetic transitions. Examples of potentially interesting candidate materials include Co_{80}Pd_{20}, which may undergo a ferromagnetic transition in the deeply supercooled liquid state, and near eutectic compounds of Fe-B, Ni-B, and Co-B, each of which demonstrate the formation of ferromagnetic metastable crystalline phases.

To improve upon the present state of the system, a new method of measuring the temperature of the coil must be developed. The new method must allow for more rapid temperature measurements, and it must be less susceptible to the deposition dependent light absorbing characteristics of the boron nitride mounting pedestal. It has been suggested that this can be accomplished by performing simultaneous DC resistance measurements on the coil. Careful consideration has been given to many aspects of this idea, and a detailed plan has been produced that should allow for simultaneous measurements of TDO frequency and of the coil’s DC resistance. Once implemented, the more rapid coil temperature characterization should
allow for significantly improved measurement capabilities, including the ability to perform measurements during free cools and through phase transitions, all the while experiencing less interference caused by vapor deposition. Many of the components necessary to construct the next generation system have already been purchased, and the construction and implementation is ready to proceed.
CHAPTER 5. THE INFLUENCE OF HIGH VACUUM AND OXIDE IMPURITIES ON SAMPLE PROCESSING

The single greatest obstacle faced throughout the development of the new ISU-ESL laboratory has been the persistent presence highly stable, insoluble oxide impurities found to be present on the surfaces of samples under investigation. These oxide impurities have interfered not only the with the testing and benchmarking of the new ESL instrumentation and measurement methods, but also the scientific investigation of the materials themselves. Based on consistencies between investigations at ISU, conversations with other researchers in the field, and literature reports of supercooling studies of a variety of materials (using ESL as well as other methods), the issues of sample contamination appear to be related to ESL processing in general, and are not limited to those studies performed at ISU. While the ESL technique has been used to study refractory elements and Zr-based alloys with good success, a wide range of materials, including pure elements as well as alloys, have displayed limited supercooling ability during ESL processing. For many of these materials (such as Cu, Ge, and Co-Pd alloys) other processing methods such as EML, CNL and melt fluxing have been used to achieve very deep supercooling, consistently in excess of 300 K. In an attempt to understand and potentially remedy the poor processing performance of these materials using ESL, an extensive effort has been carried out to determine the nature of the oxide contamination, and how to either prevent or remedy the problem. The findings are presented in this chapter.

5.1 Processing Characteristics of ISU-ESL Samples

Table 5.1 shows a list of all materials that have been processed in the ISU-ESL between October 2010 and January 2014, along with qualitative indicators of processing performance
for those materials. Poor quality indicates that a sample was difficult to process into the liquid state and/or displayed limited supercooling (<50 K) during free cools. Moderate quality indicates that the samples could be processed into the liquid state with little difficulty and that reasonably good supercooling could be achieved (>50 K), but the supercooling was less than that reported in the literature and impurities were visually present on the sample surface. Excellent quality indicates that the samples were very easy to process into the liquid state and that the supercooling was great (>250 K), highly repeatable, and generally in line with maximum supercooling expectations based on available literature reports. Excellent quality samples also showed the ability to exist in the deeply supercooled state for extended periods of time (several minutes) so that processing was not limited to free cooling, but also slow cooling (∼1 K/s) and isothermal holds.

Table 5.1  Materials that have been processed in the ISU-ESL prior to January 2014

<table>
<thead>
<tr>
<th>Composition</th>
<th>Sample purity &amp; processing performance</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zr (low oxygen)</td>
<td>Excellent</td>
</tr>
<tr>
<td>Zr (heavily oxidized)</td>
<td>Excellent</td>
</tr>
<tr>
<td>Si</td>
<td>Excellent</td>
</tr>
<tr>
<td>Ge</td>
<td>Moderate</td>
</tr>
<tr>
<td>Cu</td>
<td>Poor</td>
</tr>
<tr>
<td>B</td>
<td>Moderate</td>
</tr>
<tr>
<td>Pd</td>
<td>Poor (evaporation)</td>
</tr>
<tr>
<td>Co&lt;sub&gt;100−x&lt;/sub&gt;Pd&lt;sub&gt;x&lt;/sub&gt; 50 ≤ x ≤ 80</td>
<td>Poor to Moderate</td>
</tr>
<tr>
<td>Fe&lt;sub&gt;83&lt;/sub&gt;B&lt;sub&gt;17&lt;/sub&gt;</td>
<td>Poor to Excellent</td>
</tr>
<tr>
<td>Ni&lt;sub&gt;83&lt;/sub&gt;B&lt;sub&gt;17&lt;/sub&gt;</td>
<td>Poor</td>
</tr>
<tr>
<td>Co&lt;sub&gt;81&lt;/sub&gt;B&lt;sub&gt;19&lt;/sub&gt;</td>
<td>Poor</td>
</tr>
<tr>
<td>Fe&lt;sub&gt;66.7&lt;/sub&gt;Si&lt;sub&gt;33.3&lt;/sub&gt;</td>
<td>Poor to Excellent</td>
</tr>
<tr>
<td>Fe&lt;sub&gt;75&lt;/sub&gt;Si&lt;sub&gt;25&lt;/sub&gt;</td>
<td>Poor</td>
</tr>
<tr>
<td>Cu&lt;sub&gt;50&lt;/sub&gt;Zr&lt;sub&gt;50&lt;/sub&gt;</td>
<td>Poor to Excellent</td>
</tr>
<tr>
<td>Ni&lt;sub&gt;50&lt;/sub&gt;Zr&lt;sub&gt;50&lt;/sub&gt;</td>
<td>Poor to Excellent</td>
</tr>
<tr>
<td>Cu&lt;sub&gt;50−x&lt;/sub&gt;Ni&lt;sub&gt;x&lt;/sub&gt;Zr&lt;sub&gt;50&lt;/sub&gt;</td>
<td>Poor</td>
</tr>
<tr>
<td>Zr&lt;sub&gt;80&lt;/sub&gt;Pt&lt;sub&gt;20&lt;/sub&gt;</td>
<td>Moderate</td>
</tr>
<tr>
<td>Pd&lt;sub&gt;81&lt;/sub&gt;Si&lt;sub&gt;19&lt;/sub&gt;</td>
<td>Moderate</td>
</tr>
</tbody>
</table>

As can be seen in Table 5.1, the only materials that consistently showed an excellent processing ability are pure Si and pure Zr. The case of Zr is interesting, because even heavily
oxidized\textsuperscript{1} samples have been found to perform well. The cases of pure B and pure Pd are somewhat outliers. The vapor pressure of Pd resulted in a massive amount of evaporation, resulting in a very short experiment time with limited observations made. In the case of pure B, the vapor pressure was low enough that several melting/cooling cycles could be performed; however the degree of supercooling was rather low, only 60–70 K. There is at least one report \cite{155} indicating that supercooling in excess of 300 K should be achievable, but it is unclear what prevented deeper supercooling from being achieved in our case. Each of the remaining materials on the list can be placed into one of two primary categories based on their processing performance: non-Zr-based alloys and Zr-based alloys, with Fe-based alloys being a special subset of the former.

The first samples to be identified for investigation within the ISU-ESL research group, and the first samples to be processed using the ISU-ESL, were a series of Co-Pd alloys notable for their magnetic behavior in the deeply supercooled liquid state. However, during the processing of these samples in the ESL, it was noticed that the range of supercooling that could be achieved was far less than that for Co-Pd samples processed using EML. At the same time, it was also noticed that all of the Co-Pd samples studied in the ESL appeared to have insoluble impurity phases present on the sample surfaces, an example of which is shown in Fig. 5.1. These insoluble impurity phases act as heterogeneous nucleation sites and, as such, their presence on the sample surfaces reduces the maximum supercooling which can be achieved. However, the impact of these insoluble phases is not limited to heterogeneous nucleation and the consequently reduced supercooling. Because the insoluble phases have different emissivities than the clean metal surfaces, measurements of sample temperature are negatively affected as the apparent temperature of the sample is observed to fluctuate in a noisy/random manner as the insoluble phase moves in and out of the view of the sample from the perspective of the infrared pyrometers (similarly, this is why the insoluble phases show up as bright patches in Fig. 5.1). The varying emissivities reduce not only the reliability of all temperature measurements, but also the reliability of any measurements of the sample’s specific heat, which relies crucially

\textsuperscript{1}Though not analyzed for oxygen content, it is obvious that the samples were heavily oxidized based on the blue and yellow surface coloration, as well as the broad transition temperature for the HCP-BCC solid-solid transition
Figure 5.1 A Co$_{80}$Pd$_{20}$ sample being laser melted on a graphite substrate. The bright patch of insoluble material on the sample surface has been determined to be Al$_2$O$_3$.

upon both accurate temperature measurements as well as reliable estimations of the sample’s emissivity. Furthermore, the presence of the insoluble impurity phase can strongly interfere the ability to induce oscillations in a levitated sample, which interferes with the ability to perform reliable measurements of surface tension and viscosity. Finally, if the insoluble phase has any appreciable thickness, it will even interfere with the acquisition of reliable volume/density data. Taken altogether, the effects of the impurity phase have strongly limited the extent to which Co-Pd samples can be studies using the ESL technique.

The observation of insoluble impurity phases is not limited to the case of Co-Pd alloys. Impurity phases have also been observed to be present in samples of pure Ge and Cu, as well as Fe-B, Ni-B, Co-B, Fe-Si, and Pd-Si alloys. The impurity phases appear to be highly stable from a thermal standpoint, as extended processing of samples at high temperatures failed to remove them. They also appear to be chemically stable, resisting attack from a variety of chemical solvents and reducing agents when applied at room temperature: water, methanol, ethanol, isopropyl alcohol, acetone, hydrochloric acid, sulfuric acid, nitric acid, hydrofluoric acid, sodium hydroxide, and mixtures of hydrofluoric and acetic acid with bromine additives have all failed to remove the insoluble phases from the samples. Attempts at mechanically removing the insoluble phase, via Si-C abrasives as well as scratching with steel razor blades, have also failed to produce cleaner samples.
To gain insight into the nature of the insoluble phases, samples of pure Cu, Fe$_{83}$B$_{17}$, and Co$_{80}$Pd$_{20}$ were studied using a scanning electron microscope (SEM) which also employed energy dispersive spectroscopy (EDS) for the purpose of elemental analysis. EDS works by bombarding a material with high energy electrons (5–25 keV), resulting in the emission of x-rays which are characteristic to the element being excited, and thus can be used to fingerprint which atomic species are present in a material. When the clean portions of a sample were inspected via EDS, the results were precisely what was expected: pure Cu, Fe plus B, and Co plus Pd were found in each of the respective samples. However, when the contaminated portions of the samples were inspected, something unexpected was found: large concentrations of Al plus O. In some portions of the sample, the impurity phase was so thick that the only elements detected were Al and O. This information, combined with the observed thermal and chemical stability, would seem to indicate that the impurity phase in each of these samples is actually aluminum oxide, Al$_2$O$_3$. This is rather unfortunate, as Al$_2$O$_3$ is one of the most thermally and chemically stable materials known, and its hardness makes it resistant to attack with mechanical abrasives.

As to where the Al$_2$O$_3$ contamination originates, the answer to that questions is still unknown. One possibility is that the oxide forms from the reaction of oxygen, present in the atmosphere as well as in the residual gases under high vacuum, with elemental Al which is present as an impurity phase in the raw materials. Another possibility is that the contamination occurs as a result of material handling: Al$_2$O$_3$ is one of the most commonly used abrasives, found in a variety of sand-papers and abrasive pads (e.g. green Scotch-Brite) which are used for cleaning tools and for preparing surfaces. However, even when the highest purity starting materials were used (Al concentrations less than 0.1 ppm), and the use of Al$_2$O$_3$ abrasives were eliminated, patches of Al$_2$O$_3$ continue to be observed on samples. Because of the persistence of Al$_2$O$_3$ within a variety of materials systems, and because of the thermal, chemical, and mechanical stability of this oxide phase, a new method will need to be developed for removing the Al$_2$O$_3$ from samples that have been found to be contaminated, even when stringent preparation precautions have been taken.

We now turn our attention to Zr-based alloys, where a different sort of sample contamination has been observed. Similar to the Al$_2$O$_3$ patches on non-Zr-based samples, the oxides that
Figure 5.2  Temperature-time curve for three consecutive melting/cooling cycles of a Cu$_{50}$Zr$_{50}$ sample. The feature at (a) is associated with the dissolution of an insoluble (likely oxide) phase during heating, while the feature at (b) is associated with the precipitation of the insoluble phase during cooling. The features near 1175 K and 1205 K correspond to a solid-solid structural transformation and the melting temperature, respectively.

form on Zr-based alloys act as heterogeneous nucleation sites, reducing the degree of supercooling that can be achieved, as well as contributing to difficulties regarding temperature and thermophysical property measurement as described above. However, whereas non-Zr-based alloys show the presence of insoluble Al$_2$O$_3$ patches that persist throughout processing, Zr-based alloys show the presence of an insoluble oxide that (i) shows a definite temperature dependence to its stability and (ii) the presence of which appears to vary strongly from one alloy to the next as well as among different samples of the same alloy. An example of the temperature dependence of the oxide stability is shown in Figs. 5.2 and 5.3.

Fig. 5.2 shows the temperature vs. time data for three consecutive heating/cooling cycles of a Cu$_{50}$Zr$_{50}$ sample. The features at 1175 K and 1205 K correspond to solid-solid structural transitions and the congruent melting point of the sample, respectively. Along with the solid-solid and melting transitions and their associated transitions on cooling, two additional transitions are shown two occur at the points labeled “a” and “b”. Note that the temperature
dependence of each of these transitions is highly repeatable for this sample. The transition occurring at point "a" appears to be a dissolution transition, wherein an oxide phase which is uniformly distributed over the sample surface spontaneously dissolves and is observed to disappear. The disappearance of the oxide phase results in an associated reduction in the emissivity of the sample, which results in the abrupt drop in the apparent temperature. Upon cooling, the precipitation of the oxide phase appears to be kinetically hindered, as it does not occur until the sample has cooled to a temperature approximately 150 K lower than the dissolution temperature. The precipitation is observed to occur at feature "b", and results in a noisy region of temperature measurement during the precipitation followed by a different cooling rate for the sample after the precipitation. It should be noted that the difference in the cooling rates determined before and after the precipitation of the oxide phase might be confused for a sudden change in the temperature dependence the sample's specific heat capacity. Fig. 5.3 shows color images of the sample before and after the oxide dissolution. The presence of the oxide phase is most noticeable in the images by focusing on the bright reflections of the ESL positioning lights along the sample equator. The oxide phase results in significantly more diffuse reflection on the sample surface compared to the clean surface which is present after dissolution. Similar observations have been made for samples of Zr$_{80}$Pt$_{20}$. 

Figure 5.3 A liquid Cu$_{50}$Zr$_{50}$ sample processed in the ESL. (Left) Before dissolution, the molten sample with uniform, insoluble oxide coverage. (Right) After dissolution, the molten sample with a clean, oxide-free surface. The difference is most noticeable by comparing the reflections along the sample equator.
At the time that these observations were made, it was not immediately clear what the nature of the oxide phase was. The optical and thermal properties of the oxide are different enough from the \( \text{Al}_2\text{O}_3 \) that was observed on non-Zr-based samples that it was assumed that the present oxide was likely \( \text{ZrO}_2 \) which was forming as a result of oxygen saturation of the samples, although this assumption has not been verified using analytical methods. It is well known that researchers at other institutions have been able to successfully process Zr-based alloys using ESL on multiple occasions. It would seem then that the problem encountered by the ISU-ESL group is a matter of oxygen contamination that occurred during the sample preparation process, although the source of this contamination was unknown at the time the experiments were carried out. Assuming that the oxygen contamination could be eliminated, there is still another open question: why is the oxide phase on Zr-based samples observed to become thermally unstable and breakdown (dissolve), whereas the oxide phase on non-Zr-based samples is persistent at all temperatures? And why is it possible, with careful sample preparation, to produce high quality, clean Zr-based samples when nearly all other alloys display insoluble oxide contamination issues?

Finally, we consider the special subset of the non-Zr-based alloys, the Fe-based alloys. Three different Fe-alloys have been processed in the ISU-ESL: \( \text{Fe}_{83}\text{B}_{17} \), \( \text{Fe}_{66.7}\text{Si}_{33.3} \), and \( \text{Fe}_{75}\text{Si}_{25} \). These samples share many of the processing characteristics of the other non-Zr-based alloys in that the have been observed to be contaminated with insoluble oxide phases that appear to be patches of \( \text{Al}_2\text{O}_3 \) based on all available information. However, while materials such as pure Ge, Cu, Co-Pd and Pd-Si alloys could all be melted and processed into the liquid state with relative ease (despite substandard supercooling), all Fe-based samples that have been studied in the ISU-ESL prior to Jan. 2014 has proven to be extremely difficult to process into the liquid state. While the samples could be heated from room temperature up to the melting point without difficulty, as soon as these samples began to melt they would become unstable from a levitation standpoint, and would frequently and consistently drop onto the electrodes while either partially molten or just after becoming fully molten. Occasionally after the samples had dropped, they would become fused to the the electrodes and the vacuum chamber would have to be opened to remove the samples. However, usually the samples could be mechanically
jarred free of the electrodes by using the actuating system for the sample positioning post. In this case, the samples could then be laser-melted on the post to reform a spheroidal shape and eventually relaunched to make another attempt at melting. Even after multiple instances (several tens) of being melted under high vacuum conditions, either while levitated or while sitting on the positioning post, the samples would continue to show levitation instabilities and eventually drop. This behavior has made it very challenging to process these samples in the ESL, let alone to perform reliable thermophysical property measurements.

Because these types of levitation instabilities have only been encountered with Fe-based alloys, it has been assumed that the problem is related to the Fe content and its tendency to readily oxidize (rust), and that any alloy with a significant Fe content will be similarly problematic. Because of iron’s ferromagnetic properties, highly allotropic nature, significant abundance, and its prominent role in both industry and science, there are many different types of Fe alloys that could be very interesting to study using the ESL. Therefore, it is very desirable to determine not only what is causing these levitation instabilities, but to develop a means to remedy the problem so that Fe-based alloys may be processed in the ESL in a more consistent and reliable manner.

5.2 Gas Kinetics for Evaporation & Oxidation Rates

Before further discussing the nature of the various problems and potential remedies regarding ESL sample processing, it is useful to have a detailed discussion regarding the evaporation and oxidation rates experienced by samples. Up until very recently, concepts such as sample evaporation or oxidation have been treated only in a qualitative manner. This has frequently led to guessing games when trying to determine, for instance, how hot and for how long a sample can be processed before evaporation becomes considerable. In other cases, the effect of residual gases in terms of sample oxidation has been treated in a similarly poor manner. Such uncertainty can be avoided, because the issues of sample evaporation and oxidation can be treated quantitatively by using concepts from the kinetic theory of gases.

Within the framework of kinetic theory, the particle flux of an ideal gas passing through an
area can be shown to be [117]:

\[ Z = \frac{n\bar{v}}{4} \]  \hspace{1cm} (5.1)

where \( Z \) is the particle flux with units of number per unit time and area, \( n \) is the particle number density, and \( \bar{v} \) is the average particle velocity. The particle number density and average particle velocity can be obtained from the ideal gas law and the Maxwell-Boltzmann velocity distribution, respectively:

\[ P = nk_B T \]  \hspace{1cm} (5.2)

\[ \bar{v} = \left( \frac{8k_B T}{\pi m} \right)^{1/2} \]  \hspace{1cm} (5.3)

where \( P \) is the gas pressure, \( T \) is the gas temperature, \( m \) is the particle mass, and \( k_B \) is Boltzmann’s constant. On substituting Eqs. 5.2 and 5.3 into Eq. 5.1, the particle flux of an ideal gas is found to be:

\[ Z = P \left( \frac{1}{2\pi m k_B T} \right)^{1/2} \]  \hspace{1cm} (5.4)

Eq. 5.4 forms the basis of the quantitative approach to dealing with the concepts of sample evaporation and oxidation rates. Because the particle mass, the gas pressure, and temperature are either well known or measurable quantities, the particle flux can be easily calculated. This allows the evaporation rate to be calculated in terms of an outward flux of metal vapor particles leaving the sample surface, and the oxidation rate to be calculated in terms of an inward flux of residual gas particles striking the sample surface. For oxidation, the rate calculated with Eq. 5.4 should be considered as an upper limit; as will be discussed below, additional thermodynamic consideration must be given with regard to oxide formation.

It should also be noted that at the pressures normally encountered in ESL experiments, the mean free path of all gas particles is large in comparison to the chamber dimensions. This means that particle-particle interactions can be ignored, and the invocation of ideal gas behavior is justified.

For the purpose of calculating evaporation rates of ESL samples, Eq. 5.4 can be rewritten in practical units as

\[ Z_{evap} = 440 a_x Pr^2 \sqrt{\frac{M}{T}} \]  \hspace{1cm} (5.5)
where $Z_{\text{evap}}$ is the evaporation rate in mg/min, $P$ is the vapor pressure in Torr, $r$ is the sample radius in mm, $M$ is the molar mass of the element under consideration in g/mol, $T$ is the sample temperature in Kelvin, and $a_x$ is chemical activity of the particular element in question for the case of an alloy. The chemical activity is a thermodynamic variable that accounts for the nature of the mixing that is occurring within an alloy. In a system that exhibits ideal mixing, the chemical activities of the alloying elements will be equal to their respective mole fractions. However, in general, most metallic alloys do not exhibit ideal mixing, and the chemical activities must be obtained through thermodynamic analysis, such as that which is performed during the development of binary phase diagrams.

There are several good references for determining the vapor pressure of the elements. The RCA vapor pressure curves [156] are probably the most commonly used reference for such data. One drawback with the RCA curves is that they can be difficult to read, due to a large amount of information being packed into a single chart. The resources used most frequently in the ESL lab have been the Yaws Handbook [157] as well as the CRC Handbook [110], both of which provide coefficients for the calculation of vapor pressure as a function of temperature. The general practice has been to compare the information from each of these sources to check for consistency and to ensure the information is accurate.

As an example, we consider the case of pure liquid Si. In preparation for a Neutron-ESL experimental run, and before there was an awareness of Eq. 5.5, an experiment was carried out to determine how much mass would be lost from a 78.1 mg Si sample if it was melted and maintained at a temperature above its melting point for approximately 30 min. The melting point of Si is approximately 1687 K, and just above the melting point a 78.1 mg sample would have a diameter of 3.86 mm. During the experiment, several minutes were required to bring the sample through its melting transition, followed by a brief overheating to 1820 K, before bringing the sample to a temperature of approximately 1707 K for the remaining time. The actual mass loss of the sample over the duration of the experiment was measured to be $4.4 \pm 0.1$ mg. Using the recorded temperature data, the known size of the sample, and available vapor pressure data, the expected mass loss may be calculated via Eq. 5.5. Using data from the Yaws Handbook, the total expected mass loss would have been 3.2 mg, about 27%
lower than the actual mass loss. The discrepancy may be caused by errors in the temperature measurements or inaccuracy of the vapor pressure data. Because of the logarithmic dependence of vapor pressure on temperature, small errors in either the temperature measurement or vapor pressure data may lead to significant discrepancies in the mass loss calculation. Because the CRC Handbook does not contain vapor pressure coefficients for pure Si, an alternative means of vapor pressure calculation was carried out. This method uses thermochemical data to calculate the equilibrium vapor pressures based on the Gibbs free energy of transformation (see Sec. 5.3). Using this method, the mass loss is expected to have been 4.1 mg, in much better agreement with the measured mass loss. This would seem indicate that, at least for the case of Si, the Yaws Handbook underestimates the vapor pressure. For other elements, such as Al, the Yaws Handbook data and the thermochemical data are in better agreement.

We now turn our attention to the matter of oxidation rates, and how they are impacted by the quality of the vacuum. It has already been mentioned in Sec. 3.9 that high vacuum conditions are required in ESL systems to prevent gaseous dielectric breakdown from occurring; for this purpose it was found that a pressure of approximately $10^{-5}$ Torr or lower is sufficient. When it comes to processing samples, the usual practice has been to allow the chamber pressure to fall below $5 \times 10^{-7}$ Torr before attempting to heat and melt the sample; this value was chosen because it can be attained in a reasonably short amount of time while also being within a factor of 10 of the achievable base pressure of the chamber. But to what extent might sample processing be affected by higher or lower pressure levels? This is the question we look to answer by considering the maximum oxidation rate of samples.

Before continuing, it is necessary to consider the nature of the residual gases that are present at high vacuum. In any well behaved, unbaked high-vacuum system, the most prevalent residual gas is water vapor, which may constitute anywhere from 70–95% of the residual gas [158,159]. In addition to water vapor, other gases which may be present are CO, CO$_2$, N$_2$, and O$_2$. There are two different reasons for water vapor’s prevalence. First, water vapor readily undergoes chemisorption and physisorption processes which result in a large quantity of H$_2$O becoming adsorbed by the interior surfaces of the vacuum chamber. The effect of these processes is most noticeable during the initial pumping of the vacuum system, and it may require upwards of one
week of pumping to allow the surfaces to become sufficiently outgassed before the vacuum base level is reached. The effect of water vapor is so significant that variations in the laboratory humidity can change the time to reach the vacuum base level by 2–3 days or more. Once the base level is reached, water vapor will continue to be the dominant residual gas due to permeation through elastomer gaskets. For Viton gaskets, water vapor is 40–200 times more permeable than O\textsubscript{2} and 7 times more permeable than CO\textsubscript{2}; for neoprene these numbers are 350 times and 70 times, respectively [158, 160]. Using this information as justification, it will be assumed for simplicity throughout the remainder of this chapter that the residual gas found at high vacuum is entirely water vapor.

We can now address the question of the rate of oxidation of samples. For simplicity, we will consider the maximum oxidation rate possible, assuming that the water vapor sticking coefficient is 1. Also, because the surface area of the chamber is much greater than the surface area of a sample, the residual gas will thermalize to the chamber temperature and may be taken to have an ambient temperature of 300 K. Under these conditions, the maximum oxidation rate caused by the residual water vapor can be determined by applying Eq. 5.4:

\[ Z_{\text{H}_2\text{O}} = P \times 4.8 \times 10^{18} \]  

where \( Z_{\text{H}_2\text{O}} \) has units of mm\textsuperscript{-2}s\textsuperscript{-1} and \( P \) is the gas pressure in Torr.

For a typical sample size of 2.5 mm diameter, processed under a pressure of \( 1 \times 10^{-6} \) Torr for 1 hour, the total number of H\textsubscript{2}O particles that collide with the sample surface is approximately \( 3.4 \times 10^{17} \). Compare this number with the total number of atoms in a sample: with sample masses typically tens of milligrams, and molecular weights typically tens of grams per mole, a typical sample would contain about one millimole, or about \( 6 \times 10^{20} \) atoms. This indicates that samples containing elements that are stronger reducing agents than H\textsubscript{2} can undergo oxidation at a rate of approximately 500 parts per million atoms (ppma) per hour if processed at \( 10^{-6} \) Torr. By allowing the pressure to fall to \( 10^{-7} \) Torr or lower before attempting to process a sample, the oxidation rate can be reduced to 50 ppma per hour or less.

To what extent can these rates of oxidation affect a sample? To put it into perspective, we can compare the quantities just mentioned to the oxygen content listed on chemical assays for
a variety of materials. High purity Zr, Fe, and Cu, for example, can be purchased with oxygen contents below 500 ppma [161]. In terms of the impact of oxygen content on sample processing, two examples pertaining to Zr alloys are available to shed some light on this question. The first example pertains to studies of a rapidly quenched Zr$_{80}$Pt$_{20}$ alloy in which the oxygen content was intentionally varied to study its affect on glass formation [162, 163]. Among the results, it was shown that samples containing approximately 7000 ppma oxygen have better glass forming ability than those samples containing significantly more ($\gtrsim$ 10000 ppma) or less ($\lesssim$ 3000 ppma or less) oxygen, indicating a profound effect of the oxygen on the behavior of the supercooled liquid over a narrow concentration range. The second example comes from first-hand experience during the commissioning of the Neutron-ESL (NESL) system at Oak Ridge National Lab. During the experimental run, difficulties were encountered with the vacuum chamber and it was not possible to reduce the chamber pressure below about 2–3×10$^{-6}$ Torr, indicating an oxidation rate of 1000-1500 ppm per hour. A sample of Ti$_{39.5}$Zr$_{39.5}$Ni$_{21}$ was melted and maintained at a temperature near 1375 K for about 4 hours while diffraction data were acquired. By the end of the experiment, the sample had absorbed enough oxygen from the residual gas that the solubility limit had been exceeded, and solid oxides came out of solution and were distinctly visible on the sample surface. These examples indicate that the oxidation rates encountered during ESL experiments can have a significant impact on sample processing, and that the chamber pressure should be maintained as low as possible to prevent substantial oxygen absorption by samples during experiments.

5.3 Oxide Thermodynamics and Stability

When metallic elements are processed (or even simply placed) in the presence of oxygen, there is a possibility that the metals will react with the oxygen to form metal-oxides. However, the stability of the oxides which form will depend on both the temperature of the material as well as the partial pressure of oxygen in the environment. When multiple metallic species are present, the formation of one metal-oxide may be preferred over the other, which could have major implications for sample processing depending on the nature of the two oxide phases with respect to their metal counterparts (i.e. soluble vs. insoluble oxides). Furthermore, certain
elements, such as hydrogen and carbon, form gaseous oxides, and the reaction of a metal-oxide with either of these elements may result in the reduction of the solid oxide in favor or the gaseous oxide. Because the gaseous oxides will volatilize, reaction of metal-oxides with hydrogen and carbon results in a possible purification method. To understand the conditions under which any of these reactions may take place, the thermodynamics of the oxidation and reduction processes must be considered.

Similar to what was discussed in Sec. 2.1.1, whether or not a chemical reaction will be considered thermodynamically favorable is determined by the Gibbs free energy of reaction. Consider the following generic chemical reaction:

\[
aA + bB \rightarrow cC + dD
\]  
(5.7)

where \(a\) moles of chemical \(A\) react with \(b\) moles of chemical \(B\) to produce \(c\) moles of chemical \(C\) and \(d\) moles of chemical \(D\). If the sum of the Gibbs free energy of the products (\(C\) and \(D\)) is less than the sum of the Gibbs free energy of the reactants (\(A\) and \(B\)), then the chemical reaction will proceed to the right, and vice versa. However, if any of the reactants or products are present as a gas phase, then certain restrictions will be placed on the partial pressures of those gases. Those restrictions can be determined based on the Gibbs free energy of reaction, and in the most general sense the relationship is given as:

\[
\Delta G^o \leq -RT \ln \left( \frac{p_C^o c}{p_A^o a} \left( \frac{p_D^o d}{p_B^o b} \right) \right)
\]  
(5.8)

where \(\Delta G^o = cG_C + dG_D - (aG_A + bG_B)\) is the standard Gibbs free energy of reaction, \(p_{(A,B,C,D)}\) are the partial pressures of the gases during the reaction, \(p_{(A,B,C,D)}^o\) are the partial pressures of the gases in their standard states, \(R\) is the universal gas constant, and \(T\) is the temperature. The partial pressures of the gases in their standard states are usually taken to be either 1 bar or 1 atm (depending on the data source), and the partial pressures of any reactants present in the solid or liquid phases are taken to be equal to their standard partial pressures. For instance, if we assume that chemicals \(A\) and \(C\) are either solid or liquid while chemicals \(B\) and \(D\) are gases, and we take the partial pressures in the standard state to be 1 atm, then
Eq. 5.8 can be rewritten as:

\[ \Delta G^o \leq -RT \ln \left( \frac{(p_D)^d}{(p_B)^b} \right) \]  

(5.9)

where it is understood that the partial pressures have units of atm.

As an example relevant to the processing of samples in the ESL, we can consider the case of pure copper, which oxidizes according to the following reaction:

\[ 2Cu + \frac{1}{2}O_2(g) \rightarrow Cu_2O \]  

(5.10)

The Gibbs free energy of formation of Cu\(_2\)O as a function of temperature is given as

\[ \Delta G^o_{Cu_2O} = -1.692 \times 10^5 + 73.36T \]  

(5.11)

where \( \Delta G^o_{Cu_2O} \) has units of Joules. Based purely on Eq. 5.11, it would be expected that copper oxide should be stable to temperatures in excess of 2000 K. However, because samples processed in the ESL are processed under conditions of high vacuum, it is important to consider the partial pressure of the reacting gas. Applying Eq. 5.9, the partial pressure of O\(_2\) required for the stable formation of Cu\(_2\)O is given by:

\[ p_{O_2} \geq 760 \exp \left( \frac{2\Delta G^o_{Cu_2O}}{RT} \right) \]  

(5.12)

where \( p_{O_2} \) has units of Torr. For the oxide to be stable, the partial pressure requirement must be less than the residual gas pressure in the chamber, typically a few times \( 10^{-7} \) Torr or less. Near room temperature the partial pressure of O\(_2\) required to stabilize oxidation is incredibly low, approximately \( 4.1 \times 10^{-49} \) Torr. However, the partial pressure requirement goes up dramatically as the temperature is increased: at 1050 K, \( p_{O_2} \geq 5.1 \times 10^{-7} \) Torr and at 1350 K, just below the melting point, \( p_{O_2} \geq 2.8 \times 10^{-3} \) Torr. Because these pressures exceed the residual gas pressure in the chamber, it can be concluded that any copper sample processed in the ESL should be free of copper oxide.

Pure copper has been processed in the ISU-ESL on a number of occasions. During the first few attempts, the samples used for investigation were copper ball bearings obtained from McMaster-Carr. The samples were made of 99.95% mass purity copper, and were 2.38 mm in diameter. Before being placed in the vacuum chamber the samples were rinsed with ethanol and
acetone. During the processing of these copper ball bearings, it was observed that the samples could not be brought to their melting point. Even after processing in the ESL for 8 hours, the levitation voltage continued to rise and levitation stability suffered if the sample temperature was increased too much. One observation which was made at the time, but not understood until recently, was that despite being unable to melt these samples in the ESL, the samples appeared to be much cleaner when they were removed from the vacuum chamber; the luster had changed from a dull brown to a rather bright orange-pink. In hindsight it is quite clear what was going on. When the samples were initially placed into the chamber they had a relatively thick coating of Cu$_2$O, resulting in the dull brown appearance. Because the samples were then processed under conditions of high temperature and high vacuum for several hours, the Cu$_2$O became destabilized and was reduced to pure Cu and gaseous O$_2$, which was subsequently pumped away. Furthermore, as the reduction process was occurring, the emissivity of the sample was being continually reduced, and so the sample temperature towards the end of the experiment was likely much higher than was realized at the time. It is unclear how much further processing would have been required to be able to melt the sample, but given the lack of progress after 1+ day of processing the matter was not pursued. Better progress with pure copper has been achieved using an in-house method to prepare samples. Starting with either a 6N copper wire (Alfa Aesar) or an OFHC copper rod (McMaster-Carr), approximately 50 mg pieces of copper were cut, rinsed with hydrochloric acid, water, and isopropyl alcohol, and laser melted on a quartz substrate under high vacuum. Samples prepared in this manner could be successfully melted in the ISU-ESL, however, they were found to be contaminated with Al$_2$O$_3$ which limited the achievable supercooling.

The general chemical equation which describes the reaction of formation of a binary oxide is given as:

$$xA + \frac{y}{2}O_2(g) \rightarrow A_xO_y$$

(5.13)

where $x$ moles of element $A$ reacts $y/2$ moles of $O_2$ to form one mole of the binary oxide $A_xO_y$. It is important to note that chemical equations that describe a reaction of formation are balanced such that they describe the formation of a single mole of the product. This is true by definition. Along with the reaction of formation, there is an associated standard Gibbs
free energy of formation, $\Delta G^0_A$, which is the change in the Gibbs free energy that takes place when one mole of the product is produced. This fact, that there is a single mole of product, is being stressed because that is how the data is presented in thermochemical databases such as the NIST-JANAF Thermochemical Tables \[164\] and the Center for Research in Computational Thermochemistry (CRCT) Fact-Web \[165\]. While this is, by definition, how the data should be presented, in practice it can be very useful to use a different formulation.

When comparing the reducing strengths of several elements (stronger reducing agents form more stable oxides) it is useful to reformulate the chemical reactions such that they are taking place per mole $O_2(g)$. In this manner, Eq. 5.13 can be rewritten as:

$$\frac{2x}{y} A + \frac{2y}{2} A_x O_y$$

For this chemical reaction, the Gibbs free energy is $\Delta G^E_A = \frac{2y}{y} \Delta G^0_A$. We can also consider a second such oxidation reaction:

$$\frac{2q}{z} B + \frac{2q}{2} B_q O_z$$

with its associated Gibbs free energy $\Delta G^E_B = \frac{2q}{y} \Delta G^0_B$. The utility of this formulation of oxidation reactions becomes apparent when we try to compare the relative reducing strengths of elements $A$ and $B$. If Eq. 5.15 is subtracted from equation Eq. 5.14, the resulting chemical reaction is given as:

$$\frac{2x}{y} A + \frac{2q}{z} B_q O_z \rightleftharpoons \frac{2y}{y} A_x O_y + \frac{2q}{z} B$$

and the Gibbs free energy of this reaction is $\Delta G^E_{AB} = \Delta G^E_A - \Delta G^E_B$. As can be seen, the role of molecular oxygen, $O_2(g)$, has been removed from the picture, and the chemical reaction now appears to take place between elements $A$ and $B$ and their respective oxides. The relative reducing strengths of elements $A$ and $B$ can now be directly compared. If element $A$ is a stronger reducing agent than element $B$, then $\Delta G^E_{AB}$ will be negative and the reaction will proceed to the right. If element $B$ is the stronger reducing agent, then $\Delta G^E_{AB}$ will be positive and the reaction will proceed to the left.

Because oxidation/reduction reactions take place by essentially trading oxygen atoms between reducing elements, the process of reformulating the reactions as taking place per mole
O$_2$(g) essentially normalizes the oxidation reactions so that multiple oxide species can be directly compared against each other. This is particularly useful when it is realized that elements can form into several different types of oxides (monoxides, dioxides, trioxides, etc.), each having a different coefficient in front of the O$_2$(g) in Eq. 5.13. While the exact choice for normalization is somewhat arbitrary, normalizing per mole O$_2$(g) has the added benefit that the Gibbs free energies of reaction are more directly related to the partial pressure of O$_2$(g) required to stabilized oxide formation:

\[ p_{O_2} \geq 760 \exp \left( \frac{\Delta G^E_A}{RT} \right) \]  

(5.17)

Fig. 5.4 shows a plot of the temperature dependence of the Gibbs free energy $\Delta G^E$ per mole O$_2$ for a large number of metal-oxides. The lower an oxide is on the diagram at any given temperature, the more stable the oxide and the more potent the reducing power of the element. In cases where an element may form several oxides, only the most stable oxide is shown on the diagram. The only exception to this is pure Fe: while FeO is the most stable form for temperatures above 850 K, Fe$_3$O$_4$ is the most stable below 850 K; however, the difference is quite small. Diagrams such as this are known as Ellingham Diagrams, after Harold Ellingham who first constructed and published such a diagram in 1944 [166]. In addition to the Gibbs free energy axis, a true Ellingham Diagram would also contain three addition axis: one for the determination of the partial pressure of O$_2$ required to stabilize the oxides; one for the determination of the H$_2$/H$_2$O ratio necessary for hydrogen gas to be able to act as a reducing agent; and one for the determination of the CO/CO$_2$ ratio necessary for carbon monoxide gas to be able to act as a reducing agent. These additional axis have been left off of the digram in Fig. 5.4 because they are largely unnecessary within the current discussion. Instead, four addition Gibbs free energy lines have been drawn. The line labeled $10^{-7}$ Torr pO$_2$ indicates the stability barrier for oxides processed in the ESL. Any oxide located above this line will become unstable and eventually break down if processed under the typical vacuum conditions found in the ESL chamber. Any oxide above the line labeled $10^{-3}$ Torr pO$_2$ will experience a more rapid decomposition. The lines labeled 4N H$_2$ and 6N H$_2$ represent the purity of an H$_2$ containing gas which would be required for H$_2$ to act as a reducing agent to facilitate the removal of oxides. The use of H$_2$ reducing gases will be discussed in more detail in Sec. 5.4.
Figure 5.4 Ellingham-type diagram showing the Gibbs free energies of formation for several metal-oxides.
With Ellingham diagram in hand, we can begin to understand several of the observations which have been made regarding sample oxidation and reactivity. We first note that for several materials, oxidation will not be possible under the high vacuum conditions found in the ESL. These materials include: Au, Ag, Pd, Cu, Ni, and Co. If an oxide of any of these materials is already present on a sample, it will decompose at a rate determined by its $p_{\text{O}_2}$. At first glance, it would appear that the oxide of Ge should be stable in the ESL, at least for an overheating of less than 300 K above its melting point (1211 K). However Ge also forms a gas phase oxide, GeO($g$), and as will be shown in Sec. 5.5, the existence of gas phase oxides can destabilize solid phase oxides when processed under conditions of high vacuum. Iron oxide, which is thought to play a role in the levitation instability observed in Fe-based alloys when processed in the ESL, appears to be stable for temperatures below 1650 K, which is greater than the melting temperatures of the Fe-alloys studied in the ESL (1448 K for Fe$_{83}$B$_{17}$ and 1488 K for Fe$_{66.7}$B$_{33.3}$). It would therefore seem unlikely that the levitation instability which occurs during the melting of these materials is being caused by the decomposition of iron oxide into Fe+$\text{O}_2$. However, just as with Ge, it will be shown that the existence of gas phase oxides may be playing an important role, and in this case it is the oxides of B and Si that may be affecting the sample processing behavior. Finally, we can see that pure Al is a much stronger reducing agent than nearly all of the other materials which have been processed in the ESL. This would explain why the Al$_2$O$_3$ surface impurities have not observed to break down during the processing of samples, even after being in contact with high temperature molten metals for extended periods of time.

Studying the information contained within Ellingham diagrams has been very helpful in understanding the behavior of the Zr-based alloys. As stated earlier, provided that proper care is taken to prevent oxygen saturation during sample preparation, Zr and its alloys are the only materials other than pure Si which are found to be free of insoluble surface oxides. In the other pure elements and alloy systems studied, insoluble Al$_2$O$_3$ has been identified as the impurity phase. The reason why Zr and its alloys are not also contaminated with Al$_2$O$_3$ is quite simple: at temperatures above 1000 K, Zr is a stronger reducing agent than Al. Therefore, if any Al$_2$O$_3$ was to be present on the sample surface, it would be broken down and dissolved.
by the Zr content. This is likely why \( \text{Al}_2\text{O}_3 \) has not been found as a surface impurity in these materials.

As to why so much difficulty has been encountered with oxygen saturation in Zr-based alloys, it has been found that suboptimal procedures have been used during sample preparation. For instance, silica tubes and crucibles are frequently used to contain the alloy materials while they are being melted during the injection casting process which is used to produce spheroidal samples. Based on the information in the Ellingham diagram, we see that Zr is a much stronger reducing agent than Si, and therefore when Zr-based alloys are melted in a silica crucible, the \( \text{SiO}_2 \) will be reduced and the oxygen will be pulled into the alloy. It is not clear whether this is the main reason for the oxygen contamination, but it is clearly a contributing factor. Another contributing factor is that the injection casting system has been frequently found to be poorly sealed against atmospheric oxygen contamination. Because Zr is such a strong reducing agent, it will readily react with any amount of oxygen in the processing environment.

To alleviate these problems, a new sample preparation protocol has been developed for all Zr-based alloys. In this new protocol, the alloy master ingots are made and subsequently formed into 3 mm dropcast rods using the professional grade arc-melting station at the Ames Laboratory Materials Preparation Center (MPC). These rods can then be cut into appropriately sized pieces, and laser melted on a clean copper or graphite substrate within the high vacuum chamber of the ESL. By eliminating the use of an oxide crucible and by avoiding the use of sample processing equipment that frequently suffers oxygen contamination problems, preparing samples in this manner should help to prevent unwanted oxidation of the samples. Another advantage of this method is that by preparing the sample spheroids in the ESL chamber, the high magnification color imaging system can be used to monitor the surface quality of the samples during the melting process. This information can be used to determine if the samples are clean or contaminated at the time of preparation.

### 5.4 Oxide Reduction via Reducing Gas

One method of removing oxide impurities from a metal is to process the metal at high temperatures in the presence of a reducing gas. Two examples of commonly used reducing
gases are carbon monoxide and hydrogen gas, which react with oxygen (or other oxide species) to form carbon dioxide and water vapor, respectively:

\[ 2 \text{CO}(g) + \text{O}_2(g) \rightarrow 2 \text{CO}_2(g) \]  

(5.18)

\[ 2 \text{H}_2(g) + \text{O}_2(g) \rightarrow 2 \text{H}_2\text{O}(g) \]  

(5.19)

Based on the normalized Gibbs free energies of reactions for the formation of \( \text{CO}_2(g) \) and \( \text{H}_2\text{O}(g) \), as shown on the Ellingham Diagram in Fig. 5.4, it might be expected that CO(g) and H\(_2\)(g) processing gases would only be useful as reducing agents for the oxides species shown at higher positions on the diagram. However, it is important to realize that the energies of reaction assume that the reacting gases (H\(_2\)(g) and H\(_2\)O(g), CO(g) and CO\(_2\)(g)) are present in equal molar quantities. If high purity reacting gases are used, such that the product phases are present in diminished quantities, then there will be an additional contribution to the Gibbs free energy of reaction that will increase the reducing capability of the reacting gas.

At temperatures above 1000 K, H\(_2\)(g) will be a stronger reducing agent than CO(g) because the Gibbs free energy change associated with Eq. 5.19 is more negative than that associated with Eq. 5.18. Furthermore CO(g) is known to be toxic, and therefore represents a significant health risk. For these reasons, H\(_2\)(g) is the favored reducing gas and the remainder of this section will focus solely on its use as a reducing gas to be used for the purpose sample purification.

To understand how H\(_2\)(g) can be used as a reducing gas, consider the chemical reaction that takes place when Eq. 5.14 (generic oxidation reaction) is subtracted from Eq. 5.19:

\[ \text{H}_2(g) + \frac{2}{y} \text{A}_x\text{O}_y \rightleftharpoons \frac{2x}{y} \text{A} + \text{H}_2\text{O}(g) \]  

(5.20)

The Gibbs free energy change for this reaction is \( \Delta G_{\text{H}_2\text{A}}^{E} = \Delta G_{\text{H}_2}^{E} - \Delta G_{\text{A}}^{E} \). From Eq. 5.9, we find that the partial pressure requirements will allow the reaction to proceed to the right provided that the following condition is met:

\[ \Delta G_{\text{A}}^{E} \geq \Delta G_{\text{H}_2}^{E} + RT \ln \left( \frac{P_{\text{H}_2\text{O}}}{P_{\text{H}_2}} \right) \]  

(5.21)

In equilibrium, H\(_2\)O and H\(_2\) are present in equal quantities (according to Eq. 5.20), and in that case Eq. 5.21 simplifies to \( \Delta G_{\text{A}}^{E} \geq \Delta G_{\text{H}_2}^{E} \). However, if a high purity hydrogen gas used,
for which the water vapor content is significantly lower than the hydrogen content, then the logarithmic term in Eq. 5.21 will begin to contribute and the reducing strength of the hydrogen gas will be increased. This is how hydrogen gas can be used to reduce the oxides of materials which would otherwise be considered the stronger reducing agent.

Because hydrogen is a highly flammable gas, it is not typically used in laboratories in its pure form. Rather, it is often used as the minor constituent in a variety gas mixtures, where the major constituent is an inert gas. One of the most common reducing gas mixtures used at ISU and Ames Laboratory is a mixture of 95% Ar and 5% H_2. This gas mixture is most often used to recharge the copper catalysts which are employed to remove oxygen from glove boxes. The gas mixture is made using zero grade constituents: 99.998% pure Ar with 5 ppm H_2O content, and 99.99% pure H_2 with 10 ppm H_2O content. When considering the purity of the gas as it applies to reduction reactions, it is important to realize that the total water vapor content of the gas must be measured against the hydrogen content. For the mixture of 95% Ar and 5% H_2 zero grade gases, the H_2O content is approximately 100 ppm as measured against the hydrogen content. This corresponds to a 99.99% (4N) purity hydrogen gas with respect to H_2O, and therefore this gas mixture may be used as a reducing agent to remove the oxides of any material located above the “4N H_2” line on the Ellingham diagram in Fig. 5.4.

While 4N H_2 is not a strong enough reducing agent to eliminate the Al_2O_3 impurities from ESL samples, it may be possible to use such a gas to improve the ESL processing behavior of the Fe-based alloys. Assuming that the levitation/charge instabilities experienced by these samples are related to their iron oxide content and its decomposition during melting, then preparing these samples in a 4N H_2 reducing gas mixture should allow the iron oxides to be reduced before attempting to process the samples via levitation. To test this idea, samples of Fe_{83}B_{17} have been processed using the common 95% Ar and 5% H_2 gas mixture. To make the samples, a 3 mm diameter drop cast ingot was carefully broken into small pieces, such that the masses would correspond to 2.0–2.5 mm diameter spheres. The sample pieces were then placed on a graphite substrate inside the ESL vacuum chamber. The chamber was evacuated to less than 1 Torr, backfilled with the reducing gas mixture to 380 Torr, evacuated again, then backfilled again to a final pressure of 380 Torr. This process ensures that the chamber and gas lines are
free of atmospheric gases, and the final pressure was chosen to be sufficiently less than ambient so that the pressure differential maintained a seal on chamber’s two Viton gaskets. The samples were then melted using the ESL heating laser, and the sample temperature and surface quality were monitored using the pyrometers and high magnification color video imaging system.

When the samples were first melted, a large quantity of oxide material was observed to be present on the sample surface. However, as the samples were maintained at a temperature of approximately 100 K above the melting point, the vast majority of the oxide coverage disappeared. Within about 1 minute of processing, some oxide material was still present on the surface, but no further breakdown of oxides was observed to be taking place. A possible explanation for this behavior is that the oxide coverage was composed of primarily FeO, with some amount of Al$_2$O$_3$. While the sample was molten, the reducing gas was able to attack the FeO and reduce it to Fe, leaving only the Al$_2$O$_3$ as the insoluble oxide impurity. To ensure that all of the iron oxide contamination was fully reduced, each sample was melted, heated to 100 K above the melting point, then allowed to cool to low temperature (∼300 K), and this process was repeated two additional times for each sample. After each of the samples had been melted three times in the reducing gas, the chamber was evacuated and allowed to reach a pressure of approximately $1 \times 10^{-7}$ Torr. Then, under high vacuum, each sample was briefly melted two additional times for ∼10 s each time. This final melting step was performed to free the samples of any gas which may have become trapped during processing in the reducing gas.

The ultimate test of whether or not processing in reducing gas has improved the quality of the sample comes from attempting to levitation process these samples in the ESL. During levitation processing, it has been found that these samples could be heated from room temperature up to the melting point in under 10 minutes without noticeable levitation instability. Once the melting point was reached, the samples were slowly heated through the melting transition. The decision to proceed slowly was based on previous bad experiences where the samples would drop immediately upon melting. However, unlike all previous Fe-based samples, the newly prepared samples showed no signs of levitation or charge instability; the samples not only appeared to be positionally stable, but no voltage spikes were observed to occur on the vertical high voltage amplifier. By the time the samples were fully molten, less than 20 min had passed from the
start of processing. Furthermore, the samples showed a high degree of processing ability. It was possible to melt, overheat, free cool, and solidify the samples several times over without encountering any difficulties in terms of levitation stability. In fact, to date, none of the Fe$_{83}$B$_{17}$ prepared using reducing gas have dropped while being processed in the ESL. This represents an incredible improvement over previous attempts to melt Fe-based samples, for which the samples would drop repeatedly while partially or fully molten and several hours of processing would be required just to attempt a free cooling experiment.

Based on these experiences, it seems safe to conclude that the levitation instabilities encountered with Fe-based samples are caused by the presence of iron oxide contamination. The preparation of the samples using a reducing gas can eliminate the iron oxide, and alleviate the associated levitation instabilities. While this has been shown, it has also observed that the samples continue to have persistent Al$_2$O$_3$ contamination. The next question then becomes: is there some other way of using a reducing gas mixture to achieve reduction of Al$_2$O$_3$, and to achieve truly clean samples? The answer to this question is yes, however very tight restrictions must be placed on quality of the reducing gas.

Looking back at the Ellingham Diagram in Fig. 5.4, it can be seen that a 6N H$_2$ reducing gas becomes a stronger reducing agent than Al at temperatures above 1900 K. In terms of the total water content of a reducing gas mixture, to achieve this level of purity there must be less than 50 ppb H$_2$O in a 95:5 Ar:H$_2$ mixture; a less stringent requirement of 200 ppb H$_2$O would be necessary for a 80:20 Ar:H$_2$ mixture. One method which is commonly used to reduce the oxygen and water vapor content of gases is to install a liquid nitrogen cold trap into the gas line, which would cause the O$_2$ and H$_2$O to condense out of the gas. Unfortunately, while this method would work for gases of He and H$_2$, it cannot be applied to gas mixtures containing Ar because the boiling point Ar is higher than that of N$_2$, and therefore the Ar would also condense. The best option for Ar:H$_2$ gas mixtures would be to use a silica gel desiccant, which removes both O$_2$ and H$_2$O through chemisorption and physisorption processes. A professional grade silica gel gas purification system is available under the brand name Oxisorb®. Based on the Oxisorb® data sheet, this system can reduce the O$_2$ and H$_2$O contents of a gas to less than 5 ppb and 30 ppb, respectively, and can do so at gas flow rates greater than 1 m$^3$/hr.
Therefore, such a system would be more than adequate to purify a reducing gas mixture to be used for the reduction of $\text{Al}_2\text{O}_3$.

While it is possible to meet the purity restrictions required for a reducing gas mixture to act as a reducing agent towards $\text{Al}_2\text{O}_3$, it will not be possible to perform such a process using the same methods as were applied to eliminate FeO from Fe-based samples. During the laser melting of samples on a graphite substrate, it has been noticed that the maximum temperature which can be achieved under vacuum conditions is typically about 1700 K. Under 380 Torr of a 95:5 Ar:H$_2$ gas mixture, the maximum achievable temperature is reduced by 100–200 K, and in the presence of a gas flow the maximum temperature is expected to be further reduced. Therefore some other means of processing samples will need to be developed. The idea scenario would be to use some sort of levitation system to perform the purification. The use of ESL under gaseous environments is very challenging, owing to the dielectric breakdown of gases, and the weak dielectric strength of Ar makes matters worse (6 kV/cm dielectric strength for Ar, compared to 30 kV/cm for air/N$_2$). On the other hand, EML and aerodynamic levitation naturally make use of flowing processing gases, and therefore it may be worth exploring the use of these levitation systems for the purpose of sample purification. One other method that might work, and which would be relatively easy to explore, would be to induction heat the samples on a chilled graphite block. The exploration of these various methods should be a major focus of the ESL group going forward, as they may lead to the possibility of finally being able to produce high purity, oxide free samples.

5.5 Oxide Reduction via Gaseous Metal Oxides

5.5.1 Pure Aluminum

One of the more interesting phenomena to be encountered during this work is the ability of certain elements to display a self-cleaning mechanism which allows them to break down and eliminate otherwise stable oxides. This was first realized during a discussion with a fellow ISU graduate student who had spent some time studying pure Al and Al-rare earth binary alloys using electromagnetic levitation [75]. In the initial stages of EML processing, the samples were
heated to high temperatures (>1500 K) in a vacuum environment (10^{-6}–10^{-5} Torr). During this initial processing, the layer of Al_{2}O_{3} which was present on the sample surface was observed to disappear, and within a few minutes the samples were nearly oxide free (on a visual basis). This observation was surprising because it would not be expected for the oxide to become unstable in that range of temperature and pressure; the partial pressure of oxygen required to stabilize Al_{2}O_{3} at 1500 K is only 10^{-25} Torr. At the time that these studies were being performed, the removal of the oxide layer was attributed to the electromagnetic stirring which is experienced by EML processed samples. However, this explanation was met with some skepticism. While electromagnetic stirring may result in the oxide layer cracking and moving around the sample surface, it does not explain how the oxide became thermally unstable to the point of breaking down. On the other hand, pure Al has been processed using ESL by researchers at both Washington University [167] and Cal Tech [95,96], and in neither instance was the observation of a self-cleaning effect observed, nor was any degree of supercooling reported on. In fact, in the Cal Tech studies it is stated that Al was chosen for study specifically because of the visible surface oxides. It therefore appeared to be an open question whether the self-cleaning effect was due to the EML processing, or if it was a general feature of Al samples.

To develop further insight into the behavior of vacuum processed Al alloys, a thorough literature search was carried out to determine if such observations of the removal of Al_{2}O_{3} had been made previously. As it turns out, there is a healthy awareness of this phenomena among researchers interested in studying the surface tension and wetting behavior of pure Al and Al-based alloys [168–171]. In particular, Ref [168] discusses several different possible reaction pathways that might allow Al_{2}O_{3} to break down under vacuum conditions. Most of the reaction pathways involve Al_{2}O_{3} dissociating to form O_{2}(g) along with either an Al-suboxide gas phase or Al-vapor. None of these dissociation reactions were considered to be likely because the partial pressures of the gas phases involved were too low to produce an appreciable cleaning effect. However, another type of reaction was considered which seemed to be more plausible. In this reaction, Al_{2}O_{3} does not go through a direct dissociation, but rather it reacts with pure metallic Al to produce an Al-suboxide gas phase, specifically Al_{2}O(g). The partial pressure of Al_{2}O(g) produced by this reaction is high enough that it should result in the reduction of
Al₂O₃ at only moderate temperatures and pressures. Because this last reaction is important to understanding the oxidation/reduction behavior of not only Al and its alloys, but of several other materials systems, it will be described in detail.

We consider the following two chemical reactions for the formation of Al-oxides:

\[
\frac{4}{3} \text{Al} + O_2(g) \rightarrow \frac{2}{3} \text{Al}_2\text{O}_3 \quad (5.22)
\]

\[
4\text{Al} + O_2(g) \rightarrow 2\text{Al}_2\text{O}(g) \quad (5.23)
\]

where the (g) indicates that the suboxide is present as a gas phase. In the temperature range from 1000–2500 K, the Gibbs free energies per mole O₂ for these reactions are well described by the following:

\[
\Delta G^{E}_{\text{Al}_2\text{O}_3} = -1.121 \times 10^6 + 215.3 T \quad (5.24)
\]

\[
\Delta G^{E}_{\text{Al}_2\text{O}} = -3.472 \times 10^5 - 125.8 T + 0.01195 T^2 \quad (5.25)
\]

where the Gibbs free energies have units of Joules. If we now subtract Eq. 5.22 from Eq. 5.23, the resulting chemical reaction is

\[
\frac{8}{3} \text{Al} + \frac{2}{3} \text{Al}_2\text{O}_3 \rightarrow 2\text{Al}_2\text{O}(g) \quad (5.26)
\]

in which Al₂O₃ is reduced by pure Al, resulting in the formation of Al₂O(g). The Gibbs free energy of reaction for the reduction process described in Eq. 5.26 is similarly found subtracting Eq. 5.24 from Eq. 5.25, which results in the following:

\[
\Delta G^{E}_{\text{Al}_2\text{O} - \text{Al}_2\text{O}_3} = 7.74 \times 10^5 - 341.1 T + 0.01195 T^2 \quad (5.27)
\]

And finally, the partial pressure of Al₂O(g) in the reaction shown in Eq. 5.26 can be found by applying Eq. 5.9:

\[
p_{\text{Al}_2\text{O}} = 760 \exp \left( - \frac{\Delta G^{E}_{\text{Al}_2\text{O} - \text{Al}_2\text{O}_3}}{2RT} \right) \quad (5.28)
\]

where \( p_{\text{Al}_2\text{O}} \) has units of Torr.

The rate of the reduction reaction can be treated in a similar manner to sample evaporation rates, and therefore the reduction of Al₂O₃ by pure Al will only become substantial when the partial pressure of the product Al₂O(g) is appreciably high. At the aluminum melting point of
933.5 K, the vapor pressure of Al\textsubscript{2}O\textsubscript{(g)} is only $7 \times 10^{-11}$ Torr, indicating that the reaction is negligible. As the temperature increases above 1100 K, the vapor pressure exceeds $1 \times 10^{-7}$ Torr. At this point the vapor pressure exceeds the vacuum level and it should be possible for the reaction to proceed, albeit rather slowly. At 1410 K the vapor pressure exceeds $1 \times 10^{-3}$ Torr, and at this point the reaction should proceed on a relatively short timescale. While it would be nice to have a more quantitative analysis regarding the reaction rate, such an analysis would be difficult because of several unknown factors, for example: the thickness of the oxide layer; the effect of the oxide layer in terms of trapping the Al\textsubscript{2}O\textsubscript{(g)}; the exact partial pressure of Al\textsubscript{2}O\textsubscript{(g)} in the vacuum chamber after being produced; et cetera. Despite these unknown factors, the qualitative description of the reaction rate is still useful for determining expectations.

To test the idea of the Al self-cleaning mechanism, Al samples were processed using the ESL system. The samples were made from a 6N purity Al wire purchased from Alfa-Aesar. The exterior of the wire was thoroughly cleaned using isopropyl alcohol and acetone. The wire was then cut into small pieces and melted into spheroids via laser heating on a graphite block under high vacuum conditions. It may have been possible for the self-cleaning mechanism to occur during preparation, however it was difficult to maintain the sample at a high enough temperature. Because of aluminum’s high thermal conductivity, heat conduction from the sample to the graphite block exceeds the heating power from the laser once the sample is molten and able to wet the graphite. As such, the samples could only be heated to 1150 K for a brief period of time before cooling and solidifying. Nevertheless, high purity samples could be prepared with this method.

Before trying to process the samples, the ESL vacuum chamber was allowed to pump for several days so that a base pressure of $6 \times 10^{-8}$ Torr was achieved. During the initial processing, it was found that the samples could be brought to and through their melting point in a short period of time with little to no levitation instability. However, because of the low melting point of Al, thermionic emission charging does not play a significant role until the samples have been heated approximately 400 K above the melting point, and therefore sample charge stability throughout most of the liquid range is achieved by UV illumination only. As the Al\textsubscript{2}O\textsubscript{3} is broken down and Al\textsubscript{2}O evaporates away, it may be possible for rapid charge loss to occur.
Therefore, the sample was heated very slowly even after being fully melted; approximately 10 min passed between melting the sample and heating it to 1325 K. During the slow heating, several color images were taken of the sample to record the progress of the reduction reaction. Fig. 5.5 shows four representative images at different temperatures during the initial heating period. As can be seen, the effect of the reduction reaction is very apparent even when the sample temperature has only reached 1225 K, at which point the sample has been molten for less than 10 min. By the time the sample has reached a temperature of 1375 K and held there for 2 min, the visible oxide coverage has been reduced to only tiny speck (located on the left side of the sample along the sample equator, between light reflection spots). Within a few more minutes the sample was completely free of visible oxide.

After a few minutes of holding at 1375 K, the sample was allowed to free cool so that supercooling could be attempted to test whether the sample was truly oxide free. During the first attempt, approximately 40 K of supercooling was achieved. The sample was then remelted and brought to a temperature of 1425 K where it was held for 10.5 min before it was allowed to free cool a second time. During the second free cooling attempt, a supercooling of 98 K was achieved. At the same time that these heating and cooling cycles were being carried out, a curious behavior was noticed in the ion gauge output. During the first cycle, the apparent residual gas pressure increased from the baseline of $6 \times 10^{-8}$ Torr up to $11 \times 10^{-8}$ Torr, where it remained for the duration of the high temperature hold before dropping back to the baseline level once the sample was allowed to cool. There was a similar rise in the pressure during the second overheating attempt when the sample was held at 1425 K. However, during the second attempt, the pressure increased from baseline up to $13 \times 10^{-8}$ Torr before slowly decreasing to $8 \times 10^{-8}$ Torr over the duration of the hold, and then finally dropping back to baseline once the sample was allowed to free cool. The behavior of the pressure displayed during the second heating/cooling cycle was shown to be highly repeatable during each of the three heating/cooling cycles that followed. During these cycles, the sample was brought to a temperature of 1425 K and held for 5 min before being allowed to free cool and solidify. After solidification was complete, the sample was immediately remelted the the cycle was repeated. The average supercooling which was achieved during these cycles was $125 \pm 2.6$ K.
Figure 5.5  An aluminum sphere processed in the ESL, displaying the self-cleaning effect. Sample temperatures are: top left, 1075 K; top right, 1225 K; bottom left, 1325 K; bottom right, 1375 K.
The temperature-time data and the ion gauge reading associated with these cycles is shown in Fig. 5.6.

The behavior of the residual gas pressure during the processing of pure Al can be understood in terms of the oxidation/reduction reactions which are taking place. When the sample is brought to high temperatures around 1400 K, the increase in the gas pressure is due to the production of $\text{Al}_2\text{O}(g)$ as a result of the reduction reaction described in Eq. 5.26. As long as there is an appreciable amount of $\text{Al}_2\text{O}_3$ present on the sample surface, $\text{Al}_2\text{O}(g)$ will be produced and the residual gas pressure will remain high. This would seem to indicate that the $\text{Al}_2\text{O}_3$ was not fully removed during the initial overheating step, which resulted in the mediocre supercooling upon free cooling. However, as the $\text{Al}_2\text{O}_3$ is depleted, the production of $\text{Al}_2\text{O}(g)$ will be reduced and the residual gas pressure will be seen to decrease. This explains the behavior during the second through fifth cooling cycles, where the supercooling was observed to become more substantial. In particular, the during the fourth and fifth cooling cycles the gas pressure is seen to nearly nearly level off (Fig. 5.6). The ion gauge reading is never observed to return to baseline levels as long as the sample is hot, although this could be caused by different sensitivities of the ion gauge to $\text{Al}_2\text{O}(g)$ as opposed to $\text{H}_2\text{O}$. Because the sample is constantly being bombarded by $\text{H}_2\text{O}$, there will always be a nominal amount of $\text{Al}_2\text{O}(g)$ being produced at high temperatures.

Each time the sample is allowed to solidify and then is subsequently remelted and brought to high temperatures, the residual gas pressure is observed to increase significantly and then roll off to a nominal level. This would seem to indicate that some amount of $\text{Al}_2\text{O}_3$ has reformed on the sample surface during the low temperature portion of the processing, which must then be removed by processing at high temperature. At some point in between, there is a critical temperature above which the production of $\text{Al}_2\text{O}(g)$ is preferred and below which the formation of $\text{Al}_2\text{O}_3$ is preferred. This critical temperature can be determined by considering the particle exchange which is taking place at the sample surface. For each molecule of $\text{Al}_2\text{O}(g)$ produced an O atom is removed from the sample, whereas each $\text{H}_2\text{O}$ molecule that collides with the sample deposits an O atom (assuming unit sticking coefficient). The critical temperature for oxidation vs. reduction can therefore be determined as the temperature at which the particle
Figure 5.6  (Top) Temperature vs. time for three heating and cooling cycles for a 13 mg Al sample. The dashed line represents the melting point of 933.5 K. (Bottom) The ion gauge output during cycling of the Al sample.
fluxes of these two molecules are equal: $Z_{\text{Al}_2\text{O}} = Z_{\text{H}_2\text{O}}$. Applying Eq. 5.4 leads to the following expression:

$$p_{\text{Al}_2\text{O}} = p_{\text{H}_2\text{O}} \sqrt{\frac{m_{\text{Al}_2\text{O}} T_{\text{Al}_2\text{O}}}{m_{\text{H}_2\text{O}} T_{\text{H}_2\text{O}}}}$$ (5.29)

Because $p_{\text{Al}_2\text{O}}$ is an exponential function of $T_{\text{Al}_2\text{O}}$ (see Eq. 5.28), Eq. 5.29 cannot be solved analytically to determine an explicit expression for the critical temperature, and so it must be solved numerically. Assuming that $p_{\text{H}_2\text{O}}$ is equal to the baseline ion gauge output and that the H$_2$O is thermalized to a temperature of 300 K, the critical temperature is determined to be 1120 K. The vapor pressure of Al$_2$O(g) at this temperature is approximately $24 \times 10^{-8}$ Torr, a factor of 4 greater than the residual gas pressure.

As the sample cools below the critical temperature it will begin to gain oxygen from the residual gas. The solubility of oxygen in pure Al is incredibly small, less than 1 ppb [172] near the melting point, and therefore the Al will almost instantaneously saturate and begin forming insoluble Al$_2$O$_3$ on the sample surface. A useful indicator of the oxidation rate in a situation such as this is the time required to form a single monolayer of oxide on the sample surface. For simplicity, we will model Al$_2$O$_3$ as having simple cubic structure, such that a monolayer would have a square-grid arrangement. Then, using the known density and molar mass of Al$_2$O$_3$ (3.95 g/cc and 101.96 g/mol, respectively), the characteristic molecular length is found to be $3.5 \times 10^{-10}$ m. We must also recognize that three molecules of H$_2$O are required to generate one molecule of Al$_2$O$_3$. Then, taking this information and once again applying Eq. 5.4, the minimum time required for the formation of a monolayer of Al$_2$O$_3$ on a fresh Al surface is given by:

$$t_{\text{mono}} = \frac{5.1 \times 10^{-6}}{P}$$ (5.30)

where $t_{\text{mono}}$ has units of seconds and $P$ is the partial pressure of H$_2$O (the chamber pressure) with units of Torr. For the pressure at which the chamber was operating in the recent experiments on pure Al, this corresponds to a monolayer formation time of 85 s. In each of the three heating/cooling cycles shown in Fig. 5.6, after the samples cooled through 1120 K an average of $81 \pm 1$ s passed before recalescence occurred, indicating that slightly less than one monolayer of Al$_2$O$_3$ may have formed on the surface before solidification. In two other attempts (not
shown) the sample was cooled more slowly. During these slow cooling attempts, an average of 100 ± 6 K of supercooling was achieved, and 196 ± 1 s passed between 1120 K and recalcitrance, indicating just over two monolayers of oxide formation.

It may be possible to improve the processing ability of pure Al in the ESL by making modifications to the vacuum chamber. These modifications would lead to a lower residual gas pressure level, which would result in a lower value for the critical temperature for preferential formation of Al$_2$O(g) over Al$_2$O$_3$, as well as increase the time required for monolayer formation. These improvements would lead to not only deeper supercooling for pure Al, but may also allow for novel measurements to be performed of a variety thermophysical properties in both the equilibrium and deeply supercooled states. Furthermore, an entire class of Al-based alloys can now be considered as viable candidate materials for study using the ESL. These topics will be discussed further in Sec. 5.6. At the present time, the most important takeaway from the recent work on Al is this: the existence of a stable gas phase oxide, Al$_2$O(g), resulted in the destabilization of Al$_2$O$_3$, leading to an intrinsic self-cleaning property for Al. This behavior was theoretically predicted, and has been experimentally verified to occur for samples processed under the high-vacuum conditions found in the ISU-ESL.

### 5.5.2 Additional Gas Phase Oxides

The successful prediction and subsequent observation of a self-cleaning mechanism in pure Al begged the question: what other elements possess stable gas phase oxides, and can an understanding of those gas phase oxides be used to determine whether other samples might also exhibit self-cleaning behavior similar to that observed in pure Al? To answer this question, a search of the NIST and CRCT thermochemical databases [164,165] was carried out. Focusing the search on elements relevant to research using the ESL, it has been found that the elements C (obviously), Si, Ge, B, Ti, Zr, and Nb all exhibit stable gas phase oxides. A few other relevant elements also exhibit gas phase oxides, however, based on the Gibbs free energies of their formation, those oxides are either metastable or only marginally stable, and therefore they have been left out. To determine whether or not the gas phase oxides of the above named elements will provide a meaningful self-cleaning effect, their reducing strength can be
determined from their vapor pressures in comparison to the vapor pressure of \( \text{Al}_2\text{O}(g) \) with respect to the reduction of \( \text{Al}_2\text{O}_3 \).

The general form of the reaction in which the elements reduce \( \text{Al}_2\text{O}_3 \) to form metallic \( \text{Al} \) plus their respective gas phase oxide is given by:

\[
\frac{2x}{y} A + \frac{2}{3} \text{Al}_2\text{O}_3 \rightarrow \frac{2}{y} A_x\text{O}_y(g) + \frac{4}{3} \text{Al}
\]  

(5.31)

The change in the Gibbs free energy for this reaction is \( \Delta G_{A_x\text{O}_y - \text{Al}_2\text{O}_3}^E = \Delta G_{A_x\text{O}_y}^E - \Delta G_{\text{Al}_2\text{O}_3}^E \), and the vapor pressure of the gas phase oxide which is formed during the reaction is determined from Eq. 5.9 to be:

\[
p_{A_x\text{O}_y} = 760 \exp \left( -\frac{y}{2} \frac{\Delta G_{A_x\text{O}_y}^E - \Delta G_{\text{Al}_2\text{O}_3}^E}{RT} \right)
\]  

(5.32)

A plot of the normalized Gibbs free energies of formation for several of the gas phase metal oxides is shown in Fig. 5.7, along with a plot of the vapor pressures for these oxides as determined by Eq. 5.32. In addition to the vapor pressures, two indicator lines are shown in Fig. 5.7 (right), corresponding to vapor pressures of \( 10^{-7} \) Torr and \( 10^{-3} \) Torr. The \( 10^{-7} \) Torr line indicates the minimum vapor pressure necessary for the reduction of \( \text{Al}_2\text{O}_3 \) to occur at a meaningful rate. The \( 10^{-3} \) Torr line indicates the vapor pressure at which the reduction will occur on a timescale of minutes, as determined by the experience with pure \( \text{Al} \). As can be seen, the gas phase oxides with the greatest vapor pressures, and therefore the strongest reducing ability, are the monoxide gas phases of Al, C, Si, Ge, and B, in that order. It is interesting to note how important the oxygen content of the gas phase is. Not only are each of the strongest gases all monoxides, but particularly for the case of B, \( \text{BO}(g) \) has the highest vapor pressure and therefore strongest reducing ability despite \( \text{B}_2\text{O}_2(g) \) and \( \text{B}_2\text{O}_3(g) \) having more negative Gibbs free energies of formation. Mathematically, this is attributed to the factor of \( y/2 \) in Eq. 5.32, where \( y \) is the number of oxygen atoms per molecule.

It should also be noted that, strictly speaking, the Gibbs free energies and vapor pressures shown in Fig. 5.7 are only truly accurate for reactions between pure elements and oxide phases. If the element taking part in the reaction is part of an alloy, the Gibbs free energies of reaction and therefore the vapor pressures will both be modified due the diminished ability of the element to take part in chemical reactions. The extent to which an element’s reactivity is diminished
Figure 5.7 (Left) Gibbs free energies of formation for several gas-phase metal-oxides. (Right) Equilibrium vapor pressures for gas-phase metal-oxides in reaction with $\text{Al}_2\text{O}_3$. 
is quantified by its chemical activity, \(a\). Mathematically, the effect of the chemical activity on the Gibbs free energy of formation is:

\[
\Delta G^{o'} = \Delta G^o - RT \ln(a)
\] (5.33)

and the effect of the activity on product vapor pressures is:

\[
p^{o'}_{A_xO_y} = a_A p_{A_xO_y}
\] (5.34)

Information regarding the chemical activity of elements can be determined from thermodynamic assessments of alloy systems. The CRCT Fact-Web [165] contains a large database of binary phase diagrams, complete with chemical activity information as a function of both composition and temperature. For example, the chemical activity of B in Fe\(_{83}\)B\(_{17}\) near the melting temperature is \(2 \times 10^{-3}\), and the chemical activities of Si in Fe\(_{66.7}\)Si\(_{33.3}\) and Fe\(_{75}\)Si\(_{25}\) near their melting temperatures are \(1 \times 10^{-2}\) and \(3 \times 10^{-3}\), respectively.

With the metal-oxide vapor pressure information in hand, new insights can be made into the processing behavior of ESL samples. As mentioned earlier in this chapter, pure Si is one of the few materials which has shown reliably good processing ability, with every sample processed in the ISU-ESL being free of visible oxide impurities, and every sample being able to achieve supercooling in excess of 300 K on a consistent basis. It is very likely that this reliable processing behavior is caused by the strong reducing ability of pure Si through the production of SiO(g). At the melting point of pure Si, 1687 K, the vapor pressure of SiO(g) in reaction with Al\(_2\)O\(_3\) is \(10^{-1.5}\) Torr. This would indicate that any Al\(_2\)O\(_3\) that might have been present on the sample would be very rapidly reduced. Furthermore, because SiO\(_2\) is higher than Al\(_2\)O\(_3\) on the Ellingham diagram (and therefore less stable), its formation on molten Si under high vacuum conditions is strongly inhibited.

The vapor pressure of SiO(g) also explains why Fe\(_{66.7}\)Si\(_{33.3}\), after extensive overheating in the liquid state, was able to demonstrate excellent supercooling stability. The melting point of this alloy is 1488 K. As with all other non-Zr-based samples, after melting a sample of Fe\(_{66.7}\)Si\(_{33.3}\) it was apparent that the sample was contaminated with an insoluble stable oxide. The oxide remained on the sample surface even after several heating/cooling cycles for which the
sample was only briefly heated to a temperature of 1600 K, and the degree of supercooling that was achieved was very poor (<50 K). However, during one instance of processing the sample was heated to a temperature in excess of 1700 K and maintained at that temperature for several minutes. During this high temperature overheating, the oxide phases on the sample surface were visually observed to break down and disappear. After the high temperature overheating, the sample demonstrated excellent supercooling stability, achieving a maximum supercooling of 270 K as well as being able to remain at a supercooling of 250 K for several minutes before recalescence occurred. The cleaning effect demonstrated for this sample is likely due to the formation of SiO(g). Based on the vapor pressures shown in Fig. 5.7, and using a value of $2 \times 10^{-2}$ for the chemical activity of Si, the vapor pressure of SiO(g) at 1700 K is $1 \times 10^{-3}$ Torr, which would indicate a strong reducing ability consistent with the observed breakdown of the surface oxides.

The formation of metal oxide gas phases may also explain the difficulty that was encountered with the Fe-based alloys before it was realized that preparation under a reducing gas atmosphere could improve their performance. As was stated earlier, each of the Fe-based alloys showed very poor processing ability, frequently dropping onto the electrodes either during the melting process or shortly after being fully melted. Each of the Fe-alloys studied thus far contain a significant amount of either B or Si. If the Gibbs free energies of formation of SiO(g), B$_2$O$_2$(g), and B$_2$O$_3$ (g) are compared against the Gibbs free energy of formation for FeO, it can be seen that near the melting points of the alloys the gas phase oxides are actually more stable than FeO. This would indicate a spontaneous reaction with a correspondingly very large vapor pressure. Even after accounting for the reduced chemical activities of B and Si, the oxide vapor pressures exceed 760 Torr. If this reaction were to take place under high vacuum conditions with a levitated sample, the volatilization of the oxides could result in charge destabilization of the sample similar to that caused by the outgassing of atmospheric gases during the initial heating, but much more extreme. This explanation is consistent with the observation that samples prepared under a reducing gas atmosphere are very stable from a levitation standpoint: if there is no FeO, then there will be no volatile evaporation to result in charge destabilization.

Awareness of the existence of gas phase oxides has also been applied in an intentional
manner to improve the processing of samples. The best example of this was with pure Ge. In all attempts to process pure Ge in the ISU-ESL prior to Jan. 2014, the supercooling of the samples was typically limited to 60 K or less. When the samples were molten, small flecks of an insoluble impurity phase could be seen on the sample surface. Several different types of raw Ge were used, including 5N purity pieces from Materion as well as 6N purity pieces and a 6N zone refined ingot from Alfa Aesar. The samples were prepared by laser melting on either a clean copper or quartz substrate. The poor supercooling and presence of insoluble impurities were true for all cases, even when there was no additional handling of the raw material (i.e., no cutting of the raw material using tools). In the literature, there is a report of Ge being studied by the Cal Tech ESL group, and their supercooling was also limited to 60 K. Taken altogether, these facts would seem to imply that the problem is with the raw Ge itself, not the preparation process. Meanwhile, there are several reports throughout the literature [64, 173–178] of supercooled Ge being studied with techniques such as melt fluxing, droplet dispersion, and EML, with maximum supercoolings in the range of 190–426 K. It should, therefore, be possible to improve upon the supercoolings which have been achieved using ESL.

To test the self-cleaning theory on Ge, a 54 mg (∼ 2.6 mm diameter) sample was processed using the ISU-ESL. The sample was prepared by selecting piece from a batch of 6N purity Ge from Alfa Aesar and laser melting on a quartz substrate under high vacuum. Before processing the sample, the ESL vacuum chamber was pumped to $1.5 \times 10^{-7}$ Torr. After the sample had been levitated and fully melted (melting point 1211 K), the sample was heated to a temperature of 1563 K and held for 15 min. At that temperature, the vapor pressure of GeO(g) produced from the reaction of Ge and Al$_2$O$_3$ would be $10^{-4.5}$ Torr. After 15 min, the sample was free cooled and a supercooling of 140 K was achieved. While this was an improvement, it was still lower than the literature values of maximum supercooling. Upon remelting, careful inspection of the sample revealed that while the oxide impurity was still present on the surface, it had become noticeably smaller. To accelerate the cleaning effect, a set of heating/cooling cycles were performed during which the sample was heated to 1693 K, held for 30–180 s, and then free cooled. At that temperature the vapor pressure of GeO(g) is $10^{-3.3}$ Torr, and in total
the sample was held at 1693 K for 6 min. Following these high temperature heating/cooling cycles, the oxide patch could no longer be found on the sample surface, and supercoolings in excess of 200 K were found to be consistently achievable. A summary of the results are shown in Fig. 5.8. In addition to the improved supercooling, the sample was found to be quite stable in the deeply supercooled liquid state, being able to stay in the liquid phase for over 8 min during a supercooled isothermal hold 175 K below the melting point.

In addition to the greatly improved supercooling, an interesting trend was noticed regarding the degree of supercooling as a function of overheating temperature. Four sets of heating/free cooling experiments were performed from four different overheating temperatures: 1693 K, 1563 K, 1678 K, and 1478 K, in that order. The average supercooling achieved while free cooling from each of these temperatures was: 122 K, 231 K, 129 K, and 249 K, respectively. In all, 17 free cools were performed from overheating temperatures below 1600 K, resulting in an average supercooling of 236 ± 25 K, and 10 free cools were performed from overheating temperatures above 1600 K, resulting in an average supercooling of 125 ± 25 K. This would seem to indicate that, even after the removal of the oxide impurities, there is a strong inverse correlation between overheating temperature and the degree of supercooling that can be achieved. Why this is the case is presently unknown. It could be an extrinsic effect, resulting from a combination of the levitation forces, laser heating, and radiative cooling, and the influence these factors may have in terms of perturbing the sample. It may also be an intrinsic effect, indicating a type of thermal hysteresis with respect to the thermophysical properties of liquid Ge. Further experiments will have to be performed to verify this behavior as well as to determine the most likely explanation. It may also be possible, with reduced overheating, to extend the range of achievable supercooling beyond the maximum of 262 K achieved here.

5.6 Outlook

One of the primary goals of the ISU-ESL group going forward should be to develop a means of processing samples in a reducing gas environment. As mentioned earlier in Sec. 5.4, if samples can be processed at temperatures exceeding 1900 K in the presence of a gas mixture with a
Figure 5.8  Results of the high temperature processing of pure Ge, for which sample self-cleaning was observed.  (Top Left) A maximum supercooling of 262 K was achieved during a free cool from 1480 K.  (Top Right) A histogram of the supercoolings that were achieved after high temperature processing. Free cools were attempted in groups with overheating temperatures of 1693 K, 1563 K, 1678 K, and 1478 K, in that order. (Bottom) To test isothermal stability in the supercooled state, Ge was maintained at a supercooling of 175 K for 8.2 min before recalescence.
H₂:H₂O ratio of 10⁶ or greater, then it will be possible to eliminate the Al₂O₃ contamination from these samples. However, until such a system has been developed, it should still be possible to improve the success rate of sample processing by focusing attention on a number of key systems. Alloys systems that contain significant quantities of Al, C, Si, and B should be able to demonstrate significant self-cleaning properties, and therefore more attention should be placed on studying these alloys systems in the near future. Some examples of such systems will be discussed here.

As mentioned earlier, the ability to process and perform measurements on deeply supercooled pure Al could be improved by making minor modifications to the ESL system. The first modification to the ESL system would be to replace the Viton gaskets that are used on the top and front flanges of the system with copper gaskets. The flanges are already compatible with copper gaskets, and so no major hardware modifications would be necessary. By switching to copper gaskets, the permeation of atmospheric gases, particularly H₂O(g), will be significantly reduced, and as a result the ultimate baseline pressure of the system can be reduced below the present level of about 2.5 × 10⁻⁸ Torr. To reduce the pumping time required to reach the new ultimate baseline pressure, the vacuum chamber can be wrapped with heating tape and Al foil and a mild bakeout of the system at 50–100 °C can be performed. With the vacuum pumps already present in the lab, the combination of copper gaskets and mild baking should allow an ultimate pressure of 1 × 10⁻⁹ Torr to be achievable after about one week of pumping. The drawback to switching to copper gaskets is that access to the interior of the chamber will become more restricted. In the current configuration, a Viton sealed fast-entry entry door is used to allow quick access to the chamber interior for the purpose of placing and retrieving samples, and this functionality will be lost. Fortunately, a sample loading system has already been developed that allows several samples (> 20) to be placed into the chamber and loaded onto the electrodes without breaking vacuum. The loading system allows multiple samples of interest, as well as additional balls for testing the levitation system and performing video calibration, to be used consecutively without interruption. Therefore, the restricted access to the chamber interior is not a major drawback.

With an ultimate pressure of 1 × 10⁻⁹ Torr, it should become possible process Al into
the deeply supercooled state without the sample undergoing significant amounts of oxidation. Once again invoking Eq. 5.29, and using the same assumptions, the critical temperature for the preferential formation of Al$_2$O$_3$ vs. Al$_2$O(g) will become reduced from the previous value 1120 K to down to 1015 K. Compared to the melting point of Al, 933 K, this is a modest but still helpful improvement. However, a much more significant improvement comes from the effect of the improved vacuum on the monolayer formation time, will will increase from the previous value of 85 s up to approximately 5100 s, or about 1.4 hours. Assuming that in increase in the supercooling depth will be achieved, typical free cooling times experienced by samples (between the critical temperature and recalescence) will be approximately 150 s, indicating monolayer coverage of only 3% of the surface by the time that recalescence occurs. This should lead to not only deeper supercooling, but many measurements can also be performed during the free cooling of a sample, such as volume/density, ratio of specific heat to total emissivity, and spectral emissivity measurements, and therefore these thermophysical properties could be measured on a pristinely clean Al sample all the way down to the maximum supercooling temperature. It may also be possible to perform measurements of surface tension and viscosity during a free cool, however a new degree of automation and streamlining of the measurements would be necessary to increase the data acquisition rate. In the mean time, it should still be possible to perform these measurements in a short enough period of time that the monolayer coverage does not exceed 10%.

The ability to process pure liquid Al in such a nearly oxide-free manner, coupled with the ability to achieve deep supercoolings while simultaneously performing a variety of bulk thermophysical property measurements, would present a unique opportunity for its characterization. While there have been previous attempts at performing supercooling on pure Al, the amount of supercooling achieved in these attempts was typically less than 50 K [179,180], although in one instance a maximum supercooling of 175 K could be achieved by dispersing 20 μm powders in a sulfate salt flux [61]. The nature of these supercooling investigations centered on the thermodynamic and kinetic aspects of nucleation, particularly as they depend on the droplet size and type of emulsifying agent. No reports on the measurements of thermophysical properties in supercooled pure Al have been found, and therefore any such measurements would be new.
Furthermore, there continues to be extensive discussion as to the intrinsic values of various thermophysical properties for pure Al even for temperatures at or above the equilibrium melting point. In particular, measured values of the viscosity and surface tension appear to be quite scattered compared to those for other pure elements [171, 181, 182]. The reason for the scatter is due primarily to the strong tendency of Al to form insoluble Al$_2$O$_3$, as well as the aggressive reactivity of pure Al towards many commonly used substrate materials which results in contamination of the samples. Therefore, the ability to perform non-contact measurements on pure Al using the ISU-ESL may allow for an improved understanding of the intrinsic properties of pure Al even at temperatures above the melting point.

The demonstrated ability to process Al in the ISU-ESL opens the door not only to new measurements being applied to pure Al, but also to many Al-based alloys. Table 5.2 contains a list of Al-based alloys with known scientific interest and which have melting temperatures low enough to be compatible with high vacuum processing in the ESL. The list of materials is derived from Refs. [19, 20, 46, 62, 75, 183–185], and could likely be made much larger with a more thorough literature search. Of particular note among the list should be the compounds containing the element Mn. It has long been assumed that alloys containing Mn should not be processed in the high vacuum environment of the ESL, based on the extremely high vapor pressure of pure Mn. However, this is actually a perfect example of why it is necessary to be aware of Eq. 5.5 for the evaporation rates of samples, in particular the role of the chemical activity. Based on available vapor pressure data [157] and thermochemical data [165], the effective vapor pressures of Al and Mn at 1300 K have been tabulated in Table 5.3 for the pure states and two binary alloy compositions. As can be seen from the results, the low concentration of Mn has resulted in a significant reduction in the chemical activity, and as a consequence the effective vapor pressure of Mn in the alloys is reduced by a factor of 30–110 compared to the pure element. Therefore, alloys with a low concentration of Mn, for which the chemical activity of Mn is significantly reduced, should be compatible with high vacuum processing in the ESL.

In addition to pure Al and its alloys, alloys containing significant amounts of C, Si, and B should demonstrate self cleaning behavior, and therefore these materials should also be strongly considered for study. Examples of binary metal-metalloid systems for which there is a known
Table 5.2  List of Al-based alloys for which there is known scientific interest and which have melting temperatures low enough to be compatible with high vacuum processing in the ESL.

<table>
<thead>
<tr>
<th>Alloy</th>
<th>Solid phase</th>
<th>Melting Temperature (K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al$<em>{58}$Cu$</em>{34}$Fe$_8$</td>
<td>Quasicrystal</td>
<td>1130</td>
</tr>
<tr>
<td>Al$<em>{60}$Cu$</em>{34}$Fe$_6$</td>
<td>Quasicrystal</td>
<td>1098</td>
</tr>
<tr>
<td>Al$<em>{62}$Cu$</em>{25.5}$Fe$_{12.5}$</td>
<td>Polytetrahedral Crystal</td>
<td>1258</td>
</tr>
<tr>
<td>Al$<em>{72}$Pd$</em>{21}$Mn$_7$</td>
<td>Quasicrystal</td>
<td>1137</td>
</tr>
<tr>
<td>Al$<em>{64}$Cu$</em>{22}$Co$_{14}$</td>
<td>Quasicrystal</td>
<td>1274</td>
</tr>
<tr>
<td>Al$<em>{65}$Cu$</em>{25}$Co$_{10}$</td>
<td>Quasicrystal</td>
<td>1259</td>
</tr>
<tr>
<td>Al$<em>{67}$Cu$</em>{21}$Co$_{12}$</td>
<td>Quasicrystal</td>
<td>1293</td>
</tr>
<tr>
<td>Al$_{100-x}$Mn$_x$ 10 ≤ x ≤ 20</td>
<td>Metastable crystals and quasicrystals</td>
<td>1172–1268</td>
</tr>
<tr>
<td>Al$<em>{86}$Cr$</em>{14}$</td>
<td>Metastable crystals and quasicrystals</td>
<td>1300</td>
</tr>
<tr>
<td>Al$<em>{90}$Tb$</em>{10}$</td>
<td>Marginal Glass former</td>
<td>1277</td>
</tr>
<tr>
<td>Al–Si system</td>
<td>Anomalous Eutectic Solidification</td>
<td>850–1687</td>
</tr>
<tr>
<td>Al–Ge system</td>
<td>Enhanced Eutectic Superconductor</td>
<td></td>
</tr>
<tr>
<td>Al–Ge system</td>
<td>Enhanced Eutectic Superconductor</td>
<td>693–1211</td>
</tr>
</tbody>
</table>

interest include: Ni–B [186], Cu–Si [187], Pd–Si [10], Co–Si [188], Ni–Si [189], Fe–Si [190,191], Fe–C [1,192,193]. These systems feature a variety of interesting behavior: glass formation, metastable crystalline phase formation, and magnetic properties that depend strongly on the solidified phase as well as the microstructure. The references given are just a select few among many for these systems. The exact compositions which can be successfully studied in the ESL will depend strongly on the metalloid content and the nature of the binary mixing. As a general rule, ESL processing of the samples is expected to be easier for alloys with a higher metalloid content. There are two main reasons for this. First, increasing the metalloid content will result in a greater chemical activity of the metalloid, which will help to ensure a potent reducing effect towards unwanted stable oxides. Second, increasing the metalloid content will result in a lower density for the alloy, which will subsequently result in a lower levitation voltage. The lower levitation voltage will help to ensure stability and prevent the sample from dropping in the event of sudden charge loss as a result of the oxide reduction and outgassing processes.
Table 5.3  Effective vapor pressures of Al and Mn at 1300 K, accounting for the chemical activities of the elements in solution.

<table>
<thead>
<tr>
<th>Element</th>
<th>Composition (%)</th>
<th>Activity</th>
<th>Vapor Pressure (Torr)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al</td>
<td>100</td>
<td>1</td>
<td>$2.1 \times 10^{-4}$</td>
</tr>
<tr>
<td>Mn</td>
<td>100</td>
<td>1</td>
<td>$3.1 \times 10^{-2}$</td>
</tr>
<tr>
<td>Al</td>
<td>90</td>
<td>0.86</td>
<td>$1.8 \times 10^{-4}$</td>
</tr>
<tr>
<td>Mn</td>
<td>10</td>
<td>0.0090</td>
<td>$2.8 \times 10^{-4}$</td>
</tr>
<tr>
<td>Al</td>
<td>80</td>
<td>0.69</td>
<td>$1.4 \times 10^{-4}$</td>
</tr>
<tr>
<td>Mn</td>
<td>20</td>
<td>0.033</td>
<td>$1.0 \times 10^{-3}$</td>
</tr>
</tbody>
</table>

5.7 Conclusions

A significant level of improvement has been made regarding the processing and contamination behavior of samples processed in the ISU-ESL. Concepts such as evaporation and oxidation rates, which have been treated only qualitatively up until now, can now be treated quantitatively via Eqs. 5.5, 5.6, and 5.30. The quantitative understanding of these phenomena will allow for more precision when developing processing guidelines for a variety of alloy systems. Furthermore, the nature of the sample contamination problems has been elucidated, and potential solutions have been proposed. In the case of non-Zr-based samples, the primary contaminant has been found to be Al$_2$O$_3$, which is an extremely stable oxide, able to withstand chemical attack from most solvents as well as being thermally stable under conditions of high vacuum and high temperature, and which will not break down in the presence of most non-Zr-based metallic liquids. Due to the ubiquitous nature of this stable oxide, it does not seem possible to produce samples in a way that avoids contamination, even when the most stringent precautions are taken. Therefore, a method of purifying contaminated samples has been proposed. This method involves the processing of samples at temperatures exceeding 1900 K in the presence of a flowing reducing gas mixture that contains at least 5% H$_2$(g) content, and for which the total H$_2$:H$_2$O ratio exceeds $10^6$. Processing under these conditions should result in the breakdown of the Al$_2$O$_3$, and will thereby purify the samples. In the case of Zr-based samples, it has been found that elemental Zr is a stronger reducing agent than Al at high temperatures,
and therefore the contaminant species found on these samples is likely not Al$_2$O$_3$. Rather, the contamination of Zr-based samples seems to come as a result of oxygen saturation of the samples during sample preparation, which results in the formation of an insoluble ZrO$_2$ below a critical dissolution temperature. To resolve this problem, a sample preparation route has been proposed in which Zr-based samples are prepared in a gaseous environment only during the arc melting production of the initial sample ingot (using a professional grade arc melting system), after which further preparation can take place in the high vacuum environment of the ISU-ESL chamber. The elimination of silicate crucibles and faulty preparation equipment should allow the oxygen content to stay below the solubility limit of the alloys.

In the event that preparation of oxide-free samples continues to be problematic, a class of materials has been identified that display a self cleaning behavior, and thus these materials should be able to overcome the preparation difficulties. This class of materials includes the elements Al, C, Si, Ge, and B, as well as alloys that contain a significant quantity of these elements. The nature of the self cleaning behavior arises from the existence of stable gas phase oxides of these elements, particularly monoxide gas phases. While these gas phase oxides generally have a lower Gibbs free energy of formation compared to Al$_2$O$_3$, they are still stable enough to demand a finite partial pressure of reaction. Under the proper conditions of temperature and chemical activity (for alloys), the partial pressure of these gas phases can become large enough to produce a significant reducing capability towards Al$_2$O$_3$. This phenomena has been evidenced by that fact that samples of pure Al can be produced in an oxide free manner at temperatures above 1120 K, as well as by the fact that samples of pure Ge that have been processed at high temperature have been shown to become clean and have resulted in the deepest supercoolings achieved for pure Ge when using the ESL technique. Furthermore, samples of Fe$_{66.7}$Si$_{33.3}$ have been observed to undergo similar self cleaning mechanisms, resulting in very stable supercooling up to a maximum of 270 K below the melting point. Based on these observations, it has been suggested that until advanced sample preparation and purification methods have been developed, focusing research efforts on pure Al and Ge, as well as on alloys containing sufficient quantities of Al, C, Si, and B, will result in the ability to more rapidly achieve successful sample processing. Several materials with known scientific interest have
been pointed out, including specific Al alloy compositions, as well as several binary systems containing Al, C, Si, and B.
CHAPTER 6. ESL STUDIES OF SUPERCOOLING AND METASTABLE PHASE FORMATION IN THE Fe$_{83}$B$_{17}$ NEAR EUTECTIC ALLOY

In this chapter, the results of recent investigations of the formation and thermophysical properties of stable and metastable iron-born (Fe-B) alloys are presented, with the analysis focused primarily on the study the metastable phase formation in an Fe$_{83}$B$_{17}$ near eutectic alloy. Initial supercooling measurements using the ISU-ESL identified the formation of three metastable phases: a precipitate phase that shows stable coexistence with the deeply supercooled liquid, and two distinct bulk solidification phases. To identify the structure of the metastable phases, the Washington University Beamline ESL (WU-BESL) has been used to perform *in-situ* high energy x-ray diffraction measurements of the metastable phases. Based on the x-ray results, the precipitate phase has been identified as bcc-Fe, and the more commonly occurring bulk solidification product has been found to be a two-phase mixture of Fe$_{23}$B$_6$ plus fcc-Fe, which appears, upon cooling, to transform into a three phase mixture of Fe$_{23}$B$_6$, bcc-Fe, and an as-yet unidentified phase, with the transformation occurring at approximately the expected fcc-to-bcc transformation temperature of pure Fe. To further characterize the multi-phase metastable alloy, the ISU-ESL has been used to perform measurements of volume thermal expansion via the videographic technique, as well as RF susceptibility via the TDO technique. The results of the thermal expansion and susceptibility data have been found to be sensitive indicators of additional structural changes that may be occurring in the metastable solid at temperatures below 1000 K, and the susceptibility data has revealed that three distinct ferromagnetic phase transitions take place within the multi-phase mixture. Based on these results, it has been hypothesized that there may be an additional transformation taking place that leads to the formation of either bct- or o-Fe$_3$B in addition to the Fe$_{23}$B$_6$ phase, although further work is required to test this hypothesis.
6.1 Introduction and Motivation

Fe-B alloys are well known glass formers. When rapidly cooled at rates on the order of $10^6$ K/s, alloys with B concentrations ranging from 12–28% can be quenched into a glassy state, with the eutectic composition (approximately Fe$_{83}$B$_{17}$) requiring the lowest cooling rate [194]. In addition to being a good binary glass forming system, Fe-B also forms the basis of a large body of multi-component glass forming systems, ranging from ternary alloys such as Fe-B-Si [195] to five- and six-component bulk glass forming alloys such as Fe$_{43}$Cr$_{16}$Mo$_{16}$(C, B, P)$_{25}$ [196] with critical cooling rates on the order of 100 K/s. Much of the work in recent years has focused on the development of these multi-component bulk forming systems, particularly with respect to their glass forming ability and engineering properties such as hardness [197], corrosion resistance [196], and soft ferromagnetism [68, 198]. However, the Fe-B binary system continues to receive significant attention, in both the amorphous [199, 200] and liquid [192, 201–206] states, as it is a valuable system for performing fundamental studies to gain insight into the nature of the glass transition.

In addition to being a good binary metallic glass forming system, the Fe-B system has demonstrated a wide variety of metastable crystalline phase formation. According to the equilibrium stable phase diagram, shown in Fig. 6.1 (from Ref. [207]), Fe-B alloys with Fe contents between 66.67–100 at.% will tend to form two-phase mixtures of tetragonal Fe$_2$B and pure fcc/bcc Fe. However, when the Fe-B alloys are initially formed into a glassy state and undergo crystallization during subsequent annealing processes, it has been found that a wide variety of metastable intermetallic compounds can form [208, 209], with the three most commonly occurring phases being: body centered tetragonal (bct) Fe$_3$B, orthorhombic (o) Fe$_3$B, and fcc Fe$_{23}$B$_6$\(^1\). The apparent ease with which these phases form, and their ability to resist transformation into the stable phases, has led to some of them being mistakenly identified as stable equilibrium phases [208]. However, the most recent assessments of the Fe-B binary system, including both experimental [207] and calculated [210], have verified that the only stable

\(^1\)Other phases that have been observed, though much less frequently, include a primitive tetragonal Fe$_3$B and a supersaturated mixture of bcc-Fe with 20 at.% B referred to as Fe$_4$B [208]. Compared to the other metastable phases, the frequency with which these phases have been observed has declined significantly since the 1980s and, therefore, they will not be included in the remaining discussion.
intermetallic phase with Fe content greater than 50 at.% is Fe$_2$B. Additionally, \textit{ab-initio} calculations of the cohesive energies of several Fe-B intermetallic phases have verified that bct-Fe$_3$B, o-Fe$_3$B, and Fe$_{23}$B$_6$ are indeed metastable phases \cite{211}. The ability of near-eutectic Fe-B alloys to undergo crystallization into a wide variety of intermetallic phases has led to this being an ideal and popular binary system for performing studies of phenomena such as nucleation and phase transformation, and these metastable phases may even play an important role in the production of industrially relevant materials such as permanent magnets \cite{22}.

Recent investigations \cite{192, 205, 206} of the liquid Fe$_{83}$B$_{17}$ near eutectic composition have demonstrated that, in addition to glass formation and the crystallization of metastable phases during annealing, metastable crystalline phases can be formed when solidification occurs from the deeply supercooled liquid state. By suppressing heterogeneous nucleation using a variety of techniques (immersion in a solid flux of alumina, immersion in a molten glass slag of B$_2$O$_3$, and conical nozzle levitation), three different research groups have shown that non-equilibrium solidification of the supercooled liquid can lead to the formation of bct-Fe$_3$B and/or Fe$_{23}$B$_6$. While the studies \cite{192, 205, 206} demonstrated the possibility of metastable phase formation, no measurements were performed on the thermophysical properties of the supercooled liquid state or of the metastable solidification products and, to our knowledge, no further experimental studies of supercooled near-eutectic Fe-B liquids and their metastable solidification products have been published. Furthermore, discrepancies exist regarding the exact nature of the metastable phase formation, with Refs. \cite{205, 206} claiming formation of bct-Fe$_3$B but not Fe$_{23}$B$_6$, and Ref. \cite{192} claiming formation of Fe$_{23}$B$_6$ but not bct-Fe$_3$B. There are also discrepancies between \cite{205} and \cite{192} regarding the level of supercooling that is required before metastable phase formation can occur, with Ref. \cite{205} claiming that the supercooling must exceed 386 K before metastable phase formation occurs and Ref. \cite{192} observing metastable phase formation at supercoolings of less than 100 K. Therefore, there is much remaining to be learned regarding the nature of these metastable crystalline phases and their formation from deeply supercooled liquids in the Fe-B system.
6.2 Review of stable and metastable Fe-B phases

In this section a review will be given of the various phases that have been previously observed as crystallization products in Fe-B near-eutectic liquid and glassy alloys. The primary reference for crystallographic data such as Pearson symbols, lattice constants, and atomic environment types listed in Tables 6.1 and 6.2 is the Springer Materials Landolt-Börnstein Database, including the various “B-Fe (Boron-Iron)” data sheets [208–210] as well as the individual crystal structure data sheets: fcc-Fe [212], bcc-Fe [213], Fe₂B [214], o-Fe₃B [215], bct-Fe₃B [216], and Fe₂₃B₆ [217]. In the cases of bct-Fe₃B and Fe₂₃B₆, detailed data regarding the exact atomic positions and structure types are not available, so the structure types were based on their respective prototype structures of bct-Ni₃P and Cr₂₃C₆; the particular local atomic environments were checked against the discussion of local structures within Fe-B phases that takes place in Refs. [48, 203, 211] to ensure that the descriptions are consistent and accurate. The references for the Curie transition temperatures of each of the respective phases are: bcc-Fe and
Table 6.1 Summary of the crystal structures and ferromagnetic Curie temperatures for the various Fe-B intermetallic phases.

<table>
<thead>
<tr>
<th>Phase</th>
<th>Pearson Symbol</th>
<th>Lattice constants (Å)</th>
<th>Curie Temperature (K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>fcc-Fe</td>
<td>cF4</td>
<td>a,b,c = 3.60</td>
<td>N.A.</td>
</tr>
<tr>
<td>bcc-fe</td>
<td>cI2</td>
<td>a,b,c = 2.87</td>
<td>1043</td>
</tr>
<tr>
<td>Fe$_2$B</td>
<td>tI12</td>
<td>a,b = 5.12; c = 4.26</td>
<td>1015</td>
</tr>
<tr>
<td>o-Fe$_3$B</td>
<td>oP16</td>
<td>a = 5.40, b = 6.65, c = 4.37</td>
<td>897</td>
</tr>
<tr>
<td>bct-Fe$_3$B</td>
<td>tI32</td>
<td>a,b = 8.66; c = 4.30</td>
<td>786</td>
</tr>
<tr>
<td>Fe$_{23}$B$_6$</td>
<td>cF116</td>
<td>a,b,c = 10.67</td>
<td>698</td>
</tr>
</tbody>
</table>

Fe$_2$B [218]; Fe$_{23}$B$_6$ [22]; o-Fe$_3$B and bct-Fe$_3$B [219]. Assignments of Voronoi polyhedra were made based on the information in Refs. [220,221], many of which were also verified based on the discussions in Refs. [48,203,211]. The coordination numbers shown in Table 6.3 are based on a weighted average of the various atomic environment types shown in Table 6.2, except for the Fe$_{80}$B$_{20}$ liquid, whose coordination numbers were determined from the *ab initio* investigations of Ref. [203].

Before discussing the information contained within Tables 6.2 and 6.3, a discussion is necessary to explain how that information is defined. Within Table 6.2, the various Fe-B crystal structures are broken down into their respective Wyckoff sites, along with the atomic environment types and Voronoi polyhedra associated with each Wyckoff site. Within a crystal, a Wyckoff site is a representative atomic site characterized by a particular multiplicity and a set of symmetry relations, both of which are determined by the particular space group to which the crystal structure belongs. Given the coordinates of a single atom of a particular Wyckoff site, the positions of the remaining atoms of that type can be calculated using the allowed symmetry operations. The atomic environment types associated with each Wyckoff site are determined by creating a histogram of the number of neighboring atoms located at a particular distance away from the central atom, with the coordination polyhedron being determined by the atoms that appear to the left of a maximum gap in the histogram [222]; the first shell coordination atoms are arranged on the vertices of the respective coordination polyhedra. The Voronoi polyhedra are reciprocal-space representations of their respective coordination polyhedra, and their
Table 6.2  Comparison of the different types of short range order which exist in the various Fe-B intermetallic phases.

<table>
<thead>
<tr>
<th>Crystal Structure</th>
<th>Site</th>
<th>Wyckoff Site</th>
<th>CN</th>
<th>Atomic Environment Type</th>
<th>Voronoi Polyhedron</th>
</tr>
</thead>
<tbody>
<tr>
<td>fcc-Fe</td>
<td>Fe</td>
<td>4a</td>
<td>12</td>
<td>cuboctahedron (Fe$_{12}$)</td>
<td>(0, 12, 0, 0)</td>
</tr>
<tr>
<td></td>
<td>B</td>
<td>8h</td>
<td>14</td>
<td>15-vertex Frank-Kasper (Fe$<em>{11}$B$</em>{4}$)</td>
<td>(0, 0, 12, 3)</td>
</tr>
<tr>
<td>bcc-Fe</td>
<td>Fe</td>
<td>2a</td>
<td>14</td>
<td>rhombic dodecahedron (Fe$_{14}$)</td>
<td>(0, 6, 0, 8)</td>
</tr>
<tr>
<td></td>
<td>B</td>
<td>4a</td>
<td>10</td>
<td>four-capped trigonal prism (Fe$<em>{8}$B$</em>{2}$)</td>
<td>(0, 2, 8, 0)</td>
</tr>
<tr>
<td>o-Fe$_{3}$B</td>
<td>Fe-1</td>
<td>8d</td>
<td>14</td>
<td>14-vertex Frank-Kasper (Fe$<em>{11}$B$</em>{3}$)</td>
<td>(0, 0, 12, 2)</td>
</tr>
<tr>
<td></td>
<td>Fe-2</td>
<td>4c</td>
<td>15</td>
<td>15-vertex Frank-Kasper (Fe$<em>{12}$B$</em>{3}$)</td>
<td>(0, 0, 12, 3)</td>
</tr>
<tr>
<td></td>
<td>B</td>
<td>4c</td>
<td>9</td>
<td>tri-capped trigonal prism (Fe$_{9}$)</td>
<td>(0, 3, 6, 0)</td>
</tr>
<tr>
<td>bct-Fe$_{3}$B</td>
<td>Fe-1</td>
<td>8g</td>
<td>14</td>
<td>14-vertex Frank-Kasper (Fe$<em>{12}$B$</em>{2}$)</td>
<td>(0, 0, 12, 2)</td>
</tr>
<tr>
<td></td>
<td>Fe-2</td>
<td>8g</td>
<td>16</td>
<td>16-vertex Frank-Kasper (Fe$<em>{12}$B$</em>{4}$)</td>
<td>(0, 0, 12, 4)</td>
</tr>
<tr>
<td></td>
<td>Fe-3</td>
<td>8g</td>
<td>13</td>
<td>pseudo Frank-Kasper (Fe$<em>{10}$B$</em>{3}$)</td>
<td>(0, 3, 6, 4)</td>
</tr>
<tr>
<td></td>
<td>B</td>
<td>8g</td>
<td>9</td>
<td>tri-capped trigonal prism (Fe$_{9}$)</td>
<td>(0, 3, 6, 0)</td>
</tr>
<tr>
<td>Fe$<em>{23}$B$</em>{6}$</td>
<td>Fe-1</td>
<td>48h</td>
<td>14</td>
<td>14-vertex Frank-Kasper (Fe$<em>{12}$B$</em>{2}$)</td>
<td>(0, 0, 12, 2)</td>
</tr>
<tr>
<td></td>
<td>Fe-2</td>
<td>32f</td>
<td>13</td>
<td>pseudo Frank-Kasper (Fe$<em>{10}$B$</em>{3}$)</td>
<td>(0, 3, 6, 4)</td>
</tr>
<tr>
<td></td>
<td>B</td>
<td>24e</td>
<td>9</td>
<td>mono-capped square antiprism (Fe$_{9}$)</td>
<td>(0, 5, 4, 0)</td>
</tr>
<tr>
<td></td>
<td>Fe-3</td>
<td>8c</td>
<td>16</td>
<td>16-vertex Frank-Kasper (Fe$_{16}$)</td>
<td>(0, 0, 12, 4)</td>
</tr>
<tr>
<td></td>
<td>Fe-4</td>
<td>4a</td>
<td>18</td>
<td>pseudo Frank-Kasper (Fe$<em>{12}$B$</em>{6}$)</td>
<td>(0, 6, 0, 12)</td>
</tr>
</tbody>
</table>
Table 6.3  Average chemical coordination numbers of each of the various Fe-B phases.

<table>
<thead>
<tr>
<th></th>
<th>Total</th>
<th>Fe-Fe</th>
<th>Fe-B</th>
<th>B-Fe</th>
<th>B-B</th>
</tr>
</thead>
<tbody>
<tr>
<td>fcc-Fe</td>
<td>12.0</td>
<td>12.0</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
</tr>
<tr>
<td>bcc-Fe</td>
<td>14.0</td>
<td>14.0</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
</tr>
<tr>
<td>Fe$_2$B</td>
<td>13.3</td>
<td>11.0</td>
<td>4.0</td>
<td>8.0</td>
<td>2.0</td>
</tr>
<tr>
<td>o-Fe$_3$B</td>
<td>13.0</td>
<td>11.3</td>
<td>3.0</td>
<td>9.0</td>
<td>0.0</td>
</tr>
<tr>
<td>bct-Fe$_3$B</td>
<td>13.0</td>
<td>11.3</td>
<td>3.0</td>
<td>9.0</td>
<td>0.0</td>
</tr>
<tr>
<td>Fe$_{23}$B$_6$</td>
<td>13.0</td>
<td>11.7</td>
<td>2.3</td>
<td>9.0</td>
<td>0.0</td>
</tr>
<tr>
<td>Fe$<em>{80}$B$</em>{20}$ liquid, simulated at 800 K</td>
<td>13.2</td>
<td>12.0</td>
<td>2.2</td>
<td>8.9</td>
<td>0.4</td>
</tr>
</tbody>
</table>
construction is performed using the same rules for which Wigner-Seitz cells are constructed for their respective Bravais lattices. The various indices associated with the Voronoi polyhedra, \((n_3, n_4, n_5, n_6)\), indicate the number of faces of the polyhedra that contain 3, 4, 5, or 6 edges, respectively. In a more general geometrical sense, a Voronoi (reciprocal space) polyhedron is the geometric dual of the coordination (direct space) polyhedron. For example, a local atomic environment characterized by perfect icosahedral ordering of the atoms has for its coordination polyhedron the regular icosahedron, with each of the nearest neighbor atoms occupying one of the 12 vertices of the icosahedron. The geometric dual of a regular icosahedron is the regular dodecahedron, which has 12 pentagonal faces, and therefore the Voronoi indices associated with icosahedral ordering are \((0, 0, 12, 0)\). Some of the coordination polyhedra relevant to the discussion of short range order in Fe-B intermetallic phases are shown schematically in Fig. 6.2 (figures originally from Ref. [223] (Frank-Kasper phases) and Ref. [224] (capped trigonal prisms)).

Among the Fe-B phases shown in Table 6.2, it can be seen that the atomic environment types surrounding the iron Wyckoff sites are dominated by Frank-Kasper polyhedra. Frank-Kasper polyhedra are topologically close-packed groupings of atoms characterized by polytetrahedral ordering of the atoms: the coordinating atoms are arranged into a closed surface comprised entirely of triangular faces, each of which share the central atom of the cluster as a common tetrahedral vertex. Among the boron Wyckoff sites, the coordination polyhedra are comprised of capped trigonal prisms and capped square antiprisms. The tri-capped trigonal prismatic and mono-capped square antiprismatic structures are actually very similar in nature, and one can be described as a slightly distorted version of the other [203]. Perhaps the most important distinction that can be made between the stable Fe\(_2\)B phase and each of the metastable Fe-B phases is the nature of the short range order surrounding the boron atoms. In the Fe\(_2\)B phase, the boron atoms are 10-coordinated: they are placed between what is essentially two Fe-based square grids, rotated by 45 degrees with respect to each other, with each of the squares capped by another boron atom. This results in a boron-boron coordination number of 2, with the boron atoms essentially forming an unbroken, zig-zagging chain throughout the crystal. In contrast, in each of the metastable Fe-B phases the boron atoms are only 9-coordinated, and
Figure 6.2 Schematic coordination polyhedra which describe the various atomic environment types found in Fe-B intermetallic alloys. TOP: (left) 12-vertex Frank-Kasper (icosahedron); (middle) 14-vertex Frank-Kasper; (right) 15-vertex Frank-Kasper. BOTTOM: (left) 16-vertex Frank-Kasper; (middle) tri-capped trigonal prism; (right) four-capped trigonal prism.
the boron-boron coordination number for each metastable phase is zero.

Based on *ab initio* simulations of liquid Fe$_{80}$B$_{20}$ at 800 K [203], the most common boron centered Voronoi polyhedra for deeply supercooled Fe-B near-eutectic alloys is the (0, 5, 4, 0) type, which comprised 20% of the boron-centered clusters, followed by the (0, 3, 6, 0) and (0, 2, 8, 0) types at 15% and 10%, respectively. The iron centered Voronoi polyhedra were found to be highly coordinated and highly distorted, with the most dominant contributions being of the (0, 4, 8, $x$) and (0, 3, 8, $x$) types, where $x = \{0, 1, 2, 3, 4\}$. Upon comparison with the crystalline Voronoi types, it would appear that the most important distinction that can be made is among the boron centered sites. Based on the respective quantities of the (0, 5, 4, 0), (0, 3, 6, 0), and (0, 2, 8, 0) Voronoi polyhedra, and keeping in mind that the (0, 5, 4, 0) and (0, 3, 6, 0) polyhedra are essentially distortions of each other, it would appear that the boron-centered chemical ordering of the liquid is much more similar to any of the metastable Fe-B phases than it is to the stable Fe$_3$B phase, with the Fe$_{23}$B$_6$ structure being slightly favored over the bct- and o-Fe$_3$B phases. Furthermore, upon comparing the coordination numbers of the Fe$_{80}$B$_{20}$ liquid with those of each of the Fe-B intermetallic phases (Table 6.3), it can be seen that the Fe-Fe, Fe-B, and B-Fe coordination numbers collectively show the most agreement with the Fe$_{23}$B$_6$ phase.

Based on the discussion above, it could be argued that the nature of the chemical short-range ordering in the liquid is the most similar to the Fe$_{23}$B$_6$ phase, followed by the bct- and o-Fe$_3$B phases, and there is the least amount of similarity between the liquid and the Fe$_2$B phase. The similarities in the chemical short-range ordering may lead to an interfacial energy that is the most favorable to the formation of the Fe$_{23}$B$_6$ phase when considering solidification from the deeply supercooled melt. Another important factor to consider is the diffusion which is required to accomplish cooperative growth of a two-phase mixture out of the liquid. The closer the composition of the liquid is to one of the intermetallic phases, the less diffusion will be required to accomplish growth, resulting in more favorable crystal growth rates. The combination of the chemical short range ordering and the influence of composition on the required degree of atomic diffusion would argue that, for liquids with compositions between Fe$_{80}$B$_{20}$ and Fe$_{83}$B$_{17}$, nucleation and growth of the Fe$_{23}$B$_6$ phase should be the most favorable.
While the favorable nucleation and growth of the Fe$_{23}$B$_6$ phase is more or less in agreement with the experimental results discussed in this chapter, it should also be noted that, based on experimental observations, there appears to be a large variability from one sample to the next in terms of whether the sample will nucleate and grow into the metastable Fe$_{23}$B$_6$ + fcc-Fe mixture or directly into the stable Fe$_2$B + fcc-Fe mixture. This wide variability has led to speculation that extrinsic factors, such as insoluble surface contaminants or dissolved oxygen content, may also play an important role in determining phase nucleation and stability.

6.3 Sample Preparation and Initial Investigations

The samples were prepared by arc melting appropriate quantities of high purity starting materials on a water cooled copper hearth at the Ames Laboratory Materials Preparation Center. The starting materials were 99.99% pure Fe from Toho Zinc Corporation and 99.9999% pure B from Alfa Aesar; the purities are metals basis only. After the initial arc melting and formation of the alloy button, the button was remelted an additional three times to ensure that the composition was homogeneous throughout the volume. The composition of the samples was nominal, based on the ratio of starting materials. During the first attempts to produce 2–3 mm diameter spheroids that would be suitable for ESL processing, the alloy button was crushed using bolt cutters into small pieces with masses of approximately 90 mg. These pieces were then formed into spheroids by an additional arc melting step. However, the samples produced this way generally performed very poorly in the ESL, and an improved method of producing spheroids was sought. In the improved method, another alloy button was produced similar to the first one, but rather than crushing the button into small pieces, the button was drop cast into rods with diameters of approximately 3 mm. These rods were then cut into pieces with masses ranging from 25–75 mg. To form these pieces into spheroids, they were laser melted on a substrate of either copper or graphite. The laser melting of the samples allowed for much more control during the preparation process. In addition to the laser, a pyrometer was used to monitor the sample temperature, and therefore the maximum sample temperature and melt duration could be accurately controlled. Furthermore, this method allowed the sample surface condition to be carefully monitored by using a high resolution color imaging system.
Ultimately, the preparation method that resulted in the most successful ESL processing of these samples employed laser heating on a graphite substrate inside of a chamber backfilled to 0.5 atm pressure with a reducing gas mixture of zero grade Ar:H$_2$ with a mixing ratio of 95:5. Melting the samples in a reducing gas mixture allowed iron oxides on the sample surface to be eliminated, resulting in more reliable ESL processing of these samples. More details on this process can be found in Ch. 5, specifically Sec. 5.4.

The first attempt at processing an Fe$_{83}$B$_{17}$ sample in the ISU-ESL was done using one of the original arc melted spheroids with a mass of 93 mg. This sample proved to be challenging to process using ESL. While it could be brought up to the melting/eutectic temperature with relative ease, this sample would repeatedly drop as soon as the melting process began. After dropping, the sample could be relaunched and levitation melting attempted again, but the process was problematic. In an attempt to improve the processing of this sample, it was melted on the sample positioning post (a 3 mm diameter rod of OFHC copper) several times under the high vacuum environment. After several attempts to levitation melt the sample, including dozens of instances of the sample dropping and dozens of instances of melting the sample on the positioning post, successful processing of the sample was achieved. The likely explanation for the poor initial processing behavior of this sample is that the sample was contaminated with insoluble iron oxides. The breakup of the iron oxides was rapid enough to result in charge destabilization of a levitated sample, but not rapid enough to result in the sample quickly becoming clean. These experiences are largely what led to the use of a reducing gas during sample preparation, as described in the previous chapter.

Despite the initial difficulties with levitation processing, once the sample began to behave well it demonstrated interesting behavior. The results from a select number of melting and cooling cycles for the sample are shown in Figures 6.3, 6.4 and 6.5. In each of these figures, the dashed lines correspond to a temperature of 1447 K, which is the eutectic temperature of the sample as indicated by the phase diagram in Fig. 6.1. The dotted line in each figure is 1394 K, which corresponds to the apparent temperature of the solidification plateau during formation of the Fe$_{23}$B$_6$ phase. The sample temperature was measured using a single color pyrometer, and the emissivity setting of the pyrometer was adjusted until the apparent eutectic temperature
coincided with the expected eutectic temperature.

Fig. 6.3 shows three cooling curves that were measured for a 93 mg sample of Fe$_{83}$B$_{17}$, and together they demonstrate some of the metastable phase forming behavior of this material. In Fig. 6.3(Top Left), the sample is initially overheated to a temperature of 1630 K before being allowed to free cool. During the free cool the sample reaches a minimum temperature of 1327 K, corresponding to a supercooling of $\Delta T = 121$ K, before recalescence occurs. Initially the sample solidifies into the metastable Fe$_{23}$B$_6$ phase with with a metastable solidification plateau of approximately 1394 K, but before the sample can fully solidify it undergoes metastable-to-stable (MtS) transformation, resulting in a second recalescence event (the so-called double-recalescence). The noise that occurs in the sample after solidification of the stable phase is a result of surface texturing, and the feature that occurs at 420 s corresponds to the solid-solid structural transition from fcc to bcc for the pure Fe fraction of the sample. Fig. 6.3(Top Right) shows a second cooling curve where the same overheating was applied to the sample before allowing the sample to free cool. However, this time the sample reaches a minimum temperature of 1398 K, corresponding to a supercooling of only $\Delta T = 49$ K. After recalescence, the sample appears to solidify into a second, distinct metastable solid phase with a solidification plateau of approximately 1431 K, henceforth called the $HT$-metastable phase because the solidification product has yet to be identified. As with the Fe$_{23}$B$_6$ phase, before the sample fully solidifies into the $HT$-metastable solid phase it undergoes MtS transformation. Finally, Fig. 6.3(Bottom) shows the same sample being allowed to free cool from an overheating temperature of 1548 K. During the free cool the sample reaches a minimum temperature of 1311 K ($\Delta T = 136$ K) before recalescence occurs. After recalescence the sample appears to solidify fully into the metastable Fe$_{23}$B$_6$ phase. There is no obvious second recalescence event that would signal transformation into the stable solid phase, and the solid state cooling curve indicates a smooth reduction in the cooling rate as the sample temperature drops, which would be expected based on the model of pure radiative cooling. Attempts at calculating first and second derivatives of the temperature vs. time do not reveal any obvious thermal signatures that might indicate a thermodynamic transition, and plotting the cooling rate vs. temperature results in a plot that fits very nicely to a quadratic function of the temperature, which would be expected for
thermal radiation with a temperature dependent surface area. In other words, the cooling curve in Fig. 6.3(Bottom) provides convincing evidence that the Fe$_{23}$B$_6$ metastable solid phase phase has been captured down to near room temperature. Furthermore, the solid-solid structural transition that occurs for Fe in Fig. 6.3(Top Left) is not observed to occur in Fig. 6.3(Bottom), which would indicate one of several possibilities: that the pure Fe fraction is not present; that one of the Fe allotropes has become stabilized throughout the temperature range; or that the fcc/bcc transition temperature has become significantly broadened, such that the latent heat of transformation is released slowly over several temperatures instead of at a single temperature. As will be shown in Sec. 6.4, the correct explanation appears to be the third option.

The appearance of the HT-metastable solid phase has been much less frequent than the Fe$_{23}$B$_6$ phase. In fact, only twice has the HT-phase been observed to form. Attempts have been made to coax samples into forming this phase more frequently by supercooling the samples to a temperature between 1394 K and 1431 K and waiting for solidification to occur, but the samples nearly always solidify into the stable solid phase rather than the HT-phase. There is currently no explanation as to why it is so difficult for the sample to solidify into the HT-phase, or what distinguishes the conditions that allowed the phase to appear the two times that it has.

In an effort to achieve a greater degree of supercooling for the Fe$_{83}$B$_{17}$ samples compared to what was achieved using the 93 mg sample, a 29 mg sample was produced by crushing one of the larger samples into smaller pieces and laser melting one of the pieces on a copper substrate to form a small spheroid. The rational behind making a smaller sample is that they generally experience greater cooling rates, which may lead to a deeper level of supercooling before heterogeneous nucleation occurs. The radius of the 29 mg sample was approximately 0.68 times the radius of the 93 mg sample, and therefore the maximum cooling rates that can be achieved during a free cool increased by a factor of nearly 1.5. Several new observations were made during the processing of the 29 mg sample, one example of which is shown in Fig. 6.4. In this example, the sample melted at the stable eutectic temperature of 1447 K, was overheated to 1520 K for 20 s, and then allowed to free cool. The sample cooled to a temperature of 1309 K ($\Delta T = 136$ K), at which point a mini-recalescence event occurred, as indicated by the arrow in
Figure 6.3  Cooling curves representing different solidification behavior for a 93 mg Fe$_{83}$B$_{17}$ sample processed in the ISU-ESL. (Top Left) Solidification from the supercooled liquid results in the metastable Fe$_{23}$B$_6$ phase, which subsequently transforms to the stable solid phase. (Top Right) A second metastable solid phase is formed with a different solidification plateau, which also eventually transforms into the stable solid phase. (Bottom) The sample fully solidifies into the metastable Fe$_{23}$B$_6$ phase, but this time transformation to the stable solid phase does not occur.
Figure 6.4  A cooling curve for a 29 mg Fe$_{83}$B$_{17}$ sample, showing the formation of a metastable bcc-Fe precipitate phase followed by solidification into the stable solid phase.

Fig. 6.4. This mini-recalescence signifies the precipitation of a small volume fraction of solid material in the sample, which has been identified as bcc-Fe. However, the precipitation event does not trigger bulk solidification of the sample. Rather, the solid-liquid mixture continues to cool to a minimum temperature of 1292 K ($\Delta T = 155$ K) before recalescence occurs and the sample undergoes solidification into the stable solid phase. The maximum supercooling achieved for this sample, and the maximum supercooling among all Fe$_{83}$B$_{17}$ samples processed in the ISU-ESL, was ($\Delta T = 165$ K) and occurred in the presence of this precipitate phase.

The formation of the bcc-Fe precipitate phase does not seem to be strongly correlated with subsequent solidification into either the stable solid or the Fe$_{23}$B$_{6}$ phase. For instance, in Fig. 6.5(Top), the first heating/cooling cycle shows the formation of the precipitate phase as indicated by the solid arrow, followed by solidification into the Fe$_{23}$B$_{6}$ phase. Another interesting observation from this data set is that during the next heating/cooling cycle, the Fe$_{23}$B$_{6}$ phase does not transform into the stable solid, but rather melts directly into the supercooled liquid at the Fe$_{23}$B$_{6}$ metastable melting temperature of 1394 K as indicated by the dash-dotted arrow. Between the initial recalescence and the completion of the metastable melting, approximately 45 s passed without the sample undergoing MtS transformation. This behavior has been observed on multiple occasions for Fe$_{83}$B$_{17}$ samples processed in the ISU-ESL, although
usually the MtS transformation occurs before the sample can be melted directly into the supercooled liquid at the Fe$_{23}$B$_6$ melting temperature. Although a comprehensive study has not been carried out to determine the average lifetime of the Fe$_{23}$B$_6$ phase at high temperatures, experiments have been performed where this phase has formed and then allowed to cool to 1230 K before being held isothermally, and a maximum of 95 s has been observed for the lifetime between recalescence and MtS transformation.

Regarding the stability of the supercooled liquid, it was found that the 29 mg sample was able to remain at deep levels of supercooling for several minutes. During isothermal holds at supercooling depths of $\Delta T < 100$ K it was found that the lifetime of the supercooled liquid could exceed 400 s, although durations of approximately 100 s or less were more common. During isothermal holds at supercooling depths of $\Delta T > 100$ K it was found that the duration of the supercooled state was still on the order of 100 s, even in the presence of the bcc-Fe precipitate phase. This is shown in Fig. 6.5(Bottom). In this instance, the sample was maintained in the deeply supercooled liquid state at 1340 K ($\Delta T = 107$ K) for 160 s, at which point the bcc-Fe precipitate phase formed as indicated by the arrow. After precipitation, the solid-liquid mixture remained in the deeply supercooled state for an additional 90 s before recalescence occurred and the sample solidified into the Fe$_{23}$B$_6$ phase. This level of stability of the solid-liquid mixture could be repeatably demonstrated.

Finally, in addition to the early troubles regarding levitation instability, all of the Fe$_{83}$B$_{17}$ samples were observed to have small amounts of insoluble, stable oxide impurities floating along the surface of the samples. This has actually been true for all of the Fe$_{83}$B$_{17}$ samples studied throughout this work. As was discussed in more detail in Ch. 5, this stable oxide phase is most likely Al$_2$O$_3$. The exact source of this oxide contaminant, whether it is a result of sample handling or if it is a product of intrinsic impurities, remains unknown. The presence of this insoluble oxide phase raises questions regarding the observed behavior of the samples. First, how much could the supercooling of the samples be improved if the oxide impurity could be removed? Previous studies on Fe$_{83}$B$_{17}$ have shown that a supercooling of 200 K can be achieved [205] for samples contained on a bed of alumina powder, and supercoolings up to 460 K have been achieved using a B$_2$O$_3$ fluxing method [206]. It is actually rather odd that Ref. [205]
Figure 6.5 Two additional temperature data sets for the 29 mg Fe$_{83}$B$_{17}$ sample. (Top) Supercooling results in the formation of the bcc-Fe precipitate phase, followed by solidification into the metastable Fe$_{23}$B$_6$ phase. Upon reheating, the sample melts at the metastable melting temperature without transforming into the stable solid. (Bottom) After remaining in the supercooled liquid for 160 s, the bcc-Fe precipitate forms, but does not trigger bulk solidification of the sample.
could achieve a deeper supercooling than the ESL processed samples, considering that their samples are in contact with the same material that is thought to be the primary contaminant in the samples presently investigated. The difference may be the nature of the alumina, being a fine powder in Ref. [205] and more of an irregular solid patch on the ESL samples. Regardless, it would seem as though deeper supercooling should be achievable. The other question that must be asked is: could the insoluble oxide be influencing the phase formation behavior of the sample? Because the oxide impurity acts as a heterogeneous nucleation cite, it may also act as a seed crystal that results in the preferential formation of one metastable phase over the other, or perhaps it is the reason that metastable phase formation happens at all. While it is difficult to ascertain the full extent of the oxide phase’s influence on the phase formation behavior, such questions could be answered by preparing oxide-free samples to test whether or not the solidification of a clean sample is any different from a contaminated sample. Research into sample purification methods is ongoing.

6.4 BESL X-ray Studies

6.4.1 Experimental Details and Results

Measurements of atomic structure were performed via x-ray diffraction using the Washington University Beamline-ESL (WU-BESL) [100]. The WU-BESL is an ESL system similar to that developed at ISU, but with modifications that allow it to be incorporated into beamlines at synchrotron x-ray sources. For this particular study, the WU-BESL was installed at sector 6ID-D of the Advanced Photon Source (APS) at Argonne National Laboratory. High energy x-rays (132 keV, \( \lambda = 0.094 \, \text{Å} \)) were employed to allow diffraction measurements to be performed in transmission mode, as well as to reduce unwanted contributions to the scattered x-ray intensity, such as air scattering and fluorescence. The high vacuum chamber was equipped with beryllium windows for the entrance and exit ports of the x-ray beam, and the geometry of the system allowed for x-ray scattering angles in the range of \( 0.9 \leq 2\theta \leq 19.5 \) (degrees), corresponding to a momentum transfer of \( 1.0 \leq Q \leq 22.6 \) (Å\(^{-1}\)). The application of x-ray diffraction on liquids and polycrystalline solids results in Debye-Scherrer rings, the patterns of
which were measured using a 2-dimensional digital detector (GE Revolution 41-RT) with a resolution of 2048x2048. The Debye-Scherrer rings were integrated using the FIT2D [225] powder analysis software to produce data sets of x-ray scattering intensity vs. scattering angle $2\theta$ (or momentum transfer $Q$). Qualitative analysis of the crystal structures was performed by comparing the measured x-ray intensity with the expected patterns based on a database of known crystal structures [226], and quantitative analysis of the crystal structures was performed using the General Structure Analysis System (GSAS) [227]. More detailed information regarding the WU-BESL can be found in Ref. [100], and addition details regarding BESL systems can also be found in Ref. [99].

We will first discuss the identification of the bcc-Fe precipitate phase in deeply supercooled Fe$_{83}$B$_{17}$, which was first indicated in Fig. 6.4. Fig. 6.6 shows the x-ray diffraction patterns of the deeply supercooled liquid just prior to precipitation (Top) and after the bcc-Fe precipitate phase has fully formed (Middle), both of which were recorded during a free radiative cooling at a temperature of 1326 K before and after precipitation. To isolate the bcc-Fe phase from the liquid, the diffraction pattern before precipitation was subtracted from the diffraction pattern after precipitation. Because some volume fraction of the sample will have transformed from liquid into solid, a 1-to-1 subtraction is not appropriate; rather, some multiplicative factor must be applied to the liquid precursor. It has been found that multiplying the liquid precursor by a factor of 0.86 results in an adequate background for the isolated diffraction pattern of the precipitate phase. This would seem to indicate that approximately 14% of the volume of the sample has undergone solidification into the precipitate phase. However, care must be taken when considering the volume fraction of the precipitate phase, because the stoichiometries of the liquid phase fraction before and after precipitation are likely different and therefore a simple subtraction of the two diffraction patterns is insufficient to properly isolate the precipitate phase. Nevertheless, the 14% figure still serves as an approximate indicator of the volume fraction of the precipitate phase.

The identification of bcc-Fe as the precipitate phase was accomplished by comparing diffraction pattern of the isolated precipitate phase (Fig. 6.6 (Bottom)) with known diffraction data from crystallographic databases [226]. On first thought, the formation of bcc-Fe in this tem-
Figure 6.6  X-ray diffraction patterns for: (Top) the supercooled liquid at 1326 K, just prior to the formation of the precipitate phase; (Middle) the solid-liquid mixture after the precipitate phase has fully formed; (Bottom) the precipitate phase, isolated from the liquid fraction by subtracting the (Top) pattern from the (Middle) pattern. The precipitate phase was found to be bcc-Fe.
perature range may seem surprising. For pure Fe in the temperature range from 1183–1667 K (which includes the precipitation temperature of 1326 K), the stable allotrope is fcc-Fe; outside this temperature range the stable allotrope (near 1 bar pressure) is bcc-Fe. The natural question that arises, then, is: why does the precipitate phase take on the bcc structure instead of the fcc structure? There are at least two possible answers to this question. The first possibility is that the bcc structure has become stabilized through soluble additions of boron into the bcc-Fe crystal structure. There are a number of materials systems for which the bcc-Fe structure becomes stabilized for all temperatures between room temperature through the melting point. Two examples are the Fe-Si binary system, for which only 4% Si is required to stabilize the bcc-Fe structure, and the Fe-Zn binary system, where only 6% Zn is required to stabilize the bcc-Fe structure at all temperatures [228]. For the stable equilibrium Fe-B binary system, the solubility of B in Fe is less than 0.02% [210], and the stable binary phase diagram does not show any indication of the bcc-Fe structure becoming stabilized. However, it has been shown that for rapidly quenched Fe-B alloys that the solubility of B in bcc-Fe can be increased by up to 12% [15]. It may therefore be possible that the nonequilibrium solidification conditions that occur from the deeply supercooled liquid result in a metastable solid-solution of B in Fe that stabilizes the bcc-Fe structure in temperature ranges where the fcc-Fe structure would normally be expected. Another possible explanation for the precipitation of the bcc-Fe phase comes from consideration of the interfacial free energy and its impact on the nucleation barrier. As was discussed in Ch. 2, with regards to Eq. 2.11 for the interfacial free energy of a monatomic material, the solid-liquid interfacial free energy for a bcc-crystal is 18% smaller than for a fcc-crystal. For pure Fe, the enthalpy difference between fcc and bcc structures is only approximately 6% of the enthalpy of fusion for the bcc-liquid transformation [229]. Therefore, there would seem to be a net reduction in the nucleation barrier for the formation of bcc-Fe as opposed to fcc-Fe. It could be that one or the other, or both, or these explanations (solid-solution stabilization and nucleation barrier reduction) is behind the precipitation of the bcc-Fe from the supercooled liquid. One last comment that can be made regarding the precipitation of bcc-Fe is that the ability of the precipitate phase to coexist with the supercooled liquid, without initiating bulk solidification, would seem to indicate that the composition of Fe$_{83}$B$_{17}$ is on the Fe-rich side of
a metastable eutectic.

We now turn our attention to the bulk solidification and the formation of stable and metastable solid phases for this composition. Fig. 6.7 shows x-ray diffraction data of the supercooled liquid just prior to, as well as during, solidification of the stable and metastable solid phases. These diffraction data were recorded during back-to-back heating/cooling cycles of a single sample, and in each case the maximum supercooling before recalescence was $\Delta T = 132 \pm 5$ K, so there should be little difference between the liquid phase precursors to solidification. For both the stable and metastable solid phases, it can be seen that the most intense crystalline peaks correspond closely to the peak in the first oscillation of the liquid phase. For the each of the liquid phase precursors, the peak in the first oscillation is located at $2\theta = 2.62$ degrees. For the stable solid phase the most intense peak is located at $2\theta = 2.55$ degrees, and for the metastable solid phase the most intense peak is at $2\theta = 2.58$ degrees. In general, the distribution of crystalline peak intensities appears to roughly correspond with the first and second broad oscillations of liquid data.

To ensure that there is no significant difference between the liquid phase precursors to solidification of the stable and metastable solid phases, a direct comparison of the liquid diffraction data in Fig. 6.7 has been made. In Fig. 6.8 the two sets of liquid data are plotted together, and as can be seen there is no discernible difference between the two data sets, despite the two data sets being acquired on difference cooling cycles and despite the two liquids ultimately solidifying into different solid phases. A careful analysis of the two liquid data sets indicates that any difference between the two is below the noise threshold for performing x-ray diffraction measurements on levitated samples. Verification of the similarity of the two liquid data sets is important because it confirms that the different solidification pathways are not being caused by gross differences in the liquid structure, such as might be caused by variations in the thermal history of the sample. Instead, given that the liquid precursors appear to be nearly identical, it would seem that the different solidification products are resulting from the statistical nature of the nucleation processes occurring within the deeply supercooled liquid.

To gain further insight into the nature of the solidification products, measurements were performed on samples throughout solidification and down to low temperatures. Representative
Figure 6.7  X-ray diffraction patterns for: (Top Left) the supercooled liquid precursor just before solidification into the stable solid phase; (Bottom Left) the solid-liquid mixture during solidification of the stable solid phase; (Top Right) the supercooled liquid precursor just before solidification into the metastable solid phase; (Bottom Right) the solid-liquid mixture during solidification of the metastable solid phase.
Figure 6.8 Comparison of the supercooled liquid precursors for solidification of the stable solid phase (solid blue curve) and metastable solid phase (dashed red curve). Each pattern corresponds to the supercooled liquid at approximately 1318 K. There is no discernible difference between the two liquids.

plots of x-ray scattering intensity vs. 2-Theta for the stable and metastable solids at high and low temperatures are shown in Fig. 6.9. In these particular examples, “high temperature” is defined as being above the bcc/fcc transition temperature of pure Fe (1185 K), and “low temperature” is defined as being below the transition temperature. The measurements on the stable phase serve as a verification for the analysis of the experimental data, as the results should be very similar to what is expected based on the known stable binary phase diagram (Fig. 6.1). The results of structural analysis on the stable phase indicate a mixture of Fe$_2$B plus fcc-Fe at high temperature, and Fe$_2$B plus bcc-Fe at low temperature, just as would be expected based on the equilibrium stable phase diagram.

In the case of solidification into the metastable Fe$_{23}$B$_6$ phase, it was initially suspected that the sample may be single phase, which would indicate a width of formation for the Fe$_{23}$B$_6$ phase of approximately 4%. This understanding was made based on the lack of any clearly discernible fcc-Fe peaks in the high temperature data shown in Fig. 6.9. However, further analysis of the data has shown that fcc-Fe is indeed present at high temperatures, but its diffraction peaks overlap almost completely with those of the Fe$_{23}$B$_6$ phase. To demonstrate clearly that fcc-
Figure 6.9  Comparison of the x-ray diffraction patterns for the fully solidified stable and metastable products at high and low temperatures. (Top Left) The stable solid at 1253 K, consisting of Fe$_2$B and fcc-Fe. (Bottom Left) The stable solid at 952 K, consisting of Fe$_2$B and bcc-Fe. (Top Right) The metastable solid at 1253 K, consisting of Fe$_{23}$B$_6$ and fcc-Fe. (Bottom Right) The metastable solid at 901 K, consisting of Fe$_{23}$B$_6$ and bcc-Fe. The dashed red lines indicate peaks associated with fcc-Fe, while the dotted green lines indicate peaks associated with bcc-Fe.
Fe is present at high temperature, a simple subtraction was performed on the data to isolate the fcc- and bcc-Fe phases. The subtraction was based on the following idea: if the high temperature x-ray data of the stable/metastable phases contains diffraction peaks belonging to Fe$_2$B/Fe$_{23}$B$_6$ plus fcc-Fe, and the low temperature x-ray data contains diffraction peaks belonging to Fe$_2$B/Fe$_{23}$B$_6$ plus bcc-Fe, then performing a subtraction of (high temperature) minus (low temperature) diffraction data should remove the intermetallic phase contribution to the diffraction profile, revealing fcc-Fe peaks with positive intensity and bcc-Fe peaks with negative intensity. In order to allow the intermetallic phases to be as cleanly subtracted as possible, the low temperature data were corrected to account for thermal expansion and the Debye-Waller effect. The results of the subtractions are shown in Fig. 6.10. As can be seen, the subtraction method results in a nearly perfect removal of the Fe$_2$B phase, clearly revealing the fcc-Fe peaks with positive intensity and bcc-Fe peaks with negative intensity. Difficulty was encountered when trying to accomplish a subtraction with the same level of cleanliness on the metastable phase, primarily due to the poor powder averaging of the sample which resulted in significant oscillations in the peak intensities from one data frame to the next. Nevertheless, the fcc-Fe and bcc-Fe peaks are still clearly discernible, indicating that the metastable solidification product was indeed a mixture of Fe$_{23}$B$_6$ plus fcc-Fe at high temperature, with the fcc-Fe transforming to bcc-Fe upon cooling. It has been observed that the peaks associated with bcc-Fe tend to appear rather slowly as the sample cools, indicating that the fcc/bcc Fe transition is occurring over a range of temperatures, instead of a single well-defined temperature as in the case of the Fe$_2$B-Fe mixture.

In addition to the Fe$_{23}$B$_6$ and pure-Fe phases being identified in the metastable phase x-ray data, two additional peaks have been observed to appear in the low temperature diffraction data as shown in Fig. 6.11. These peaks are not associated with Fe$_{23}$B$_6$, Fe$_2$B, or either of the pure Fe phases, and therefore they indicate the formation of a new phase. The appearance of these peaks occurs at approximately the same time as the fcc-to-bcc Fe transition near 1165 K, although it is unclear whether it is a causal relationship or merely coincidental. Because there

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2Not all of the fcc- and bcc-Fe peaks have been specifically indicated in the data. Only those peaks most helpful for identifying fcc- and bcc-Fe in the metastable phase have been indicated.
Figure 6.10  Residual x-ray intensities after performing subtractions of (high temperature) minus (low temperature) x-ray data for the stable phase (TOP) and for the metastable phase (BOTTOM).
are only two clearly discernible peaks of appreciable intensity, and because only one of these peaks is not overlapping significantly with peaks from either the Fe$_{23}$B$_6$ or bcc-Fe phases, it has not been possible to determine the nature of this additional phase. Attempts have been made to match the peak locations with those of other known Fe-B phases, such as bct- and o-Fe$_3$B, and based purely on the locations of these two peaks it appears that it may be possible that the additional phase is o-Fe$_3$B. However, developing a positive match of the identity has proven difficult due to the lack of clearly distinguishable peaks.

Attempts at performing quantitative analysis of the x-ray data using Rietveld analysis have proven to be very challenging due to the poor powder averaging of the samples and the large number of overlapping peaks. Even with the relatively well behaved Fe$_2$B plus bcc/fcc Fe phase mixture, the analysis has struggled to accurately determine both the lattice parameters and the phase fractions of the constituent phases. In the case of Fe$_2$B, the Rietveld analysis has resulted in spurious values of the lattice parameters, including a sudden expansion in both the a and c lattice parameters at the bcc/fcc transition of Fe. By analyzing the temperature dependence of
individual Fe$_2$B peaks, it was found that expansion was not actually occurring in the Fe$_2$B itself, and it has been concluded that the apparent expansion in the Rietveld refined data was caused by a misassignment of some fraction of the Fe$_2$B/Fe peaks. Attempts are ongoing to tighten the Rietveld refinement parameters in order to perform an accurate quantitative assessment of not only the stable phase data, but also the metastable phase data. Assuming that the quality of the Rietveld analysis can be improved, it may be possible to form a positive identification of the third phase that develops below the bcc/fcc Fe transition in the metastable phase data.

6.4.2 Additional Discussion Regarding Metastable Phase Formation

To summarize the results of the preceding sections, while performing measurements of the atomic structure of the solidification products of deeply supercooled Fe$_{83}$B$_{17}$, three important observations have been made. First, when the degree of liquid supercooling exceeds approximately $\Delta T = 125$ K, a bcc-Fe precipitate phase has been found to occur, and approximately 14% of the sample volume undergoes solidification into this precipitate phase. The combination of the precipitate phase being Fe, along with the (meta)stable coexistence of the deeply supercooled liquid plus bcc-Fe precipitate phase, seems to indicate that the alloy composition of Fe$_{83}$B$_{17}$ lies on the Fe-rich side of a metastable eutectic. Second, when the degree of liquid supercooling exceeds approximately $\Delta T = 75$ K, it becomes possible for the sample to undergo bulk solidification into a two-phase mixture of metastable Fe$_{23}$B$_6$ plus fcc-Fe, which has a metastable melting temperature of approximately 1394 K. As the metastable solid cools, the fcc/bcc Fe transition is found to occur at approximately 1165 K and the transition occurs over a broad range of temperatures instead of a single, well defined temperature. Third, it has been shown that the metastable Fe$_{23}$B$_6$ phase can be maintained down to low temperatures during a free radiative cooling with cooling rates less than 25 K/s.

There are a number of comparisons that can be made between the present study and previous studies [192, 206] regarding phase identification of the solidification products of deeply supercooled Fe$_{83}$B$_{17}$ liquids. In the present study we have shown that bulk metastable solidification results in the formation of the Fe$_{23}$B$_6$ plus fcc-Fe. This is in partial agreement with the results of Ref. [192], which also identified Fe$_{23}$B$_6$ as the metastable solidification product.
of an aerodynamically levitated Fe$_{83}$B$_{17}$ sample, but claimed that the sample was single phase at high temperature with bcc-Fe appearing at lower temperatures. It is likely that fcc-Fe was actually present in the study performed in Ref. [192], but that it was not properly identified at high temperatures due to the overlapping x-ray diffraction peaks. The formation of Fe$_{23}$B$_{6}$ plus fcc-Fe is in even stronger contrast to the results of Ref. [206], which found bct-Fe$_{3}$B as the primary metastable solidification product of Fe$_{83}$B$_{17}$ samples processed using the B$_2$O$_3$ melt fluxing technique. However, there is an important distinction to be made between the results found when using levitation techniques such as ESL (present) and CNL [192] versus the results found when using the melt fluxing technique [206]. When levitation techniques have been used, the primary solidification products were measured in-situ and were found to be primarily Fe$_{23}$B$_{6}$ immediately upon solidification. When B$_2$O$_3$ melt fluxing was used, the crystal structure of the solidified sample was measured ex-situ, and the structural measurements were performed only at room temperature; in this case bct-Fe$_3$B and bcc-Fe were found. In none of the studies have measurements of the atomic structure been performed in-situ beginning in the liquid, through solidification and down to room temperature in a single continuous acquisition; the present study goes down only to 900 K, and Ref. [192] goes down to 800 K. Therefore, it may be possible that additional crystallographic transformations are taking place between 800 K and 300 K, such as the transformation of Fe$_{23}$B$_{6}$ directly into bct-Fe$_3$B plus bcc-Fe, as well as the possible formation of additional transitory phases such as α-Fe$_3$B.

Another comparison that can be made between the present study and previous studies concerns the conditions that are required for metastable phase formation to take place. For the melt fluxed samples in Ref. [206] it was stated that metastable phase formation from the deeply supercooled liquid was not found to occur unless the degree of supercooling exceeded $\Delta T = 386$ K. This is in contrast to the present studies as well as Ref. [192] (using CNL), where it has been found that metastable phase formation occurs for supercooling levels in the range of $75 \leq \Delta T \leq 165$ K. Even though structural measurements on the melt fluxed samples were not performed in-situ, if metastable phase formation had occurred from shallower supercooling levels it should have been obvious in the temperature profiles in a similar manner to the observations that were discussed in Sec. 6.3. One possible explanation for the different metastable
phase formation behavior is that external influences are playing a role in the nucleation processes, such as surface impurities (known to exist in the present studies) or the $\text{B}_2\text{O}_3$ flux itself. Further studies will be required to sort out these differences.

There is an additional difference between the conditions for metastable phase formation between the present study and the CNL study [192]. In the CNL study it was stated that for the metastable Fe$_{23}$B$_6$ phase to remain present down to low temperatures (800 K), cooling rates on the order of 180 K/s were required, whereas cooling rates of 30 K/s resulted in MtS transformation occurring before the sample reached low temperature. In the present study, we have shown that it is certainly possible for the Fe$_{23}$B$_6$ phase to be maintained to low temperatures using cooling rates less than 30 K/s. However, we have also found that the stability of the metastable phase can vary significantly from one sample to the next. For some samples, the metastable solid phase will readily form and can be maintained down to low temperature for nearly every melting/solidification cycle that is applied to the sample. For other samples, it has been found that metastable phase formation may not occur during every melting/solidification cycle, and that when the metastable phase does form it consistently undergoes transformation into the stable solid phase before the sample has fully solidified. For yet other samples, the ease of formation and stability of the metastable phase lies somewhere in between. One possible explanation for this behavior is that the stability of the Fe$_{23}$B$_6$ phase is sensitive to the oxygen content of the sample, and that their may be a significant variation in the oxygen content from one sample to the next. It is well known that variations in oxygen content can have a strong impact on phase stabilization in metallic systems (see for example Refs. [162,163]), and given the well documented issues with oxidation of Fe-based samples, oxygen variability among different samples is certainly plausible. Another possibility is that the metastable phase formation and stability are sensitive to the exact composition of the samples and that, due to the sample preparation procedures being used, there is sizable variation in the exact composition from one sample to the next. It may also be due to a combination of factors. Additional studies will be required to determine the precise cause of the variability.
6.5 Thermophysical Measurements Using the ISU-ESL

Very recently, a large series of measurements have been performed on the thermophysical properties of a 50 mg sample of Fe$_{83}$B$_{17}$ in both the stable and metastable solid states. These include measurements of the temperature dependence of volume expansion, RF susceptibility as measured using the TDO method, and spectral emissivity in the spectral range from 1050–1650 nm. Combined with the free cooling experiments on the metastable solid, the volume expansion and spectral emissivity measurements should also enable calculations of the specific heat capacity. The primary purpose of these measurements was to gain additional insight into the nature of the metastable phase formation, temperature evolution of the metastable phase during cooling, and MtS transformation during reheating. Similar measurements have been made on the stable solid phase to provide a point of comparison when analyzing the results for the metastable solid phase. While the results from these experiments are still in the initial stages of data processing and analysis, significant progress has been made in terms of processing the volume thermal expansion and RF susceptibility data, and in this section those results will be shown along with some comments regarding their interpretation.

6.5.1 Volume Thermal Expansion

Measurements of the volume thermal expansion were performed using the machine vision video volume method described in Sec. 3.7. When performing these measurements on solid samples, it is important to recognize that the assumption of axial symmetry for the sample profile is no longer valid, as it is in the case of liquid samples. The reason for this is that, during solidification, the combination of liquid-solid density variations along with the development of crystal microstructure lead to a topology for the sample that is not isotropic. Because the levitated samples will inevitably have some amount of axial rotation, their 2-dimensional cross-sectional areas (and therefore their calculated volumes) will be observed to fluctuate at a rate corresponding to their axial rotation rate. The combination of the samples not having axial symmetry along with some degree of axial rotation can lead to an apparent fluctuation (noise level) in the volume data as great as $\pm 2\%$, based on observations made using the ISU-ESL.
To reduce the extent of these fluctuations in the recent experiments, the sample rotation rate was intentionally increased to approximately 6–8 Hz via the photon pressure of intentionally misaligned heating lasers as described in Sec. 3.3. Additionally, the video volume data was acquired at either 25 or 75 Hz, and averaged over 6–8 frames of data. As a result of the data averaging, the noise level could be reduced by a factor of 10 or more. It is also important to consider how the averaging impacts the temperature resolution of the data. During a free radiative cooling of the sample, the maximum cooling rate is approximately 30 K/s. For a 25 Hz acquisition rate for the volume data being averaged over 8 frames, this corresponds to a temperature averaged width of 10 K. However, this represents the upper limit for the temperature width of the averaging for the recent experiments. As the sample cools during a free radiative cooling there will be a corresponding reduction in the cooling rate and therefore a reduced width of the temperature averaging of the volume data. In addition to the free cooling trials, measurements have been performed during which the sample temperature was ramped at a specific rate of 3 K/s. For these measurements, the temperature width of the averaging is only 1 K.

Fig. 6.12 displays representative volume thermal expansion data for the liquid, metastable solid, and stable solid, all of which were acquired sequentially. The data acquisition begins at point (a), with the sample in the stable solid phase at a temperature of 1420 K. The heating laser power was then increased in a single step such that sample was melted and then allowed to heat to a maximum temperature of 1565 K (point (b)), at which point the heating laser power was removed and the sample underwent a free radiative cooling. At point (c) the liquid sample reached its minimum temperature of 1368 K, corresponding to a supercooling of $\Delta T = 79$ K, at which point the sample underwent recalescence and solidification into the metastable solid phase. As the sample continued to cool while in the metastable solid phase, there appear to be three inflection points in the volume thermal expansion data that separate regions that would otherwise be characterized by linear thermal expansion behavior. The inflections occur at points (d), (e), and (f). As the sample temperature approached of 650 K, the high power laser was reapplied to prevent the sample temperature from falling below the sensitive range of the infrared pyrometers. After a two minute pause near 650 K, the sample temperature
was increased at a constant ramp rate of 3 K/s. As the sample heated through point (f) there was once again an inflection in the thermal expansion behavior, and between points (f) and (e) there appears to be a deviation in the absolute volume of the sample during heating compared to that during cooling. At point (e) the sample experienced a large deviation in its volume compared to that which occurred during cooling, indicating the beginning of the MtS transformation that takes place during reheating of the metastable sample. From this point forward, the sample was in the stable phase of Fe$_2$B plus Fe. At point (g) there was a reduction in the sample volume that corresponds to the bcc-to-fcc transition of Fe. The sample continued to heat until it returned to point (a) (1420 K), where it was held for two minutes. After the hold, the sample temperature was ramped from 1420 K back down to 660 K at 3 K/s, held for two minutes, and then ramped back up to 1420 K at 3 K/s. During cooling, the fcc-to-bcc transition of Fe occurred at point (h), and during heating the bcc-to-fcc transition occurred at point (i). After returning the sample to 1420 K, the full round of measurements was repeated an addition two times. The results (not shown) are nearly identical to those shown in Fig. 6.12, indicating that the results are systematic and not representative of random conditions in the sample or measurement system.

We will begin the discussion by commenting on the solidification behavior of the alloy. It is clear in Fig. 6.12 that the volumes (and therefore densities) of the liquid and the metastable solid phase have a greater degree of similarity than the liquid and the stable solid phase. When the sample reaches point (c) and undergoes solidification into the metastable solid phase, its volume contracts by 1.9%. However, if the sample had undergone solidification into the stable solid phase, its volume would have contracted by 3.1%. This indicates that the average atomic packing density of the liquid and the metastable solid phase have a greater degree of similarity than the liquid and the stable solid phase, which may be a more general indicator of the relative similarity between the types of the atomic ordering found in these phases. Combined with the discussions regarding the nature of the chemical short-range ordering in Sec. 6.2, these observations may explain, in part, why the metastable Fe$_{23}$B$_6$ phase is commonly found as the primary solidification product for this alloy.

Focusing our attention on the metastable solid, we note the multiple inflection points in the
data that occur during cooling. From the x-ray diffraction measurements discussed earlier, we know that the metastable phase solidifies into a mixture of Fe$_{23}$B$_6$ plus fcc-Fe. The inflection in the thermal expansion data at point (d) may correspond to the point at which fcc-Fe transforms into bcc-Fe. However, the inflection point (d) occurs at a temperature of approximately 1210–1250 K, whereas the bcc-Fe is not observed in the x-ray data until the sample reaches 1165 K. One possible explanation for the discrepancy is that the onset temperature for the fcc/bcc Fe transformation is difficult to determine via the x-ray data due to the low volume fraction of the phase, the poor powder averaging of the sample, and the rotation of the levitated sample. The combination of the poor powder averaging and sample rotation result in a large degree of fluctuation in the diffracted peak heights, and it is difficult to differentiate between noise in the data and the appearance of a diffraction peak associated with the early stages of a transformation. For these reasons, the onset temperature for the fcc/bcc Fe transformation
may be higher than that indicated by the x-ray data. Another factor that may contribute to the discrepancy is that the volume thermal expansion measurements and the x-ray diffraction measurements were performed on different samples with different masses (50 mg for the volume expansion measurements and 67 mg for the x-ray diffraction measurements), leading to differences in the extrinsic behavior of the samples.

As the metastable solid continues to cool, we see two additional inflections at points (e) and (f), which occur at temperatures of approximately 980 K and 850 K, respectively. While point (f) lies outside the range of available x-ray diffraction data (down to 900 K), point (e) lies within that range and it is therefore surprising that no differences have been noticed to take place between 900–1000 K in the x-ray data. However, the lack of an obvious signature in the x-ray data may be caused by the similar issues previously stated with respect to point (d). It may also be that a reexamination of the x-ray data is in order to see if something has been missed. Although we have not found a correlation between the volume thermal expansion data and the structural measurements from the x-ray data, as will be shown in the following section the inflections at points (e) and (f) do appear to be correlated with transitions observed in the RF susceptibility data. This will be expanded upon below, and a possible explanation will be given for the observed behavior.

As the metastable solid is reheated at a rate of 3 K/s, it can be seen that there is a deviation between points (f) and (e) in the volume expansion data compared to what was observed during cooling. The underlying cause of this deviation is not clear, but one possibility is that the deviation is caused by a hysteretic effect, and that had the sample been able to reach higher temperatures without undergoing MtS transformation there would be a closed loop that forms within the cooling and heating data similar to that which is observed for the stable solid data. It may also be that the deviation is indicating that a non-reversible transformation has taken place within the metastable solid. Further structural measurements will be required to fully explain what is occurring in this region. As the sample is heated through point (e), it can be seen to undergo a MtS transformation, with the transformation spanning approximately 90 K and requiring approximately 30 s to complete. After transformation, the volume of the sample coincides well with what was measured for the stable solid under similar heating conditions.
At point (g) the Fe phase fractions undergoes the bcc-to-fcc transformation. The deviation in the allotropic transformation temperature between the green and black heating data is likely a result of the different thermal histories of the sample.

Finally, we note that for the stable solid, there is a clear hysteresis in the volume thermal expansion related to the first order allotropic transformation. On cooling, the transformation occurs at point (h) with a temperature of 1147 K. On heating, the transformation occurs at point (i) with a temperature of 1224 K. Because there is some amount of bending in the temperature data for the transformations (possibly caused by changes in the sample emissivity), these temperatures are determined at the midpoint of the transformations as indicated by the volume data. On both heating and cooling the sample temperature was changing at a rate of 3 K/s, and if the heating and cooling transformation temperatures are averaged we find a value of 1186 K for the equilibrium transformation temperature, which agrees well with the value of 1185 K as indicated on the equilibrium stable phase diagram in Fig. 6.1.

In addition to the measurements taken during heating and cooling cycles, the effect of the heating rate on the MtS transformation was also tested. Fig. 6.13 shows the volume thermal expansion of a sample while being heated at a rate of 3 K/s (black line) vs. a rate of 18 K/s. As can be seen, increasing the heating rate by a factor of 6 has increased the MtS transformation temperature by approximately 80 K, as well as increasing the Fe allotropic temperature by approximately 40 K.

6.5.2 RF Susceptibility and Ferromagnetic Transitions

RF susceptibility measurements have been carried out using the TDO technique as described in Ch. 4. The primary goal of these measurements was to determine how well this technique can distinguish between ferromagnetic transitions that are taking place in compounds with two or more ferromagnetic crystalline phases. In the stable compound, both Fe$_2$B and bcc-Fe are ferromagnetic with Curie temperatures of 1015 K and 1043 K, respectively. In addition to bcc-Fe, the metastable solid phase contains Fe$_{23}$B$_6$, which has a Curie temperature 698 K, and if there are any additional transformations occurring which result in the formation of either bct- or o-Fe$_3$B, it would be apparent based on their Curie temperatures of 786 and
897 K, respectively. While the initial goal of the TDO experiments was simply to observe the ferromagnetic transitions, the data has been found to contain additional information that may help develop new insights into the nature of the metastable solid phase of Fe$_{83}$B$_{17}$.

We recall from Ch. 4 that, for a ferromagnetic metal, the relationship between the shift in the TDO frequency and a change in the material properties can be shown to be:

\[ \Delta f \propto \sqrt{\rho_e (1 + \chi)} \]  \hspace{1cm} (6.1)

where \( \Delta f \) is the frequency shift, \( \rho_e \) is the electrical resistivity, and \( \chi \) is the magnetic susceptibility. For the sake of simply observing phase transitions, whether electrical or magnetic in nature, it is not necessary to know the constant of proportionality between the material’s properties and the frequency shift, as the transitions can be revealed by analyzing the frequency data directly. Transitions from a paramagnetic state to a ferromagnetic state are indicated by a sudden increase in the TDO frequency, and vice versa. Similarly, a transformation that results in an increase in the electrical resistivity will also be indicated by an increase in the TDO frequency. However, for conducting samples it is expected that changes in the resistivity will
result in much smaller frequency shifts than those produced by a paramagnetic-ferromagnetic transformation (10s vs 1000s of Hz, respectively). As was discussed in Ch. 4, it is also important to characterize the temperature of the TDO coil to prevent unwanted frequency drifting. Because the focus of these experiments was simply to observe ferromagnetic transitions, the coil temperature was allowed to drift near room temperature and only the first order temperature correction was applied, neglecting the temperature gradient correction as was done when performing measurements on low-carbon steel (Sec. 4.5.2).

Fig. 6.14 shows a series of TDO measurements performed on an Fe$_{83}$B$_{17}$ sample, during heating and cooling in both the stable solid and metastable solid states. The measurements begin in the high temperature metastable solid phase at a temperature of 1394 K just after solidification has completed, and data is acquired while the sample undergoes a free radiative cooling (red line). As the sample cools, the TDO frequency increases by 110 Hz at 1044 K, indicating the Curie transition for the bcc-Fe phase fraction of the metastable solid; this is emphasized in inset-b. As the sample continues to cool, there is an inflection in the data at approximately 965 K during which the frequency shifts by approximately 20–40 Hz, indicating that this may be associated with a change in the electrical resistivity of the sample. As the sample continues to cool further, it appears to undergo two additional ferromagnetic transitions at approximately 850 K and 795 K, with associated frequency shifts of 1260 Hz and 370 Hz. After the sample reaches a minimum temperature of 660 K it is held for two minutes, after which it undergoes a controlled ramp of 0.25 K/s (green line). On heating, the low temperature ferromagnetic transitions are once again observed, reproducing both the transition temperatures and frequency shifts that were observed on cooling. As the sample temperature increases above 900 K, the heating data begins to deviate from the cooling data, likely indicating the beginning of the MtS transformation. The transformation appears to be complete when the sample reaches a temperature of 970 K, as indicated by an inflection in the frequency data. The inflection in the heating data occurs at nearly the same temperature that occurs in the cooling data; it is unclear whether this is coincidental or if the two inflections are correlated. After MtS transformation, the sample continues to heat as the stable solid phase mixture of Fe$_2$B plus bcc-Fe. At 1014 K the frequency data peaks and then shifts by 130 Hz, indicating
the ferromagnetic transition of Fe\textsubscript{2}B. At 1043 K the frequency shifts again, this time by 900 Hz and corresponding to the ferromagnetic transition of bcc-Fe. After heating to 1120 K and holding for two minutes, the sample temperature is ramped down to 935 K at 0.25 K/s, held for two minutes, and then ramped back up to 1120 K at 0.25 K/s. During this cooling/heating cycle the sample once again undergoes two clearly distinguishable ferromagnetic transitions at 1043 K and 1016 K, with frequency shifts of approximately 1300 Hz and 90–150 Hz, corresponding the the ferromagnetic transitions of bcc-Fe and Fe\textsubscript{2}B, respectively.

Based on the results in Fig. 6.14, the primary goal of performing TDO measurements on Fe\textsubscript{83}B\textsubscript{17} has clearly been met. In the stable solid phase, the ferromagnetic transitions of Fe\textsubscript{2}B and bcc-Fe are clearly distinguishable and, based on the nearly overlapping cooling (blue line)
and heating (black line) data, the measurements are reproducible. A noteworthy feature of the measurements on the stable sample is the different way in which the Fe$_2$B and bcc-Fe ferromagnetic transitions manifest themselves in the frequency data. The transition for bcc-Fe is characterized by a sizable step-change in the frequency, whereas the transition for Fe$_2$B is characterized by a comparatively smaller peak in the frequency with the magnitude remaining approximately the same on either side of the transition. These different manifestations have previously been attributed to differences in the nature of the magnetic phases, with step-changes characteristic of itinerant ferromagnets and peaks characteristic of local moment magnets [144]. However, local-moment ferromagnetism is usually associated with rare earth elements, so this explanation does not seem to apply to the present case of Fe$_2$B. Providing a proper explanation for the peak associated with the Fe$_2$B transition will be the topic of future work.

Turning our attention to the metastable solid phase, we note that there are three as-yet unidentified transition temperatures indicated in the frequency data: an inflection near 965 K and two step-shifts near 850 K and 795 K. Additional TDO measurements (not shown) have been performed down to 580 K, and there appear to be no further transitions taking place between 580–795 K. Two of these transitions appear to coincide with inflections that were observed in the volume thermal expansion data near approximately 980 K and 850 K. The combination of inflection points in both the volume thermal expansion and RF susceptibility data indicate that their may be an additional structural transformation occurring in the temperature range of 965–980 K. While an additional, unidentified phase was found to occur in the x-ray data, it appeared along with bcc-Fe around 1165 K, and no further transformations have been noted in the available x-ray data which goes down to 900 K. However, subtle structural transitions cannot be strictly ruled out because of the previously noted fluctuations in the peak intensities coupled with the tendency for peaks to overlap, particularly with the rather complicated diffraction pattern of the Fe$_{23}$B$_6$ structure. One possibility is that their may be a transformation of the Fe$_{23}$B$_6$ phase into a mixture of Fe$_{23}$B$_6$ plus bct- or o-Fe$_3$B, which would also be accompanied by the production of addition bcc-Fe. This hypothesis is based on the fact that their appear to be two reversible ferromagnetic transitions occurring at 795 K and 850 K. Of the three metastable Fe-B phases, the one whose Curie temperature most closely matches
one of these temperatures is bct-Fe$_3$B, with a Curie temperature of 786 K, while the Curie temperatures of Fe$_{23}$B$_6$ and α-Fe$_3$B (698, and 897 K, respectively) match less well. It may be possible that the Curie temperatures of these phases have some variability depending on the exact composition of the sample in which they are found. For instance, in Ref [22] Fe$_{23}$B$_6$ was observed during the crystallization of glassy Nd$_4$Fe$_{77}$B$_{19}$; the resulting Fe$_{23}$B$_6$ structure was single phase, indicating that the Nd atoms had become fully dissolved. The addition of Nd atoms into the Fe$_{23}$B$_6$ structure may result in a significant reduction in the Curie temperature compared to stoichiometrically pure Fe$_{23}$B$_6$. Similar arguments could be made regarding each of the Fe$_3$B phases, with variability in the Curie temperature occurring as a function of the precise stoichiometry of the phases. However, explanations which invoke the formation of additional Fe$_3$B phases appear to be at odds with the results of the previously discussed CNL diffraction measurements which have found Fe$_{23}$B$_6$ and bcc-Fe, but neither Fe$_3$B phase, at temperatures down to 800 K. Here again, the discrepancy may be caused by difficulties associated with properly resolving all of the diffraction peaks, or with the fact that the results come from different samples processed under different conditions.

Determining the precise nature of the transitions in the TDO data, as well as the inflections in the volume thermal expansion data, will be a topic of future work. Ideally, additional structural measurements should be performed using the WU-BESL system, using a detector mode that is optimized for performing measurements of crystal structure (the present experiments were optimized for measurements of liquid S(Q)), acquiring data while free cooling down to a temperature of 600 K or lower if possible, as well as acquiring data during reheating to capture the MtS transformation. In the event that the WU-BESL system is unavailable, important insights could still be made by preparing samples into the metastable solid phase using the ISU-ESL, and performing structural measurements during heating from room temperature through the MtS transformation using standard (non-levitation) powder diffraction methods. In addition to the structural measurements, further insight could be made by performing non-RF measurements of the magnetic susceptibility and electrical resistivity. Magnetic susceptibility measurements could be made using either a Faraday balance or a vibrating sample magnetometer, and electrical resistivity measurements could be made using the standard four-probe
method provided that a suitable means of attaching wires to a spherical sample can be found. Performing magnetic and electrical measurements in this way will allow the individual contribution of these properties to be more accurately determined than is possible using only the TDO technique.

6.6 Supercooling Studies on Fe$_{79.5}$B$_{20.5}$

It has now been well demonstrated that solidification of Fe$_{83}$B$_{17}$ from the deeply supercooled liquid can lead to the formation of the metastable Fe$_{23}$B$_6$ crystal structure. The samples are multiphase, containing Fe$_{23}$B$_6$ plus fcc-Fe at high temperatures, with an additional (unidentified) phase forming as the sample cools through the fcc/bcc Fe transition. Based on these results, an interesting question to ask is: is it possible to create a sample of single phase, stoichiometrically pure Fe$_{23}$B$_6$? To attempt to answer this question, a sample was studied for which the alloy composition was nearly the same as the Fe$_{23}$B$_6$ line compound composition, i.e. approximately Fe$_{79.3}$B$_{20.7}$.

Unlike previous investigations using the ISU-ESL to study Fe-alloys, the sample for this study was not prepared from an arc melted ingot with the desired composition. Rather, the sample for this study began as one of the previously prepared Fe$_{83}$B$_{17}$ alloys, and the Fe-content was reduced by processing the sample at very high temperatures under high vacuum conditions using the ESL. Accounting for the chemical activities of the elements in solution, the effective vapor pressure of Fe is approximately $10^7$ times greater than the effective vapor pressure of B, and therefore it can be safely assumed that any mass lost during high temperature processing can be associated with a reduction of the Fe-content of the sample. To minimize the amount of gross deposition that occurred during the processing, a sample with a relatively low starting mass of 24.5 mg was chosen, corresponding to an approximate sample diameter of 1.85 mm. During the high temperature processing, the sample was heated to temperatures of 1775 ± 25 K for a total duration of 430 s. The high temperature processing was not performed in a single step, but in multiple steps with durations between 30–130 s so that systematic changes in the liquidus temperature and supercooling levels could be monitored. After processing the sample for several minutes near 1775 K, 19 additional melting/solidification cycles were performed.
Figure 6.15  A 19.7 mg sample of Fe$_{79.5}$B$_{20.5}$ being processed in the ESL, showing recalescence into the stable solid phase. The dashed blue line indicates the eutectic temperature of 1447 K and the dotted red line indicates the liquids temperature of 1545 K.

for which the sample overheating was limited to a maximum temperature of approximately 1625 K for only brief periods of time to minimize any further mass loss; during this time, the sample temperature was in the range of 1550–1625 K for a total of 136 s. At the end of the experiment, the final mass of the sample was 19.7 mg. Assuming that the initial composition of the sample was exactly Fe$_{83}$B$_{17}$, and that the mass loss was entirely due to the loss of Fe, then the final composition of the sample was Fe$_{79.5}$B$_{20.5}$, which is very close to the line compound composition for Fe$_{23}$B$_6$. An example temperature profile of the Fe$_{79.5}$B$_{20.5}$ sample is shown in Fig. 6.15.

One of the benefits of preparing the Fe$_{79.5}$B$_{20.5}$ sample using high temperature processing to shift the Fe content is that, under these conditions, it becomes possible for the reduction of stable oxides such as Al$_2$O$_3$ to take place. In fact, surface oxides that were visibly present at the beginning of the experiment were found to be visibly removed by the end of the high temperature processing. As a result, the sample had a relatively high level of purity and displayed excellent supercooling. The average and maximum degrees of supercooling were 251 ± 25 K and 273 K, respectively, as measured from the liquidus temperature of 1545 K.
Even if the supercooling is measured from the eutectic temperature of 1447 K, the maximum supercooling of 178 K is still the deepest supercooling achieved for any of the Fe-B alloys studied in the ISU-ESL. The success of this sample processing has led to the idea of producing Fe$_{83}$B$_{17}$ alloys by starting with samples on the Fe-rich side of the eutectic and performing similar high temperature processing to bring the composition back to the eutectic. It may also be possible to apply this method to other eutectic systems.

With regard to the formation of the Fe$_{23}$B$_6$ metastable solid, this experiment seems to have prompted more questions than it set out to answer. Despite the excellent supercooling behavior of the sample, during the final 19 melting/solidification cycles the sample was never found to undergo solidification into the Fe$_{23}$B$_6$ phase. As to why this is the case, there are at least three possibilities. First, it may be that the insoluble impurity phase was acting as a seed crystal for the metastable solid, and without the seed crystal solidification into the metastable phase is no longer preferred. Another possibility is that the Fe$_{23}$B$_6$ phase is stabilized by dissolved oxygen and, due to the formation and volatilization of boron-oxide gas phases during the high temperature processing, the oxygen content of the sample became depleted to the point where the Fe$_{23}$B$_6$ phase could no longer be stabilized. Finally, it may also be that the additional Fe content of the Fe$_{83}$B$_{17}$ alloys, which resulted in the solidification of a two-phase mixture of Fe$_{23}$B$_6$ plus fcc-Fe, actually served to improve the stability of the phase. Here again, additional work will be required to determine the precise reason for the lack of formation of the Fe$_{23}$B$_6$ phase from the deeply supercooled Fe$_{79.5}$B$_{20.5}$ liquid.

6.7 Conclusions

A wide series of measurements have been performed on the Fe$_{83}$B$_{17}$ near eutectic alloy. Beginning with early supercooling investigations, it was found that the alloy exhibits a variety of metastable phase formation behavior from the supercooled liquid, including the formation of a metastable precipitate phase that exists in stable coexistence with the deeply supercooled liquid, as well as bulk solidification into two distinct metastable phases. Using high energy x-ray diffraction, two of these phase have been identified: the precipitate phase is bcc-Fe, and the metastable phase characterized by a solidification plateau of 1394 K is a two phase mixture of
Fe$_{23}$B$_6$ plus fcc-Fe; the second bulk metastable phase has yet to be identified. Upon cooling, the fcc/bcc Fe transition was observed to occur at approximately 1165 K. Compared to the fcc/bcc Fe transition in the stable phase mixture, which occurred rather sharply at a single temperature, the fcc/bcc Fe transition in the metastable phase mixture appeared to take place over a broad range of temperatures. At approximately the same temperature as the fcc/bcc Fe transition, additional diffraction peaks associated with a new phase were observed to appear, although this new phase has yet to be positively identified. In addition to the structural measurements, measurements of volume thermal expansion and RF susceptibility have been carried out. These measurements have proven to be sensitive indicators of structural and magnetic transitions that may be occurring within the metastable solid. Based on inflection points in the volume thermal expansion and RF susceptibility data, as well as the identification of two ferromagnetic transitions occurring at approximately 795 and 850 K, it has been hypothesized that the Fe$_{23}$B$_6$ structure may be undergoing a partial transformation into either bct- or o-Fe$_3$B. To elucidate the nature of the low temperature metastable solid phases, a series of measurements have been proposed including measurements of atomic structure optimized for crystal structure determination, dc magnetic susceptibility, and dc electrical resistivity.
CHAPTER 7. CONCLUDING REMARKS

An electrostatic levitation (ESL) laboratory for performing non-contact measurements on materials in the high temperature liquid and solid phases has been successfully developed at Iowa State University (ISU). During the development of the ISU-ESL, a number of upgrades have been made to improve the levitation and processing stability of samples, including: an improved design for the electrode geometry, which results in a natural lateral restoring force that has greatly reduced the number of failed sample launches and has generally improved sample positional stability; replacing the HeNe positioning lasers with high power quasi-monochromatic LEDs, which has reduced unwanted drifting of the sample position; improved sample charging via vacuum-UV (21 eV) illumination; and two-beam laser heating, which results in improved temperature uniformity as well as reducing photon-pressure induced recoil in the sample position during free cooling experiments. Measurement capabilities for several thermophysical properties have been implemented, including: volume/density, ratio of specific heat to total hemispherical emissivity, surface tension and viscosity, electrical resistivity, and magnetic susceptibility. The measurements of electrical resistivity and magnetic susceptibility have been developed at ISU, and they make use of an inductively coupled tunnel diode oscillator (TDO) to transform measurements of resistivity and susceptibility into measurements of frequency. The validity of the TDO technique has been demonstrated by performing measurements of the electrical resistivity of high purity Zr as well as by observing the paramagnetic-ferromagnetic transition in a sample of low-carbon steel.

The sample processing and measurement capabilities of the ISU-ESL have been used to characterize metastable phase formation in an Fe\textsubscript{83}B\textsubscript{17} near eutectic alloy. Based on observations of latent heat release during free cooling experiments, three distinct metastable phases have been found to form from the deeply supercooled liquid. To characterize the structure of
the metastable phases, the Washington University Beamline ESL (WU-BESL) has been used to perform in-situ high energy x-ray diffraction measurements. From the x-ray analysis, two of the metastable phases have been identified: bcc-Fe has been identified as a metastable precipitate phase that exhibits stable coexistence with the supercooled liquid, and a two-phase mixture of Fe$_{23}$B$_6$ plus fcc-Fe has been identified as a bulk metastable solidification product. The third bulk solidification product, which forms much less frequently than the Fe$_{23}$B$_6$ phase, remains unidentified, although it is suspected that this phase involves either the bct- or α-Fe$_3$B phases. It has also been found that as the Fe$_{23}$B$_6$ plus fcc-Fe mixed phase cools through the fcc-to-bcc Fe transition, two additional peaks appear in the x-ray diffractogram. Due to the complicated nature of the diffractogram of the Fe$_{23}$B$_6$ phase mixture, which is characterized by poor powder averaging and several broad, overlapping peaks, it has not yet been possible to positively identify the phase associated with the additional peaks; it is suspected that the additional phase may be α-Fe$_3$B, although this has yet to be definitively proven. To develop further insights into the nature of the Fe$_{23}$B$_6$ metastable phase mixture, as well as its transformation into the stable solid phase, measurements of the volume thermal expansion and RF susceptibility via the TDO method were carried out. Each of these measurements have proven to be sensitive indicators of change occurring with the sample, as seen by subtle inflexion points in both the thermal expansion and the susceptibility data, as well as the detection of multiple (2–3) ferromagnetic transitions in both the stable and metastable polyphase alloys. Based on the results of the thermal expansion and susceptibility data, in particular the detection of three seemingly distinct ferromagnetic phase transitions in the metastable phase mixture, it has been hypothesized that the metastable sample may have undergone a transformation that resulted in the coexistence of Fe$_{23}$B$_6$ and one of the Fe$_3$B phases, which would indicate (to a limited degree) a confirmation of the identity of the unidentified peaks in the x-ray diffractogram. However, such a statement cannot be made for certain without high quality, unambiguous structural data, and therefore it has been suggested that additional structural measurements be carried out. The in-situ measurement capabilities of the WU-BESL would be preferred, but standard power diffraction measurements starting at room temperature with a metastable sample should also provide valuable insight. To verify the existence of multiple low temperature ferromag-
netic phases, corroborating measurements of the magnetic susceptibility should be carried out with non-RF methods such as a Faraday balance or a vibrating sample magnetometer, and to fully understand the signals in the TDO frequency data, dc resistance measurements should be carried out using a four probe method. For the dc susceptibility and resistivity measurements, experiments will have to be carried out starting from room temperature with a sample that has previously been shown to solidify into the metastable phase.

Going forward with the ISU-ESL, there a number of key areas that should be focused on in terms of measurement capability, including: validation of surface tension and viscosity measurements, improved measurements of the electrical resistivity and magnetic susceptibility via the TDO technique, and improved temperature and spectral emissivity measurements using the multiwavelength spectrometer. Additionally, developing a means to reliably purify samples will be important to ensure that optimal sample processing conditions can be achieved.

Regarding the surface tension and viscosity measurements, while the capability for inducing sample oscillations and measuring the oscillation frequency and decay rate have recently been demonstrated, a complete analysis of the results has not yet been carried out to determine the values of surface tension and viscosity of samples. Before attempting to perform these measurements on any given sample, benchmarking tests should be performed on 1–2 well characterized samples to validate the measurement system. Samples of pure Zr and pure Si are suggested, because in addition to being well characterized, surface tension and viscosity measurements for these materials via ESL have been previously demonstrated [89, 230], and the tendency for these samples to be free of surface impurities will help to prevent issues with contaminant induced damping of the oscillations.

Regarding the electrical resistivity and magnetic susceptibility measurements, the system in its present state has already proven useful for performing relative measurements of the electrical resistivity as well as for identifying ferromagnetic transitions. With the upgrades outlined in Sec. 4.6, it should be possible to improve both the temperature characterization of the coil as well as to increase the data acquisition rate. In the present implementation, the temperature characterization is performed using a platinum RTD, which not only has a large time constant for performing temperature measurements but, due to its length and orientation,
also produces an offset between the measured temperature and the actual temperature of the coil. By converting from the use of an RTD to direct measurements of coil resistance, the issues related to slow time constants and gradients in the temperature characterization will be minimized. This will allow TDO measurements to be performed with much greater heating and cooling rates for the samples, such as those experienced during free cooling, and should also lead to a significant increase in the upper limit for sample temperatures. As with the earlier benchmarking of the TDO technique, the best material for testing the upgraded system will likely be pure Zr, owing to its well characterized electrical resistivity, low vapor pressure, and tendency to be free of insoluble oxides. Benchmarking with Zr will also provide a good test of the ability to perform measurements on samples at high temperatures (2128 K melting point), and with large cooling rates (> 200 K/s) during free cooling.

Regarding the improved temperature and spectral emissivity measurements, there has already been some progress using the multiwavelength spectrometer to perform improved single color temperature measurements as well as spectral emissivity measurements on pure Zr (Appendix A). The sensitive spectral range of 1050–1650 nm, combined with the spectral resolution of approximately 2.5 nm, allows for a wide range of single color and two color ratio temperatures to be calculated, which may lead to an improvement in the sample temperature determination. The combination of improved accuracy for temperature measurements, combined with spectral emissivity measurements, may also lead to an improved understanding of the total hemispherical emissivity and therefore an improvement in specific heat measurements (because free cooling measurements can be used to measure the ratio of specific heat to total hemispherical emissivity). Furthermore, because the emissivity is related to the electrical resistivity, the ability to perform spectral emissivity measurements can be used to compliment TDO measurements.

Finally, provided that sample purification methods can be developed, two materials systems that should be investigated are Co$_{80}$Pd$_{20}$ and Pd$_{81}$Si$_{19}$. Previous attempts have been made at studying these materials in the ISU-ESL, but Al$_2$O$_3$ contamination of the samples limited the useful results that could be obtained. For Co$_{80}$Pd$_{20}$, it is been previously shown [33] via electromagnetic levitation that it is possible to supercool a liquid sample to temperatures within approximately 10 K of the liquid Curie temperature. However, in nearly all cases it has
been found that the sample recalesces before it can cool through the liquid Curie temperature and transform in a supercooled liquid ferromagnet. These results have been interpreted as a magnetically induced reduction in the nucleation barrier, which ultimately prevents the liquid from cooling into the ferromagnetic state. However, it has recently been shown that liquid samples studied using the $\text{B}_2\text{O}_3$ melt fluxing method can be cooled to a temperature well into ferromagnetic liquid range [29]. This has reopened the question of whether or not deeply supercooled $\text{Co}_{80}\text{Pd}_{20}$ can be cooled into a ferromagnetic liquid state. The combination of the levitation stability available using the ISU-ESL, combined with the ability to measure ferromagnetic transitions using the TDO technique, make this laboratory well suited to address the nature of deeply supercooled $\text{Co}_{80}\text{Pd}_{20}$.

Using the $\text{B}_2\text{O}_3$ fluxing method, it has recently been shown that $\text{Pd}_{81}\text{Si}_{19}$ can be cooled into a bulk glassy alloy (6 mm diameter sphere) at cooling rates below 10 K/s [10]. This makes $\text{Pd}_{81}\text{Si}_{19}$ unique among binary glass formers, as it is the only known binary alloy for which glass formation may be achieved during ESL processing. During free radiative cooling in the ESL, typical cooling rates for samples near 1000 K are on the order of 10 K/s. Therefore, provided that a $\text{Pd}_{81}\text{Si}_{19}$ sample could be produced free of oxides, binary glass formation in the ESL may be possible. If so, this would allow for wide variety of thermophysical properties to be measured during the vitrification process, as well as during devitrification with a variety of heating rates. Furthermore, these measurements could be performed multiple times on a single sample to ensure that the results are systematic. Because $\text{Pd}_{81}\text{Si}_{19}$ is a binary alloy, the experimental results can be corroborated with simulation methods to gain additional insight into the atomic structure of the alloy. Such information may be used to develop an improved understanding of glass formation in metallic systems.
APPENDIX A. ADDITIONAL DETAILS REGARDING EMISSIVITY AND TEMPERATURE MEASUREMENT

A.1 Multiwavelength Pyrometer

During the development of the ISU-ESL, a multiwavelength pyrometer (FAR Associates model FMPI) was purchased with the intent of improving sample temperature measurement capability as well as to enable spectral emissivity measurements. The FMPI was billed as an autotuning pyrometer, capable of performing infrared temperature measurements without the need for user input, eliminating the uncertainties associated with unknown emissivity values that complicate single-color and two-color ratio pyrometry methods. The underlying principle of operation for the FMPI is the calculation of several two-color ratio temperatures, using multiple wavelengths within the 1050–1650 nm waveband, along with a proprietary algorithm that operates to ensure consistency among the various calculated ratio temperatures. The maximum uncertainty in the temperature measurements was stated to be 0.75% of the measured temperature. Combined with the calibration of the internal spectrometer to a NIST traceable blackbody source, the spectral emissivity can be determined from the measured intensities and the calculated temperatures.

Upon receiving the FMPI, benchmarking tests were performed on a variety of samples including pure Zr, Si, Cu, Ge, and low-carbon steel. By and large, the capability of the FMPI to perform accurate measurements of the melting and solid-state transitions in these materials was found to be below expectations. Of particular note among the various tests are those performed on samples of pure Zr and Si. Pure Zr is considered to be a secondary reference point for performing temperature measurements as defined by ITS-90, with a melting temperature of $1854 \pm 8 ^\circ C$ [231]. In addition to the melting temperature, pure Zr exhibits a well characterized
hexagonal closed packed (hcp) to body centered cubic (bcc) structural transformation. According to most binary phase diagrams [228] the hcp-bcc transformation occurs at 863 °C, and a broad analysis of measurements has placed the transformation temperature at 868±6 °C [232]; regardless of the exact temperature, the hcp-bcc transition has been found to be an isothermal transition. As with Zr, the melting point of pure Si has been considered a reference point by IPTS-68, with the melting temperature determined to be 1414 ± 2 °C [233]. During the benchmarking tests, high purity Zr samples were prepared from crystal bar zirconium produced by ATI Wah Chang, which is generally considered the highest purity zirconium commercially available. The high purity Si samples were optical grade Si ball lenses manufactured from 5N purity single crystal stock.

The results of benchmarking tests on pure Zr are shown in Fig. A.1. During these tests, a 60 mg, 2.6 mm diameter sphere of Zr was ramped at 1 °C/s through the hcp-bcc structural transformation as well as through the melting temperature. Results of the temperature measurements for the hcp-bcc transition are shown in Fig. A.1(Top). The single color pyrometer was calibrated such that the transition would appear at approximately 863°C, and the FMPI data are as determined by the instrument. The FMPI data indicate that the transition occurred over a broad range of temperatures from 875–905°C, with an average temperature of 890 ± 9°C. This behavior differs significantly not only with the expected transformation temperature of 868±6 °C, but also with the fact that the transition should occur isothermally. For comparison, the single color pyrometer data indicated that there was a reduction in the emissivity of the sample near 1600 nm, as evidenced by the reduction of the apparent temperature through the transition. While the exact value of the single color temperature is somewhat arbitrary, due to the user input value for the emissivity, that fact that the apparent temperature decreased throughout the transition is legitimate evidence of a reduction in the emissivity of the sample. The results of melting point measurements are shown in Fig. A.1(Bottom). The value of the emissivity used for the single color pyrometer was the same as that used during the measurements of the hcp-bcc transition. The melting temperature as determined by the single color pyrometer was approximately 1833 °C, and there was an apparent increase in the sample emissivity through the melting transition. The temperatures determined by the FMPI
pyrometer for the melting transition deviated significantly from what was expected, with the onset of melting appearing at $1812 \pm 16 \, ^\circ C$, followed by the apparent melting temperature reducing to $1797 \pm 16 \, ^\circ C$. Even after the sample had completely melted and increased to a temperature approximately $40 \, ^\circ C$ above the melting point (based on the increase in apparent temperature of the single color measurements), the maximum temperature read by the FMPI pyrometer was $1835 \, ^\circ C$, well below the expected melting temperature.

The results of benchmarking tests on pure Si are shown in Fig. A.2. Upon melting, Si transforms from a semiconducting solid into a liquid characterized by metallic conductivity, and there is an associated reduction in the sample emissivity upon melting. For the single color pyrometer data, the values of the emissivities used to reproduce the expected melting temperature of the sample on the solid and liquid sides of the melting transition were 0.43 and 0.13, respectively, and temperature data in between are not shown due to large fluctuations in the apparent temperature during melting. For the temperatures determined by the FMPI pyrometer, the melting of the sample was found to begin at an apparent temperature of $1320 \pm 12 \, ^\circ C$, and the temperature was found to increase steadily throughout the transition, to a maximum apparent temperature of $1382 \pm 12 \, ^\circ C$, followed by an increase in the temperature indicating the completion of melting. Each of these temperatures is significantly below the expected melting temperature of $1414 \pm 2 \, ^\circ C$.

As a result of the benchmarking tests on pure Zr and Si, it has been concluded that the FMPI pyrometer is not able to perform accurate, self-tuning measurements of sample temperatures, and therefore the temperature data produced by this instrument should not be considered trustworthy. However, despite these unsatisfactory results, the calibrated spectral intensity data that are measured using this instrument may still be used to improve the accuracy of temperature measurements as well as spectral emissivity measurements, using in-house analysis methods as shown in the next section.

### A.2 Case Study: Zirconium

Using the calibrated spectral intensity data, calculation of a number of single-color and two-color ratio temperatures can be carried out using the following equations which were derived...
Figure A.1 Comparison of temperatures measured using the FMPI pyrometer (blue line) and the single color pyrometer (red line) for two scenarios of pure Zr. (Top) While heating through the hcp-bcc solid state transition. The dotted line is the expected transition temperature of 863 °C. (Bottom) While melting and subsequently cooling. The dashed line is the expected melting temperature of 1884 °C.
in Ch. 3:

Single-color:

\[ T = \frac{hc}{\lambda k_B} \ln \left( \frac{2\pi hc^2}{W\lambda^5 \epsilon\lambda \delta\lambda} \right)^{-1} \]  \hspace{1cm} (A.1)

Two-color ratio:

\[ T = \frac{hc}{k_B} \frac{\lambda_1 - \lambda_2}{\lambda_1\lambda_2} \ln \left( \frac{w_1\lambda_1^5 \epsilon_2}{w_2\lambda_2^5 \epsilon_1} \right)^{-1} \]  \hspace{1cm} (A.2)

As an example, a variety of single-color temperatures have been calculated based on the spectral intensities acquired while heating pure Zr through its hcp-bcc structural transition. As shown in Fig. A.3, single-color temperatures have been calculated at nominal wavelengths of 1050, 1125, 1200, 1300, 1500, and 1600 nm. The bandwidths for these lines were ±5 nm, and the single color emissivity values were determined using standard single-color methods of tuning the emissivity until the characteristic temperature appeared at the desired temperature. During calculation of these temperatures, two trends were noticed. First, for most of the colors there was a change in the apparent temperature as the sampled progressed through the transition. At longer wavelengths the apparent temperature was reduced through the transition and at shorter wavelengths it increased through the transition. At the single color wavelength of 1125 nm there
Figure A.3  Single color temperatures calculated using Eq. A.1 for the intensities of the various spectral lines, measured using the calibrated spectrometer. The data were acquired simultaneously and are spaced 25 s apart for clarity. The dotted line is the expected transition temperature of 863 °C for the hcp-bcc transition in pure Zr. From left to right, the nominal single-color wavelengths are 1050, 1125, 1200, 1300, 1500, and 1600 nm.

Figure A.3  Single color temperatures calculated using Eq. A.1 for the intensities of the various spectral lines, measured using the calibrated spectrometer. The data were acquired simultaneously and are spaced 25 s apart for clarity. The dotted line is the expected transition temperature of 863 °C for the hcp-bcc transition in pure Zr. From left to right, the nominal single-color wavelengths are 1050, 1125, 1200, 1300, 1500, and 1600 nm.

appeared to be little to no change in the apparent temperature, just as would be expected for an isothermal transition. The second observation is that, to ensure the average apparent transition temperature was 863 °C, the emissivity values (from low to high wavelength) were chosen to be 0.35, 0.3375, 0.3275, 0.3175, 0.304, and 0.298, respectively, indicating a non-gray spectral emissivity.

Because the single-color temperature calculated for the 1125 nm line appeared to be the most reliable, it was used along with the calibrated spectral intensity data to calculate values of the spectral emissivity before and after the structural transition. The spectral emissivity was calculated by dividing the measured intensities by those that would be expected from a blackbody at the same temperature. The results of the emissivity calculation are shown in Fig. A.4. As is evident, not only do the spectral emissivities display non-gray behavior, but there is a marked change in the slope of the spectral emissivity before and after the transition. The
change in the spectral emissivity is consistent with the observed variations in the single color temperatures throughout the transition. For example, the apparent temperature as measured by the single color pyrometer at 1600 nm was found to be reduced throughout the transition, which is consistent with the reduction in the sample emissivity at 1600 nm as measured using the spectrometer data and the 1125 nm single-color data. Furthermore, the change in the slope of the spectral emissivity may explain some of the difficulties with the multi-wavelength pyrometer algorithm. Two-color ratio temperatures have been calculated using the measured intensity data at 1100 nm and 1600 nm with fixed emissivity ratios (not shown), and they have been found to reproduce the temperature vs. time behavior of the multi-wavelength pyrometer shown in Fig. A.1 for pure Zr. This would seem to indicate that while the algorithm was in fact calculating ratio temperatures, it was not adequately accounting for the changes taking place in the slope of the spectral emissivity as the sample was heated through the structural transition and melting point.

In summary, while the FMPI multi-wavelength pyrometer may not be capable of performing...
measurements of temperature with the advertised accuracy, the information available from the calibrated spectrometer is still useful for improving temperature measurements and performing spectral emissivity measurements using in-house data analysis methods. These methods have been applied to pure Zr, and have led to an improved understanding of the sample temperature and spectral emissivity in the region of the hcp-bcc structural transition. Such success can likely be obtained with other materials systems, provided that trustworthy data is available regarding characteristic transition temperatures.
APPENDIX B. ADDITIONAL INFORMATION REGARDING TDO MEASUREMENTS

B.1 Validity of $\Delta f$ Approximation

In Ch. 4 the following expression was derived to relate the TDO frequency shift to a sample’s electrical resistivity and magnetic susceptibility:

$$\frac{\Delta f}{f_0} = \frac{3}{4} \varphi \left(1 - \frac{3}{2a} \sqrt{\frac{\rho}{\pi f_0 \mu_0}} \sqrt{1 + \chi}\right) \quad (B.1)$$

where $f_0$ is the base frequency of the TDO, $\Delta f$ is the frequency shift, $\varphi$ is the sample filling factor, $a$ is the sample radius, $\rho$ is the electrical resistivity, $\chi$ is the dc magnetic susceptibility, and $\mu_0$ is the permeability of free space. This equation was derived using the following approximation for the real component of the complex susceptibility as determined in Ref. [138]:

$$\chi'_{\text{app}} = -\frac{3}{2} + \frac{9}{4\theta} (1 + \chi) \quad (B.2)$$

where $\theta = a/\delta$ and $\delta$ is the classical skin depth. To ensure the validity of Eq. B.1, the accuracy of the approximation for $\chi'$ as shown in Eq. B.2 has been determined.

The full analytic solution for the complex susceptibility of a magnetic conducting sphere in an ac magnetic field was shown to be [138]:

$$\chi' = -\frac{3}{2} \left(1 + \frac{PR + QS}{R^2 + S^2}\right) \quad (B.3)$$

$$\chi'' = \frac{3}{2} \left(\frac{PS - QR}{R^2 + S^2}\right) \quad (B.4)$$

where

$$P = 3(1 + \chi) \theta (\cos \theta \cosh \theta + \sin \theta \sinh \theta) - 3(1 + \chi) \sin \theta \cosh \theta \quad (B.5)$$
Figure B.1 Deviation in the approximation for the real component of the complex susceptibility.

\[ Q = 3 (1 + \chi) \theta (\cos \theta \cosh \theta - \sin \theta \sinh \theta) - 3 (1 + \chi) \cos \theta \sinh \theta \]  \hspace{1cm} (B.6)

\[ R = -\chi \theta (\cos \theta \cosh \theta + \sin \theta \sinh \theta) + \chi \sin \theta \cosh \theta - 2\theta^2 \cos \theta \sinh \theta \]  \hspace{1cm} (B.7)

\[ S = -\chi \theta (\cos \theta \cosh \theta - \sin \theta \sinh \theta) + \chi \cos \theta \sinh \theta + 2\theta^2 \sin \theta \cosh \theta \]  \hspace{1cm} (B.8)

Fig. B.1 shows a plot of the percent deviation in the approximation for the real component of the complex susceptibility. For values of \( \theta \geq 3.05 \) the deviation is less than 0.5\%, and so provided that condition is met, Eq. B.1 may be considered valid.

### B.2 Filling Factor Determination

The coupling of a sample to an inductor arises from the perturbation of the inductor’s magnetic field caused by the sample, and the filling factor is representative of the extent to which the magnetic energy content of the field has changed. In the case of an ideal solenoid, the filling factor is equal to the ratio of the sample and solenoid volumes, and is independent of the sample position. However, in cases where the magnetic field is nonuniform, the filling factor is less well defined and will also depend on the position of the sample. The coils used
in the ISU-ESL implementation of the TDO technique are essentially current loops, and the vertical component of the magnetic field along the axis of a loop is given by:

\[ B_z = \frac{\mu_0}{4\pi} \frac{2\pi R^2 I}{(z^2 + R^2)^{3/2}} \]  

(B.9)

where \( B_z \) is the vertical magnetic field component along the axis, \( R \) is the radius of the loop, \( I \) is the current, and \( z \) is distance along the axis from the loop. As a sample moves along the coil axis, the magnitude of the magnetic field occupied by the sample volume will change and, therefore, so will the filling factor. Because the filling factor is related to the energy stored in the field, it will be proportional to \( B_z^2 \), and therefore the position dependence of the filling factor will be given approximately by:

\[ \varphi \propto \frac{R^4}{(z^2 + R^2)^3} \]  

(B.10)

The position dependence of the filling factor as described by Eq. B.10 has been verified in the lab. A 9 mm diameter coil was wound around a plastic (high-density polyethylene) rod with a 2.5 mm hole bored along rod’s axis. A 2 mm Cu sample was fixed to the end of a wooden stick, and was translated through the plastic rod in 0.51 mm increments. The base frequency of the TDO was 9.5 MHz, and the frequency shift was recorded at each position. Results from this experiment are shown in Fig. B.2 along with a fit of the data to Eq. B.10. As can be seen, the filling factor of the sample is indeed characterized by Eq. B.10. In addition to the data, the sample filling factor was calculated based on Eq. B.1, the measured frequency shifts, and the room temperature resistivity of Cu. When the sample is near the center of the coil, the filling factor reaches its maximum value of \(4.7 \times 10^{-3}\). As the sample is translated away from the coil the filling factor is rapidly reduced, and at distances of 5 mm and 7.1 mm from the coil the value of the filling factor was reduced to \(4 \times 10^{-4}\) and \(1 \times 10^{-4}\), respectively. Therefore, to maximize the filling factor during ESL experiments, samples should be levitated as close to the coil as possible before levitation stability becomes compromised.

The easiest way to determine the filling factor of a sample is to measure the frequency shift caused by placing the sample near the coil and then removing it (the extraction method). In the ISU-ESL implementation, this will ideally be done by ejecting the sample from the
electrode gap shortly after performing the desired experiments, as opposed to before and after loading the sample. This will help to avoid deviations in the frequency that may be caused by mechanically disturbing the system during sample loading, differences caused by pumping from air or N\textsubscript{2} atmospheres down to high vacuum, as well as temperature drifting of the circuit between loading and launching of the sample. Unfortunately, due to the natural restoring forces of the electrodes, ejecting the sample has been found to be challenging to accomplish on a reliable basis. If the sample cannot be ejected, there is a second method of determining the filling factor of a levitated sample. Provided that the room temperature resistivity of the sample is known, then the filling factor can be determined by vertically translating the sample in the electrode gap and carefully measuring both the sample displacement and the shift in the TDO frequency. Then, the frequency and position data can be fit to Eq. B.10, and the extraction frequency and therefore the filling factor can be calculated through extrapolation of the fit.

Figure B.2 (Blue dots) TDO frequency shift and filling factor for a 2 mm diameter Cu sample being translated through a 9 mm diameter coil with TDO operating frequency of 9.5 MHz. (Black line) Results of fitting the data to Eq B.10 for the filling factor position dependence.
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[56] Based on a quote prepared for Iowa State University by Cambridge Isotope Laboratories, Inc. The quote was generated in April 2013.

[57] Based on prices for Alfa Aesar product numbers 13394, 14174, 13374, and 40419, which are slugs of 99.99+-% purity gold and 99.95+-% purity platinum. Prices obtained via the Alfa Aesar website during July 2014.


