Thermal expansion studies on the magnetic-crystallographic transformation of Gd5(Si\text{subscript} x)Ge\text{subscript} 1-x)4

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Thermal expansion studies on the magnetic-crystallographic transformation of Gd$_5$(Si$_x$Ge$_{1-x}$)$_4$

by

Mangui Han

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

MASTER OF SCIENCE

Major: Materials Science and Engineering

Program of Study Committee:
David C. Jiles, Major Professor
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Ames, Iowa
2002

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This is to certify that the master’s thesis of

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has met the thesis requirements of Iowa State University

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ABSTRACT

By employing thermal expansion measurement, the objectives of this thesis are to understand the unusual phase transition mechanism of Gd$_5$(Si$_x$Ge$_{1-x}$)$_4$, the effect of impurities in starting material Gd on the Curie point transition, etc. The main results are contained in two published papers.

In the first paper, measurements of thermal expansion of single crystal Gd$_5$(Si$_{1.95}$Ge$_{2.05}$) during cooling and heating were conducted for the first time. A very steep change in strain with temperature was observed when the material underwent a phase transformation. This was an unusual simultaneous magnetic and structural phase transformation from a ferromagnet with orthorhombic crystal structure below the transition temperature $T_c$ to a paramagnet with monoclinic crystal structure above $T_c$. This transition temperature $T_c$ was found to depend on magnetic field, and to exhibit hysteresis depending on whether the material was being cooled or heated. When the material was subjected to a magnetic induction B in the range 0 - 2.5 Tesla, the transition temperatures, on both cooling and heating, were found to increase linearly with temperature by about 4.9 K/Tesla. This rate of change of transition temperature with magnetic field was in good agreement with calculations based on the assumption that the additional energy due to the magnetic field can suppress the thermal vibration of Gd atoms and that the additional thermal energy per Gd
atom needed to cause the phase transition to occur is equal to the additional magnetic energy of each Gd atom caused by the magnetic field.

In the second paper, two polycrystalline Gd$_5$(Si$_{2.09}$Ge$_{1.91}$) samples were made by using high purity Gd and commercial Gd respectively but with Si and Ge starting materials of the same purity. Thermal expansion results showed that both samples exhibited a first order phase transformation. Magnetic force microscopy has been used to demonstrate the magnetic phase transformation process from paramagnetic to ferromagnetic upon cooling. It was found that the Curie temperature was lower and the thermally-induced strain higher in the sample made from lower purity Gd starting materials compared with the sample made from high purity Gd metal. These results indicate that the impurities (mainly C, O, N and F) in the Gd starting material can significantly alter the strain and Curie temperature of Gd$_5$(Si$_x$Ge$_{1-x}$)$_4$ alloys.
Driven by the increasing demand for clean and efficient use of energy, scientists all over the world are looking for some substitutions of oil, coal. For example, hydrogen energy, solar energy. Magnetic refrigeration which is based on the magnetic caloric effect (MCE) has been used for a long time to get ultra-low temperature in scientific research [1], but there seemed no hope for application at ambient temperature. In recent years, an increasing attention has been paid to find magnetic refrigerants that can be used at higher temperature (T>200K), especially near room temperature. It is well-known that heavy-rare-earth elements (such as Tb, Gd, Er, Dy, Ho etc.) and their compounds have high magnetic moments and therefore are considered as the best candidate materials for finding a large MCE. One of example is gadolinium ([Xe]6s^24f^75d^1). Gadolinium is unique for its high magnetic moment (~8.0µB per atom) and for its high Curie temperature (293K) lying just below room temperature. Above the Curie temperature, it is paramagnetic. Below the Curie temperature, it is ferromagnetic. Through the Curie temperature, it undergoes a so-called second order magnetic phase transition and results in a significant entropy change, which suggests its promising application in magnetic cooling. Among them, gadolinium has been demonstrated to achieve cooling between 270 K and 310 K [2]. Complex intermetallic compounds of 4f and 5f elements often exhibit intriguing electrical and magnetic behavior due to their highly localized magnetic electrons, which can be particularly striking during first order phase transitions. In 1967, the first literature about Gd₅ (SiₓGe₁₋ₓ)₄ intermetallic appeared [3]. Since 1996 scientists...
in Ames Laboratory have conducted a systematic research on rare earth containing intermetallic compounds which order magnetically between 250 and 310K for use in a magnetic refrigerator to cool below room temperature, and discovered the existence of a giant magnetocaloric effect in the Gd₅(SiₓGe₁₋ₓ)₄ alloys, where x ≈ 0.5, especially in Gd₅(Si₀.₅Ge₀.₅)₄, the reversible magnetic field induced magnetic entropy change are the largest ever observed experimentally in a magnetic refrigerant material by about a factor of 2 or more [4]. Later, a series of exciting findings were found on this material, such as giant magnetostriction (MS), giant magnetoresistance (MR) effects [5]. Although all magnetic materials exhibit MR, MCE, and MS effects to some extent, normally only one of these properties, in a given material is distinctly strong, and usually MS, MR and MC are not associated with each other. Several alloys in the Gd₅(SiₓGe₁₋ₓ)₄ system, however, exhibit simultaneously large values of all the three effects. Therefore, this complex material presents a unique assembly of materials where MS, MR and MC are expected to be extraordinarily pronounced. It is feasible that similar peculiarities of the electronic structure are responsible for these anomalous behaviors. Therefore, uncovering the underlying physics will be very helpful for looking for a better magnetic refrigerant material or magnetic response material in the future. In this thesis, an emphasis is given to thermal expansion which was conducted to understand the phase mechanism, magnetic-crystalline interaction, and the effect of impurities in Gd starting material on the phase transition.
CHAPTER 2. LITERATURE REVIEW

2.1 PRINCIPLES OF MAGNETIC REFRIGERATION

The MCE, which was originally discovered in 1881 [6], is the response of a magnetic substance to an applied magnetic field, which results in a change in its temperature. The MCE has been successfully utilized for about 70 years to achieve ultra low temperatures by employing a process known as adiabatic demagnetization. This is accomplished by cooling a magnetic solid in a large magnetic field \( H \) to as low a temperature as possible by ordinary means, then thermally isolating the solid from its immediate surrounding and finally turning off the magnetic field. The sample will reach its minimum temperature when \( H=0 \). Since the 1950's a few continuously operating MR systems working at various temperatures from \( \sim 1 \) to \( \sim 300 \)K have been constructed and tested, but most were inefficient and at best ran for a short time.

The principle of continuous MR using a ferromagnetic material is as follows. Initially the spins of the unpaired electrons are randomly aligned in the absence of a magnetic field. When a magnetic field is applied the spins align causing the entropy to decrease because of increasing magnetic order in the system and the sample to heat up. The MCE heat is removed from the magnetic material by a heat transfer fluid (gas or liquid) and is rejected. When the magnetic field is turned off the spins randomize, cooling the magnetic substance and heat is extracted from the system to be cooled using a heat transfer fluid completing the cycle [7].
Magnetic refrigeration is an environmentally friendly cooling technology. It does not use ozone-depleting chemicals (such as chlorofluorocarbons), hazardous chemicals (such as ammonia), or greenhouse gases (hydrochlorofluorocarbons and hydrofluorocarbons). Another important difference between vapour-cycle refrigerators and magnetic refrigerators is the amount of energy loss incurred during the refrigeration cycle. The cooling efficiency of magnetic refrigerators working with Gd has been shown to reach 60% of the theoretical Carnot limit, compared to only about 30% in the best gas-compression refrigerators. The use of magnetic refrigerators with such high energy efficiency will result in a reduced consumption of fossil fuels, in this way contributing to
a reduced CO₂ release into the atmosphere. However, with the currently available magnetic materials, this high efficiency is only realized in high magnetic fields of typically 5T. Therefore, a need exists for new magnetic materials displaying larger MCE, which then can be operated in lower fields of about 2T that can be generated by permanent magnets. The cooling and heating that occurs in the magnetic refrigeration technique is proportional to the size of the magnetic moments and to the applied magnetic field. This is why research in magnetic refrigeration is now almost exclusively conducted on superparamagnetic materials and on rare-earth compounds. Following the discovery of a sub-room-temperature giant MCE in the ternary compound Gd₅(SiₓGe₁₋ₓ)₄, there are incentives from both fundamental science and practical engineering points of view to study the MCE in Gd-based materials. The common feature of these compounds is that they undergo first-order structural and magnetic phase transitions, which lead to a giant magnetic-field-induced entropy change, across their ordering temperature [8]. Using material Gd₅(SiₓGe₁₋ₓ)₄, scientists at Ames Laboratory who developed the material and their coworkers in the Milwaukee-based Astronautics Corporation of America have successfully demonstrated the world's first room temperature, permanent-magnet, magnetic refrigerator [9]. Previous successful demonstration refrigerators used large superconducting magnets, but this is the first to use a permanent magnet and operate at room temperature based on the design developed by Lee and Jiles. This magnetic refrigerator employs a rotary design. It consists of a wheel that contains segments of gadolinium powder and a high-powered, rare earth permanent magnet. The wheel is arranged to pass through a gap in the magnet where the magnetic field is concentrated. As
it passes through this field, the gadolinium in the wheel exhibits a large magnetocaloric effect: it heats up. After the gadolinium enters the field, water is circulated to draw the heat out of the metal. As the material leaves the magnetic field, it cools further as a result of the magnetocaloric effect. A second stream of water is then cooled by the gadolinium. This water is then circulated through the refrigerator's cooling coils, as shown in Figure 2.

Figure 2 As gadolinium enters a magnetic field and becomes magnetized, the material's magnetic moments align, causing it to get hot. A fluid (red) carries that heat away. As the gadolinium exits the field, the atoms absorb heat from the recirculated fluid (blue) that chills a space.

This magnetic refrigerator can ultimately provide the cooling power required for specific markets, such as home refrigerators, air conditioning, electronics cooling, and fluid chilling. The permanent magnets and the gadolinium don't require a power supply to make them work, the only energy it takes is the electricity for the motors to spin the wheel and drive the water pumps.
2.2 MAGNETOSTRICTION

The existence of magnetostriction was first discovered many years ago by Joule [10]. The magnetization of a ferromagnetic material is in nearly all cases accompanied by changes in dimensions. The resulting strain is called magnetostriction. In other words, magnetostriction is a change in dimension of a magnetic material caused by a change in its magnetic state. It can be classified into two types from a phenomenological viewpoint: spontaneous magnetostriction arising from the ordering of magnetic moments into domains at the Curie temperature, and field induced magnetostriction, which is sometimes called technical magnetostriction or Joule magnetostriction. Spontaneous magnetostriction within domains arises from the creation of domains as the temperature of the ferromagnet passes through the Curie temperature. Field-induced magnetostriction arises when domains that have spontaneous magnetostriction are reoriented under the action of a magnetic field [11]. On the fundamental level, Magnetostriction is mainly due to spin-orbit coupling: when an external field tries to reorient the spin of an electron, the orbit of that electron also tends to be reoriented. The orbit is strongly coupled to the lattice and therefore causes a change in dimensions as it is reoriented. Because the orbit is strongly coupled to the lattice, it also resists the attempt to rotate the spin axis. This coupling is thus also responsible for magnetocrystalline anisotropy. It is relatively weak, because applied fields of a few hundred Oersteds usually suffice to rotate the spins away from the magnetic easy direction. The relation between magnetostriction and spin-orbit coupling can be crudely pictured in the figure 3, which is a row of atoms in a crystal. The black dots represent atomic nuclei. The arrows show the net magnetic moment per atom,
and the oval lines enclose the electrons belonging to, and distributed nonspherically about, each nucleus. The upper row of atoms depicts the paramagnetic state above $T_c$. If we assume that the spin-orbit coupling is very strong, then the effect of the spontaneous magnetization occurring below $T_c$ would be to rotate the spins and the electron clouds into some particular orientation determined by the crystal anisotropy, left to right, say. The nuclei would be forced further apart, and the spontaneous magnetostriction would be $\Delta L/L'$. If we then apply a strong field vertically, the spins and electron clouds would rotate through 90 degrees, and the domains of which these atoms are a part would magnetostrictively strain by an amount $\Delta L/L$. The rare earth metals are exceptions to the above statements. Many of them are only ferromagnetic at temperatures far below room temperature, and their orbital moments are not quenched, i.e., the spin-orbit coupling is strong. Moreover, the electron cloud about each nucleus is decidedly nonspherical. When an applied field rotates the spins, the orbits rotate too and considerable distortion results. Through this interaction, crystal energy can be reduced via the magnetostrictive deformation in the so-called magnetoelastic energy.

\[ \text{Figure 3 Mechanism of magnetostriction (After D. C. Jiles, [11])} \]
As we know, gadolinium has a particularly stable 4f shell, it is an S state ion is spherically symmetric, and is therefore unaffected by the crystal field. Furthermore, the coupling of the lattice and electronic degrees of freedom arising from spin-orbit interaction is expected to be negligible. However, we observed a colossal strain around the transition (between ferromagnetic state and paramagnetic state) for Gd$_2$Si$_2$Ge$_2$. Therefore, this discovery gives us a hint that there may be some other mechanism involved for this compound system. On the technological level, the bulk strain of a magnetic material can be changed by the application of a magnetic field which rearranges the domain structure, and the magnetostriction can then be utilized for energy conversion devices, such as sensors, actuators, controllers, switches, and transducers.

2.3 MAGNETORESISTANCE

Magnetoresistance is the relative change of the electrical resistance of a magnetic material caused by the action of a magnetic field. On the fundamental level, magnetoresistance results from field dependent changes of charge carrier scattering or electronic structure. On the technological level, the resistance of the material can be affected by the application of a magnetic field. The discovery of giant MR (GMR) in artificial magnetic multilayers [12] and colossal MR (CMR) in naturally layered manganites [13] due to a metal/insulator transition resulted in tremendous worldwide research effort on both classes of materials. This work showed the importance of a layered structure when layers of magnetically ordered atoms are separated by layers of
non-magnetic atoms [14]. Giant MR in particular has been utilized in micro-magnetic read heads for the magnetic disk drives in the data storage industry.

2.4 STRUCTURE OF \( \text{Gd}_5(\text{Si}_x\text{Ge}_{1-x})_4 \)

First reports about the phase relationships in the pseudobinary \( \text{Gd}_5\text{Si}_4-\text{Gd}_5\text{Ge}_4 \) system appeared in 1967 [27]. In that literature, it was suggested that the crystal structures of the binary silicide and germanide of gadolinium with the 5:4 stoichiometry, the partial pseudo-binary phase diagram, and the magnetic properties of \( \text{Gd}_5(\text{Si}_x\text{Ge}_{1-x})_4 \) alloys. In the same year, Holtzberg and his coworkers found the existence of the three extended single-phase solid solution regions in this pseudo-binary system [3], specifically, the \( \text{Gd}_5\text{Si}_4 \)-based (Si-rich) and the \( \text{Gd}_5\text{Ge}_4 \)-based (Ge-rich) solid solution, both with the Sm\(_5\)Ge-type crystal structure, and an unidentified intermediate intermetallic phase between the two. In spite of this discrepancy, in preliminary studies, the \( \text{Gd}_5(\text{Si}_x\text{Ge}_{1-x})_4 \) alloys were considered as just another common series of intermetallic alloys. For \( \text{R}_5(\text{Si}_x\text{Ge}_{1-x})_4 \) system, where \( \text{R} \) denotes a rare earth element, although some studies of \( \text{R}=\text{Nd} \) and \( \text{R}=\text{Dy} \) system show some similarities in phase sequence and structures compared to the system with \( \text{R}=\text{Gd} \), the available published relationship between crystal structure and phase about \( \text{R}_5(\text{Si}_x\text{Ge}_{1-x})_4 \), where \( \text{R} \) is limited to \( \text{R}=\text{Gd} \). In 1997, the phase diagram as function of both concentration and temperature in \( \text{Gd}_5(\text{Si}_x\text{Ge}_{1-x})_4 \) which was based on as-cast alloys was proposed by Pecharsky and Gschneidner [4]. For \( \text{Gd}_5(\text{Si}_x\text{Ge}_{1-x})_4 \), there are two extend substitutional solid solution based on both \( \text{Gd}_5\text{Si}_4 \) \((0.5 < x \leq 1)\) and \( \text{Gd}_5\text{Ge}_4 \) \((0 \leq x \leq 0.2)\), and one intermediate intermetallic phase \((0.24 \leq x \leq 0.5)\). It is reported the room
temperature structure of binary $R_5Sli(Ge)_4$ intermetallics is tetragonal $Zr_3Si_4$ or orthorhombic $Sm_5Ge_4$-type. In reference [5], it is reported that the $Gd_5Si_4$-based and $Gd_5Ge_4$-based orthorhombic phase are different. The Si-rich $Gd_5Si_4$-type solid solution has the so-called orthorhombic I crystal structure, while the Ge-rich $Sm_5Ge_4$-type solid solution belongs to the so-called orthorhombic II crystal structure. In spite of this difference, it is believed that both structures are fabricated from essentially equivalent infinite in two dimensional layers as shown in Figure 4. Gd atoms are located in the corners of cubes and rhombic prism.

![Figure 4 The basic building block (slab) of Gd$_5$Si$_4$ and Gd$_5$Ge$_4$ phases (After K. A. Gschneidner Jr., etc, [5])](image)

The remaining Gd atoms (blue) are located inside the cubes and are coordinated by octahedra formed by Si or Ge atoms, which are green and red in Figure 4. Inside the layer, Si and Ge are very close to one another to form partially covalent bonds. On the slab surface, Si(Ge) atoms (red) are connecting the adjacent layers by covalent so called inter-layer Si$_2$ bonds and form the Gd$_5$Si$_4$-type structures. In the silicide Gd$_5$Si$_4$, all layers are connected to one another by covalent inter-layer Si(Ge)-Si(Ge) bonds, while in the
germanide $\text{Gd}_5(\text{Ge}_4)$, all of the inter-layer $\text{Si(Ge)}$-$\text{Si(Ge)}$ bonds are broken as shown schematically in Figs. 5a and 5c, respectively. Within $0.5 < x < 1$, the crystal structure of $\text{Gd}_5\text{Si}_4$-based solid solution remains the same as the $\text{Gd}_5\text{Si}_4$ with all layers interconnected via the $\text{Si(Ge)}$-$\text{Si(Ge)}$ bonds (see Figure 5a). In the intermediate phase (with $0.24 < x < 0.5$), one half of inter-layers $\text{Si(Ge)}$-$\text{Si(Ge)}$ bonds break and the room temperature crystal structure of the alloys becomes monoclinically distorted and is composed of alternating strongly and weakly bonded layers (Figure 5b).

![Figure 5](image)

*Figure 5* Relationships between the room temperature crystal structure of $\text{Gd}_5(\text{Si}_x\text{Ge}_{1-x})_4$ alloys: (a) $0.5 < x \leq 1$, (b) $0.24 \leq x \leq 0.5$, and (c) $0 \leq x \leq 0.2$. The layers (tilted by $90^\circ$ with respect to Figure 1) are shown in light blue. The red circles represent exterior $\text{Si}$ and/or $\text{Ge}$ atoms (depending on the composition) connecting the layers. The thick red lines indicate the presence of covalently bonded pairs and strongly interacting layers. (After K. A. Gschneidner Jr., etc. [5])

Within the composition range $0 \leq x \leq 0.2$, at room temperature, the crystal structure of the $\text{Gd}_5\text{Ge}_4$-based solid solution restores the orthorhombic symmetry, where the layers remain essentially the same as in $\text{Gd}_5\text{Si}_4$, but all of the $\text{Si(Ge)}$-$\text{Si(Ge)}$ bonds are broken, see Figure 5c. As shown above, these intermetallic phases are formed by periodic
arrangement of well-defined building blocks— the layers of strongly interacting 4f, 3p and 4p elements. When the composition is altered, the interaction between the layers varies, it results the drastic change in bonding, crystal structures, and properties, while interaction inside the layer remain essentially the same. It follows that the properties of bulk $Gd_5(Si_xGe_{1-x})_4$ are critically dependent on the bonds connecting inter-layers.

Choe et al. [18] showed that the major difference between the three crystallographic modifications found in the $Gd_5(Si_xGe_{1-x})_4$ system is due to difference bonding arrangements between the well-defined sub-nanometer thick slabs in these distinctly layered intermetallic structures, as shown in figure 5. Therefore, following both the earlier [3, 27, 28] and more recent work [4, 18], we will refer to the three different structure types known to date in the $Gd_5(Si_xGe_{1-x})_4$ system as follows. The Sm$_5$Ge$_4$-type (Figure 9a), where none of the slabs are interconnected via covalent-like Ge–Ge bonds, is the same as the orthorhombic II crystal structure and it belongs to space group $Pnma$. The Gd$_5$Si$_2$Ge$_2$-type (Figure 9b) is the monoclinic phase, which belongs to space group $P112/a$, and here the covalent-like (Si,Ge)–(Si,Ge) bonds connect the slabs into pairs, but no (Si,Ge)–(Si,Ge) bonds are found between the pairs of the slabs. The Gd$_5$Si$_4$-type (Figure 9c) is the orthorhombic I crystal structure and it has the same symmetry as the Sm$_5$Ge$_4$-type structure, i.e. the space group is $Pnma$, but here all the slabs are interconnected via covalent-like Si–Si bonds. The variation in the interslab bonding in the two orthorhombic crystal structures is clearly manifested through the considerable changes in both the lattice parameters and specific interatomic distances [4, 18]. On the lattice scale, the
difference between the Gd$_5$Si$_4$-type and Sm$_5$Ge$_4$-type crystal structures is detected via the noticeably anisotropic change of the unit cell dimensions [4]: a-(Gd$_5$Ge$_4$) = 1.029 a-(Gd$_5$Si$_4$); b-(Gd$_5$Ge$_4$) = 1.006 b-(Gd$_5$Si$_4$) and c-(Gd$_5$Ge$_4$) = 1.005 c-(Gd$_5$Si$_4$). It is easy to see that during the Gd$_5$Si$_4$-type to Sm$_5$Ge$_4$-type phase change, the $a$ lattice parameter expansion exceeds that of the other two lattice parameters by nearly a factor of 5. On the atomic resolution scale, the distances between the Si(Ge) atoms which belong to different slabs increase from 2.5–2.6 Å (Gd$_5$Si$_4$) to 3.4–3.5 Å (Gd$_5$Si$_4$) [4, 18] indicating much stronger interactions between the slabs in the former when compared with the latter.

Figure 6 Magnetic and crystallographic phases in the Gd$_5$(Si$_x$Ge$_{1-x}$)$_4$ system in zero magnetic field. (After K. A. Gschneidner Jr., etc, [5])

\[ Transition \text{ temperature (K)} \]

\[ Gd_5Ge_4 \quad x (Si) \quad Gd_5Si_4 \]

\[ Curie \quad Electronic \]

\[ P \quad P \quad F \quad F \quad F \quad F \]
We have just discussed the dependence of crystal structures on composition. Because interest in this material arose due to its colossal magnetic-caloric effect, so the magnetic properties are required to be discussed here.

When \( x \) is in the range \( 0.5 < x < 1.0 \), it is found that when the orthorhombic Gd\(_5\)Si\(_4\)-based solid solution alloy is heated, a second order magnetic phase transitions from a ferromagnet to paramagnet occurs, see Figure 6. It is well-known, pure Gd element orders magnetically below 294K. Based on Figure 6, Curie temperatures of these alloys within this composition range are higher than 294K. It is believed that this is due to the fact that in addition to the indirect Ruderman-Kittel-Kasuya-Yoshida (RKKY) 4f-4f exchange, there also exist a direct Gd-Si(Ge)-Gd superexchange in the orthorhombic Gd\(_5\)Si\(_4\)-type phase because of distinct inter-slab bonding in Gd\(_5\)(Si\(_x\)Ge\(_{1-x}\))\(_4\) alloys.

When the Ge concentration is increased so that the material composition is in the range of \( 0.24 \leq x \leq 0.5 \), as shown in Figure 6, if the temperature rises from low temperature to high temperature, half of the covalent inter-slab Si(Ge)-Si(Ge) bonds have been broken and this results in a change from a orthorhombic structure to a monoclinic structure and a change from the ferromagnetic states to the paramagnetic states. It is believed that at low temperatures the alloys with orthorhombic and ferromagnetic structures have strong interactions between all slabs.
On increasing the concentration of Ge, it goes into the range of Gd$_5$Ge$_4$-based solid solution (0 ≤ x ≤ 0.2). On cooling, it is believed that it first undergoes an electronic transition without change of the crystal structure and then a ferromagnetic ordering, which is again coupled with the crystallographic transition forming the Gd$_5$Si$_4$-type structure [15], where all slabs are connected to one another, see Figure 5. The nature of the high temperature electronic transition is unclear but the magnetic susceptibility data indicate antiferromagnetic-like behavior, probably without the formation of long-range magnetic order. There is no evidence to show the existence of the intermediate monoclinic phase in the Ge-rich solid solution region: the inter-slab bonds, which exist at low temperature, are completely destroyed together with ferromagnetism without forming the intermediate phase with only a half or a fraction of the inter-slab bonds. The magnetic interactions in the Gd$_5$(Si$_x$Ge$_{1-x}$)$_4$ system are, therefore, especially dependent on the bonding between the slabs.

As shown in Figure 5, within the range 0 ≤ x ≤ 0.5, breaking and reforming of the Si(Ge)-Si(Ge) bonds between the slabs has the most pronounced effect on the superexchange interaction, although the RKKY interactions must also be affected. It is believed that the long-range ferromagnetic order exists only as long as all slabs are connected together enabling the Gd-Si(Ge)-Gd superexchange [16, 17]. Once some or all inter-slab bonds are broken, the superexchange interaction disappears, and ferromagnetism disappears. It should be noted that for x ≤ 0.5 the dependence of the crystal and magnetic structures of Gd$_5$(Si$_x$Ge$_{1-x}$)$_4$ on external magnetic field and pressure in addition to temperature. The
reversible breaking and reforming of the half or all of the covalent Si(Ge)-Si(Ge) inter-
layer bonds occurs as the materials are magnetized-demagnetized or pressurized-
depressurized just above their Curie temperatures [18]. When the crystal structure change
was triggered by magnetic field, pressure and temperature, which is accompanied by a
tremendous shear movements of the slabs relative to one another, i.e., the inter-slab
distances change by as much as ~0.8 to ~1.1 Å for the breaking of half or all the inter-
layer bonds, respectively [4,15], while the intra-slab distances hardly change at all
(Figure 7 top). By itself, the mechanism responsible for the ability of the magnetic field to
change chemical bonding in the crystal lattice of a metallic alloy is quite unusual and will
require an extensive theoretical and experimental effort before it is fully understood. It is
found in the Gd₅(SixGe₁₋ₓ)₄, due to the changes in inter-layer bonding, structure, electron
and magnetism result in a series of unusually powerful magneto-responsive properties
(Figure 7), including the giant magnetocaloric effect (i.e., 25 to 200% larger than that
observed in the standard magnetic refrigerants [19, 20]), colossal magnetostriction (ten
times larger in Terfenol-D [21]), and giant magnetoresistance (i.e. the same as found in
artificial multi-layered thin films [22, 23]. Gd₅(SixGe₁₋ₓ)₄ is also found to exhibit an
unusual Hall effect [29]. It should be pointed out the giant magnetoresistance observed
near the corresponding phase transformation temperature in Gd₅(SixGe₁₋ₓ)₄ can be either
positive or negative depending upon the Si to Ge ratio [24, 25, 26]. In addition, changing
the chemical composition can enable us to precisely control these materials to display the
largest required response almost at any temperature between ~20 and ~300K, please refer
to Figure 6.
Figure 7 Correlation between the magnetic responses of the Gd₅(SiₓGe₁₋ₓ)₄ materials and their crystal structures for 0 ≤ x ≤ 0.5. At low temperatures the compounds are ferromagnetic (A) with all slabs (light connected via the Si(Ge)-Si(Ge) covalent bonds. Depending on the composition, the materials paramagnetic with either one-half (B) or none (C) of the slabs connected above the Curie temperatures as shown by long horizontal arrows at the top of the figure. The transitions from state A to B C are coupled with shear movement of the slabs by ~0.8 (A→B) or ~1.1Å (A→C) as indicated by red horizontal arrows. When a magnetic field is applied above Curie temperature, the reverse magnetic-martensitic transitions occur (B→A or C→A, as shown by long horizontal arrows in the resulting in the giant magnetocaloric effect, giant magnetostriction, and colossal magnetostriction. These are shown at the bottom of the figure for the Gd₅(Si₂Ge₂) composition (i.e., for x = 0.5). Unit cells of the three crystallographic modifications existing in the Gd₅(SiₓGe₁₋ₓ)₄ system are highlighted in yellow. (After K. A. Gschneidner Jr., etc, [5])
However, for Gd$_5$(Si$_x$Ge$_{1-x}$)$_4$, there is no a special concentration at which all three magnetic responses can reach maximum values. It is found that largest magnetocaloric effect occurs at $x=0.24$. The colossal magnetostriction is found at a maximum in the Gd$_5$Ge$_4$ solid solution region due to the fact that the transformation is between zero inter-slab bonds and fully bonded system. As for the composition where the maximum giant magnetoresistance can be obtained has not been found due to the lack of enough experimental data with respect to concentration and a change of the sign of magnetoresistance in the monoclinic solid region.

As discussed above, the structural phase transformation in Gd$_5$(Si$_x$Ge$_{1-x}$)$_4$ is characterized by a large shear displacement of atomic layers, with results in the change of crystallographic symmetry and magnetic order. Both the crystallographic and magnetic structures change simultaneously. Such a transformation is called a magnetic-martensitic transformation, which is extremely rare. It is believed that all the unusual properties discussed above are associated with this magnetic-martensitic phase transformation. The coupled magnetic-crystallographic phase transformation in the Gd$_5$Si$_4$-Gd$_5$Ge$_4$ system may be extremely sensitive to small changes in the phase composition of the alloy. Besides, the start and end of the magnetic-martensitic transition depends strongly on the direction of change (i.e. increasing or decreasing) of either or both the temperature and magnetic field as shown in Figure8 for Gd$_5$(Si$_2$Ge$_2$). This diagram is typical for any composition excluding $x=0$. 
Figure 8 The phase diagram of Gd₃(Si₂Ge₂). At low temperatures and high magnetic fields the compound is ferromagnetically ordered and all slabs are interconnected as shown in the icons. At high temperatures and low magnetic fields the compound is magnetically disordered (paramagnetic) and only 1/2 of the slabs are interconnected as also shown in the icon. The red area is the region where the paramagnetic/monoclinic phase transforms into the ferromagnetic/orthorhombic phase during magnetic field increase and/or temperature reduction. The blue area is the region where the ferromagnetic/orthorhombic phase transforms into the paramagnetic/monoclinic phase during magnetic field reduction and/or temperature increase. Both the red and the blue areas indicate the two regions where the Gd₃(Si₂Ge₂) system is both structurally and magnetically inhomogeneous, i.e., it consists of the two phases, ferromagnetic/orthorhombic and paramagnetic/monoclinic. (After K. A. Gschneidner Jr., et al. [5])

Based on both X-ray powder diffraction, magnetic and thermodynamic measurements, Pecharsky et al [30] published a refined composition–magnetic ordering temperature diagram of the Gd₃(SiₓGe₁₋ₓ)₄ system for the as-prepared alloys shown in the figure 9.

Similarly to both Holtzberg et al. [3] and Pecharsky and Gschneidner [4], which has been discussed before, it is also composed of three extended solid solutions in the as-prepared
Figure 9 The magnetic phase diagram of the Gd₅SiₓGe₄₋ₓ pseudo-binary system. The thin solid lines indicate magnetic phase boundaries, and the vertical dotted lines delineate the regions where the alloys are single phase materials (the compositions within shaded areas are two phase alloys). The circles (open and solid) refer to magnetic transition temperatures of the monoclinic Gd₅SiₓGe₂-type phase, the solid squares indicate the magnetic transition temperatures of the orthorhombic Gd₅Si₁₋ₓ-based phase, and the solid triangles and diamonds refer to the magnetic transition temperatures of the orthorhombic Gd₅Ge₂-based phase, respectively. (After A.O. Pecharsky, et al. [30])

pseudo-binary Gd₅Si₄–Gd₅Ge₄ system but with different composition ranges. The first is Si-rich Gd₅(SiₓGe₁₋ₓ)₄, when 0.575 ≤ x ≤ 1 compared to previous range 0.5 ≤ x ≤ 1. The second solid solution is Gd₅Si₂Ge₂-type monoclinic region when 0.4 < x ≤ 0.503, compared to the previous range 0.24 ≤ x ≤ 0.5. The third single phase region is Sm₅Ge₄-type solid solution when 0 < x ≤ 0.3. When compared with the previous phase diagram given by Gschneidner, and Pecharsky [4], the diagram presented in Figure11 reflects the
slight reduction of the extent of the two single-phase regions, i.e. the Gd₅Si₄-based solid solution and Gd₅Si₂Ge₂-type phase. The diagram also reflects the expansion of the homogeneity range of the Gd₅Ge₄-based solid solution region. In addition to these changes, Ref [30] establishes the presence of a two-phase region separating the Gd₅Si₄-type and Gd₅Si₂Ge₂-type phases. It is noted that the heat treatment has considerable effect on the extent of the phase regions in the Gd₅(SiₓGe₁₋ₓ)₄ system and has not been studied thoroughly.

2.5 FUNDAMENTALS OF THERMAL EXPANSION STUDY

Thermal expansion is a common phenomenon when an object is heated or cooled, its volume, length, or area will change. Correspondingly, it is called linear expansion, volume expansion, and area expansion. All these three types can be expressed in terms of one common parameter, i.e. linear expansion coefficient (α).

Figure 10 illustration of relationship between linear expansion, area expansion and volume expansion
The linear thermal expansion coefficient is the fraction change in length of object when it is cooled down or heated up per degree. Mathematically, it can be expressed as:

\[ \alpha = \frac{\Delta L}{L \times \Delta T} \]

From this equation, we can derive the equation for area expansion and volume expansion.

If the linear expansion is put in the form

\[ L = L_0 [1 + \alpha \Delta T], \text{ then } A = L^2 = L_0^2 [1 + 2\alpha \Delta T + \alpha^2 \Delta T^2] \]

In most cases the quadratic term above can be neglected since the typical expansion coefficient is on the order of a few parts per million per degree C. The approximate expression then becomes

\[ A = A_0 [1 + 2\alpha \Delta T] \]

This is equivalent to the expression:

\[ \frac{\Delta A}{A_0 \times \Delta T} = 2\alpha \]

By the same way, the volume can be expressed as:

\[ V = L_0^3 (1 + 3\alpha \Delta T + 3\alpha^2 \Delta T^2 + \alpha^3 \Delta T^3) \]

In most cases the quadratic and cubic terms above can be neglected since the typical expansion coefficient is on the order of parts per million per degree C. The approximate expression then becomes
\[ V = V_0 (1 + 3\alpha \Delta T) \]

which is equivalent to

\[
\Rightarrow \frac{V - V_0}{V_0} = \frac{V_0(1 + 3\alpha \Delta T) - V_0}{V_0}
\]

\[
\Rightarrow \frac{\Delta V}{V_0 \times \Delta T} = 3\alpha
\]

The basic physics underlying thermal expansion derives from the energy-displacement relationship for atoms in a solid as schematically shown in figure 11:

\[ \text{Figure 11 Lennard-Jones Potential} \]

As the temperature is raised, the amplitude of vibration increases. The asymmetrical nature of the potential well means that this is accompanied by an increase in the average inter-atomic spacing.
Intermetallics compounds containing rare earth elements exhibit a wide variety of properties, which arise from the relative importance of the lattice and electronic degrees of freedom and their possible interplay. For systems in which coherent lattice and magnetic degrees of freedom are involved, polarized neutron scattering can sometimes be employed to determine not only the temporal and spatial dependence of the magnetic moments but also the absolute magnitude. In many cases, it is not possible to experimentally separate the different contributions and unambiguously identify the mechanism or mechanisms involved. In order to quantify the influence of certain mechanism, studies have been restricted. This has led to considerable interest in compounds in which the sole magnetic element is gadolinium. Gadolinium has a particularly stable 4f shell, it is an S state ion, is spherically symmetric and is therefore unaffected by the crystal field. Furthermore, the coupling of the lattice and electronic degrees of freedom arising from spin-orbit interaction is expected to be negligible.

2.6 CRITICAL BEHAVIOR AT THE ORDERING TEMPERATURE

The bulk properties of magnetic materials show anomalous behavior in the vicinity of the transition temperatures such as the Curie and Neel points. The anomalous behavior is due to coupling between the particular bulk property and the magnetic structure. The effects are known as critical phenomena. The bulk susceptibility, the specific heat, elastic moduli, magnetostriction, magnetoresistance and thermal expansion, all reveal characteristic critical behavior at the magnetic transition temperatures. Measurement of such behavior gives an insight into the nature of the magnetic coupling. Therefore the
study of such properties close to phase transitions is of fundamental interest. For specific heat anomaly, a ferromagnetic material has a greater specific heat than that of a nonferromagnetic material and goes through a maximum at the Curie temperature. It is well-known that when heat is added to any metal, part of it increases the amplitude of thermal vibration of the ions (called the lattice specific heat \( C_l \)) and remainder increases the kinetic energy of the valence electrons (electron specific heat \( C_e \)). If the metal is ferromagnetic, then still additional heat is required to disorder the spins (magnetic specific heat \( C_{\text{mag}} \)). The number of spins disordered per degree rise in temperature increases with the temperature in accordance with the appropriate Brillouin function, and becomes very large just below the Curie temperature, where the magnetization decreases rapidly with temperature as the magnetic order breaks up. Thermal expansion and magnetostriction also undergo unusual behavior at phase transition such as at the Curie and Neel points. This arises because there is the sudden appearance of spontaneous magnetostriction at the order-disorder transition temperature.

2.7 CLASSIFICATION OF PHASE TRANSITIONS

2.7.1 DEFINITION OF PHASE TRANSITION

As we know, interactions can affect the behavior of systems, modifying the properties from those of the corresponding ideal (non-interacting) system. An example of these is the Van der Waals interaction between molecules of a gas. But a gas is still recognizable as a gas, albeit with somewhat altered properties, because the interaction did not change the fundamental nature of the system. However, there is another consequence of
interactions if the interaction is sufficiently strong, by altering a thermodynamic variable such as temperature, pressure etc. there can suddenly occur a dramatic change in the system’s properties. There is then a transition to a qualitatively different state. We refer to this as a phase transition. In 1933 Paul Ehrenfest came up with a classification of phase transitions based on the discontinuity in derivatives of the free energy function [31]. This classification is still used today to compare phase transitions.

Magnetic interactions are responsible for magnetic phase transitions. Usually the temperature of the phase transition is approximately related to the interaction energy by \( kT \approx E_{\text{int}} \). Thus the exchange interaction between electronic spins \( JS_1 \cdot S_2 \) leads to a ferromagnetic transition at the Curie temperature \( T_c \approx J/k \). However in some cases it might not be immediately clear how to quantify the “interaction”.

Many phase transitions involve a symmetry change. At the highest temperature, a system will be at its most disordered and usually most symmetric. It will therefore have the lowest symmetry possible, and this will be the symmetry of the system’s Hamiltonian. As the temperature is lowered, when there is a phase transition, that symmetry is frequently broken. Consider a magnet in zero magnetic field. The Hamiltonian contains \( JS_1 \cdot S_2 \) which is rotationally invariant. Above the transition temperature (Curie temperature), there is no spontaneous magnetization and the system has rotational symmetry. But when cooled through the ferromagnetic transition a magnetization appears spontaneously. The rotational symmetry is broken.
2.7.2 CLASSIFICATION OF PHASE TRANSITIONS

When two phases coexist they have a common temperature and a common pressure (or some field). Thus the phases will each have the same Gibbs free energy.

![Diagram](image)

Figure 12 Variation of Gibbs free energy for two phases

In figure 12, we show the variation of $G$ for two different phases of a system – say solid and fluid. The actual stable state will correspond to the lower $G$, so we see that the phase transition occurs at the point where the Gibbs free energy is the same for both phases. That is to say it is the point where the Gibbs free energy of the two phases cross. The observed locus of the Gibbs free energy $G$ will thus display a kink at the phase transition.

Traditionally phase transitions have been characterized (by Ehrenfest) on the basis of the nature of the kink in $G$. If the $n^{th}$ derivative of $G$ with respect to $T$ (at constant $p$ or equivalently at constant $H$) is discontinuous then the transition is defined as $n^{th}$ order.

Now since $\frac{\partial G}{\partial T} \bigg|_p = -S$, we see that the discontinuity in $\frac{\partial G}{\partial T}$ is the change in entropy between the two phases. And since the latent heat is the heat absorbed, given by $T \Delta S$, it follows that there is latent heat involved with a first order transition, but not with higher orders. Nowadays the classification scheme is not used in quite this way; there are only
first and second order transitions. First order transitions are defined as above, and the
temperature variations of $G$, $S$, $V$ and $C_p$ are shown by four crude graphs in figure 13.
And all transitions which are not first order are called second order. So if there is latent
heat involved in a phase transition then it is first order, otherwise it is second order. In
this thesis, we follow this classification.

![Figure 13. Characteristics of a first-order phase transition. (a) Gibbs function; (b) entropy; (c) volume; (d) heat capacity](image)

Another of the characteristics of a first order transition is coexistence. As stated above,
the latent heat is a signature of a first order transition. If a phase transition has latent heat
then it may be possible for two phases to coexist; adding a small amount of heat will
result in the conversion of a small amount of the ordered phase to the disordered phase.
Similarly, changing the volume at constant temperature will alter the proportions of the two phases.

A graph of $C_p$ against $T$ serves to distinguish among the three types of transitions, as shown in figure 14. The name of "lambda transition" is for the fact that the shape of $C_p$-$T$ curve in the third graph resembles the Greek letter lambda. It can be seen in graph (a) that as a substance in any one phase approaches the temperature at which a first-order phase transition is to occur, its $C_p$ remains finite up to the transition temperature. It becomes infinite only when a small amount of the other phase is present, and its behavior before this takes place shows no evidence of any premonition of the coming event. However, in the case of a lambda transition, as is evident in graph (c), $C_p$ starts to rise before the transition points is reached, as though the substance, in the form of only one phase, "anticipated" the coming phase transition.

Figure 14. Distinguishing characteristic among the three types of phase transitions. (a) First-order; (b) second-order; (c) lambda.
For second order transition as defined above: there is no latent heat associated with the transition. This means that there can not be a region of coexistence and the system must change continuously from one phase to the other as shown in figure 15. One example of a commonly occurring second order transition is the transition between the ferromagnetic state and paramagnetic state. The essential phenomenon is that below a certain temperature a spontaneous magnetization will occur in the absence of an applied magnetic field. It is understood that the interaction responsible for ferromagnetism is the exchange interaction between electron spins. The origin of the exchange interaction arises from the necessity to antisymmetric the electronic wave function, together with the Coulomb repulsion between electrons. This means that the symmetric and the antisymmetric wave functions have different energies and this may be written as an effective spin-dependent Hamiltonian:

\[ H_x = -\hat{h} J \sum_{i,j}^{n,n} S_i \cdot S_j \]

This is called the Heisenberg Hamiltonian. Note that this interaction is normally written as rotationally invariant for simplicity, although it can be anisotropic. The sum is over all interacting pairs and \( J \) is called the exchange integral.

2.8 THERMODYNAMICS OF THERMAL EXPANSION

2.8.1. SPECIFIC HEAT

Specific heat is defined as the heat (\( \delta Q \)) required to rise the temperature (\( T \)) of a unit of mass of a substance by one degree. \( C_y = (\delta Q/\delta T)_y \), where \( y \) indicates the control
parameter that is kept constant, usually pressure or volume. From the first law of
thermodynamics, the heat absorbed by a system is distributed as, $\delta Q = dU + \delta W$, where $U$
is the internal energy and $W$ the work done by the eventual expansion (compression), or
by the change in the magnetization ($M$) under magnetic field ($H$). If the volume of the
system does not change, (i.e, $dV=0$), $C_v = dU/dT$ is obtained. If the specific heat
measurement is performed under adiabatic conditions (isolated), which implies at
constant pressure ($C_p$). In this case, $C_p = dH/dT$, where $H= U + pV$ is the enthalpy of the
system, which includes the expansion of the system during the heat and cooling process.
The difference between $C_p$ and $C_v$ is given by $C_p - C_v = TV\alpha^2/\kappa$, where $\alpha$ is the thermal
expansion and $\kappa$ the compressibility. As seen from this equation, thermal expansion and
heat capacity are closely related. According to the second law of thermodynamics, the
change in entropy $dS(T)$ is related to the heat transfer $\delta Q$ through the equation $dS = \delta Q/T$.
Then, specific heat can be expressed as, $C_p = T(dS/dT)_p$, therefore the experimental
measurement of $C_p(T)$ provides a direct measure of the entropy evolution of the system,
$S(T) = \int C_p/T \,dT$.

One of the most important aspects of the knowledge of the entropy $S(T)$ is that it
provides information on the first term of the free energy variation ($dG = -SdT +Vdp -
MdH$). For this reason access to the evolution of $C_p/T$ constitutes one of the basic tools
for the characterization of any new system. For a magnetic system, the heat capacity is
composed of three parts: $C_p = C_{mag} + C_{ele} + C_{phon}$, where $C_{mag}$ is the magnetic
contribution, $C_{ele}$ is the electrons contribution, $C_{phon}$ is the lattice or phonon contribution.
Anomalies are observed in many bulk properties around the ordering temperature. One of them is heat capacity. The magnetic component $C_m$ given by $C_m = (dE_{ex}/dT)$, where $E_{ex}$ is the total exchange energy self-energy of the material per unit volume.

$$E_{ex} = -\mu_0 \alpha M_s^2$$

$$C_m = -2\mu_0\alpha M_s \frac{dM_s}{dT}$$

### 2.8.2. CLAUSIUS-CLAPEYRON EQUATION

This is the key tool for analyzing first-order phase transitions, especially for understanding the location and slope of the "coexistence curves", where the two phases are in equilibrium with each other. Here, we just give the Clausius-Clapeyron equation, a detailed derivation is given by Stanley [32].

For a general system,

$$\frac{dT_c}{dP} = \frac{\Delta V}{\Delta S}$$

For a magnetic system,

$$\frac{dT_c}{dH} = \frac{\Delta M}{\Delta S}$$

### 2.9 EFFECT OF MAGNETIC FIELD, PRESSURE AND ALLOYING ON TRANSFORMATION

Behavior under an external magnetic field can be used to distinguish the nature of the magnetic order. In a ferromagnet, the presence of a magnetic field broadens the transitions because of the enhancement of magnetic correlations above $T_c$. As a consequence the generalized thermodynamic order parameter $\xi(T)$ (the magnetization $M$) is the order parameter in a magnetic system) does not onset with infinite but with finite slope and from higher temperatures.
In view of the mechanical energy involved, the application of external pressure is not usually expected to produce drastic changes in a magnetic transition by itself, aside from the change in $T_c$ which is due to the reduction of the interatomic distances that affects the strength of the exchange interaction. However, its effect can be strongly enhanced by other mechanisms such as the hybridization of the local and conduction electron states related to the Kondo effect. The variation of $T_c$ with pressure is related to $\Delta C_m (T_c)$ by the Ehrenfest relation, $\frac{dT_c}{dP} = V T_c \Delta \alpha / \Delta C_m$.

The effect of alloying may produce stronger variations in transition temperature because the chemical potential itself is affected in the substitution process. Local structural pressure and disorder are also typical effects of atomic substitution, with the obvious consequence of the broadening of $\Delta C_m (T_c)$. 
CHAPTER 3. EXPERIMENT METHODS

3.1 EXPERIMENTAL TECHNIQUES FOR MEASUREMENT OF THERMAL EXPANSION

Determination of the thermal expansion requires the measurement of strain and in order to determine the thermal expansion coefficient, both strain and temperature changes are needed. A diverse range of techniques can be employed for this purpose, such as mechanical dilatometry, optical interference, X-ray diffraction, laser-based speckle pattern interferometry, electrical pulse-heating techniques, high-resolution microscopy and neutron diffraction. But the most widely used technique is the strain gauge method, which is the technique employed in this thesis. This technique is effective for measurement of bulk strains measured over a surface area of 1 mm$^2$ and greater.

3.2 STRAIN GAUGE MEASUREMENT

Strain is the amount of deformation of a body due to an applied force. More specifically, strain ($e$) is defined as the fractional change in length, as shown in figure 15.

![Figure 15](image)

Strain can be positive (tensile) or negative (compressive). Although dimensionless, strain is sometimes expressed in units such as in./in. or mm/mm. In practice, the magnitude of measured magnetically-induced or thermal-induced strain is very small. Therefore, strain
is often expressed as microstrain, which is simply expressed in units of $10^{-6}$, i.e. 1 ppm (part of per million). A detailed description about types of strain gauge, and strain gauge measurement circuits is given in Appendix A.

3.3 STRAIN GAUGE

While there are several methods of measuring strain, the most common is with a resistive strain gauge. The most widely used gauge is the bonded metallic strain gauge, a device whose electrical resistance varies in proportion to the amount of strain in the device. Other resistive strain gauges are also available, for example the piezoresistive strain gauge is a semiconductor device whose resistance varies nonlinearly with strain.

The metallic strain gauge consists of a very fine wire or, more commonly, metallic foil arranged in a grid pattern. The grid pattern maximizes the amount of metallic wire or foil subject to strain in the parallel direction (Figure 16). The cross sectional area of the grid is minimized to reduce the effect of shear strain and Poisson strain. The grid is supported on a thin flexible backing, which is bonded directly to the test specimen. Therefore, the strain experienced by the test specimen is transferred via the bond to the strain gauge, which responds with a linear change in electrical resistance. Strain gauges are available commercially with nominal resistance values from 30 to 3000$\Omega$, with 120, 350, and 1000$\Omega$ being the most commonly used values.
It is essential that the strain gauge be properly bonded onto the test specimen so that the strain is accurately transferred from the test specimen, though the adhesive and strain gauge backing, to the resistive foil itself. Manufacturers of strain gauges are the best source of information on proper mounting of strain gauges. A fundamental parameter of the strain gauge is its sensitivity to strain, expressed quantitatively as the gauge factor (GF). Gauge factor is defined as the ratio of fractional change in electrical resistance to the fractional change in length (strain):

$$GF = \frac{\Delta R / R}{\Delta L / L} = \frac{\Delta R / R}{\varepsilon}$$

The gauge factor for metallic strain gauges is typically around 2. Ideally, the resistance of the strain gauge should change only in response to applied strain. However, strain gauge material, as well as the specimen material to which the gauge is applied, will also respond to changes in temperature. Strain gauge manufacturers attempt to minimize sensitivity to temperature by processing the gauge material to compensate for the thermal expansion of the specimen material for which the gauge is intended. While compensated strain gauges reduce the thermal sensitivity, they do not totally remove it. For example, consider a...
gauge compensated for aluminum that has a temperature coefficient of 23 ppm/°C. With a nominal resistance of 1000Ω, GF = 2, the equivalent strain error is still ppm/°C. Therefore, additional temperature compensation is necessary.

3.4. STRAIN GAUGE MEASUREMENT CIRCUITS

In practice, the strain measurements made during thermal expansion or magnetostriction rarely involve quantities larger than a few millistrain (ε×10^{-3}). Therefore, to measure the strain requires accurate measurement of very small changes in resistance. For example, suppose a test specimen undergoes a strain of 500 ppm. A strain gauge with a gauge factor GF = 2 will exhibit a change in electrical resistance of only 2·(500×10^{-6}) = 0.1%. For a 120 Ω gauge, this is a change of only 0.12Ω. To measure such small changes in resistance, and compensate for the temperature sensitivity discussed in the previous section, strain gauges are almost always used in a bridge configuration with a voltage excitation source. The general Wheatstone bridge, illustrated in figure 17, consists of four resistive arms with an excitation voltage, V_{EX}, that is applied across the bridge.

![Wheatstone bridge](image)

*Figure 17 Wheatstone bridge*

The output voltage of the bridge, V₀, will be equal to:
From this equation, it is apparent that when $R_1/R_2 = R_4/R_3$, the voltage output $V_o$ will be zero. Under these conditions, the bridge is said to be balanced. Any subsequent change in resistance of one arm of the bridge will result in a nonzero output voltage.

Therefore, if we replace $R_4$ in Figure 15 with an active strain gauge, any changes in the strain gauge resistance will unbalance the bridge and produce a nonzero output voltage. If the nominal resistance of the strain gauge is designated as $R_G$, then the strain-induced change in resistance, $DR$, can be expressed as $DR = R_G \cdot GF \cdot e$. Assuming that $R_1 = R_2$ and $R_3 = R_G$, the bridge equation above can be rewritten to express $V_o/V_{EX}$ as a function of strain (see Figure 18). Note the presence of the $1/(1+GF\cdot e/2)$ term that indicates the eventual nonlinearity of the quarter-bridge output with respect to strain at high strain levels.

![Figure 18 Quarter-Bridge Circuit](image)
3.5 CLOSED-CYCLE REFRIGERATOR SYSTEM

Closed cycle refrigerator (CCR) systems provide low temperature environments (to 10 K and below) for the thermal expansion measurement in this thesis. As a result, these systems are very simple to operate and inexpensive to maintain. When combined with an automatic temperature controller, closed cycle systems become useful tools for studying the properties of materials over a wide range of temperatures, both below ambient and to a lesser extent above ambient temperature.

Closed cycle systems recirculate a fixed volume of gas to provide cooling to the sample mounting stages, and no gas is added or removed during operation. CCR utilizes the Gifford-McMahon thermodynamic cycle, based on the controlled compression and expansion of helium gas. A compressor is used to provide the high pressure helium gas needed for the cycle. Flexible metal gas lines deliver the compressed helium gas to the refrigerator, and return the low pressure gas to the compressor for recirculation. The refrigerator includes two cold stages, one for cooling the sample and one for cooling a radiation shield that surrounds the sample.

CCR systems are available in two general configurations, sample in vacuum (cold finger), and sample in exchange gas (top loading). In our experiment, we adopt the former configuration.
3.6 FUNDAMENTALS OF MAGNETIC FORCE MICROSCOPY (MFM)

The magnetic force microscopy which was first reported by Martin and Wickramasinghe was developed from the earlier atomic force microscope of Binnig, Quayte and Gerber in which the alternating voltage on the probe tip is replaced with an alternating magnetic field. The device samples the magnetic field gradients close to the surface of specimen. The method is therefore basically a scanning force probe technique based on magnetic forces between the magnetized tip of the microscope and specimen, as shown in the figure 20 and figure 21.

Figure 20 Magnetic probe scanning over the surface of a material (After D. C. Jiles [11])
In this thesis, a magnetic force microscopy manufactured by the Digital Instrument Co. is used to image the magnetic samples. The drawing in Figure 21 is used to show how it detects magnetic field variation on the surface of magnetic material. Today spatial resolutions of 50nm are routine. There are two main modes of operation: constant height and variable height. In the first mode, it operates by scanning the tip attached to the end of an oscillating cantilever across the sample surface. A laser light from a solid state diode is reflected off the back of the cantilever and collected by a position sensitive detector (PSD) consisting of two closely spaced photodiodes whose output signal is collected by a differential amplifier. Angular displacement of cantilever results in one photodiode collecting more light than the other photodiode producing an output signal (the difference between the photodiode signals normalized by their sum) which is proportional to the deflection of the cantilever. The change in phase angle of vibration of the tip can be related to the magnetic force gradient at the surface. The typical scanning
height in this mode of operation is 100-200nm. The second mode relies on moving the tip closer to the surface by controlling the tip-sample spacing. This can be used to image static magnetic fields. The magnetization in the tip is modulated and the force on the tip is detected in the same way as before, using the laser interferometer to measure vibration amplitude, phase and frequency of the tip. The image formed as result of magnetic force microscopy is obtained by measuring the force or the force gradient, and these images can be used to study magnetic structures such as domain walls, closure domains, Bloch lines and, in the case of magnetic recording media, intentionally magnetized regions of a material. In fact today, it is in the area of magnetic recording media that the MFM is finding the most applications [11].
REFERENCES


CHAPTER 4 THERMAL EXPANSION OF SINGLE CRYSTAL

Gd₅(Si₁.₉₅Ge₂.₀₅) SHOWING UNUSUAL FIRST-ORDER TRANSFORMATION


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ABSTRACT

Measurements of thermal expansion of single crystal Gd₅(Si₁.₉₅Ge₂.₀₅) during cooling and heating were conducted for the first time. A very steep change in strain with temperature was observed when the material underwent a phase transformation. This was an unusual simultaneous magnetic and structural phase transformation from a ferromagnet with orthorhombic crystal structure below the transition temperature Tc to a paramagnet with monoclinic crystal structure above Tc. This transition temperature Tc was found to depend on magnetic field, and to exhibit hysteresis depending on whether the material was being cooled or heated. In the absence of a magnetic field Tc is 267 K on cooling and 269 K on heating. However, when the material was subjected to a magnetic induction B in the range 0 - 2.5 Tesla, the transition temperatures, on both cooling and heating, were found to increase linearly with temperature by about 4.9
K/Tesla. This rate of change of transition temperature with magnetic field was in good agreement with calculations based on the assumption that the additional energy due to the magnetic field can suppress the thermal vibration of Gd atoms and that the additional thermal energy per Gd atom needed to cause the phase transition to occur is equal to the additional magnetic energy of each Gd atom caused by the magnetic field.

*index Terms*—Thermal expansion, Phase transitions, First order transformation, Hysteresis, Single crystal

**INTRODUCTION**

The rare earth intermetallic compound system Gd₅(SixGe₄₋ₓ)₄ (0.24 ≤ x ≤ 0.5) has been found to exhibit the giant magnetocaloric effect [1]. Subsequent research revealed that the magnetic and structural phase transformations occur simultaneously at near room temperatures [2, 3], with the transition temperature depending on the composition of the material (particularly the Ge to Si ratio) and whether the temperature is increasing or decreasing. Below the transition temperature Tᵥ, the material is ferromagnetic with an orthorhombic crystal structure (space group Pnma), whereas above Tᵥ, it is a paramagnet with a monoclinic crystal structure (space group P 112₁/a) [4]. Specific heat capacity and magnetization measurements of polycrystalline Gd₅(SixGe₄₋ₓ)₄ showed that the transformation could be triggered reversibly by external magnetic field or temperature [3]. Since this alloy system is under consideration for magnetic refrigeration in the vicinity of room temperature, much attention has been given recently to the investigation of the properties of this compound system. These materials have been reported to show
colossal magnetostriction near the phase transformation [5], however until now little attention has been given to thermal expansion and magnetostriction in these materials.

According to the established phase diagrams for both the magnetic structure and the crystal structure $\text{Gd}_3(\text{Si}_{1.95}\text{Ge}_{2.05})$ is very similar to $\text{Gd}_3(\text{Si}_2\text{Ge}_2)$ which exhibits a maximum magnetocaloric effect at 276 K. The materials around this composition are the among the most promising for magnetic refrigeration. At the transition temperature for $\text{Gd}_3(\text{Si}_2\text{Ge}_2)$, the $a$-axis undergoes a 0.8% change. This arises as a result of the transition between orthorhombic and monoclinic structures. Therefore, in view of the large magnitude of this strain, thermal expansion was measured along the $a$-axis of single crystal $\text{Gd}_3(\text{Si}_{1.95}\text{Ge}_{2.05})$.

**EXPERIMENTAL DETAILS**

The $\text{Gd}_3(\text{Si}_{1.95}\text{Ge}_{2.05})$ single crystal ($5\text{mm} \times 4\text{mm} \times 1\text{mm}$) was grown by the Bridgman method. Appropriate quantities of gadolinium 99.996% (metals basis, wt. %), silicon (99.9999%) and germanium (99.999%) were cleaned and arc melted several times under an argon atmosphere. The as-cast ingot was electron beam welded into a tungsten Bridgman style crucible for crystal growth. The ingot was then heated to 2000°C and held at this temperature for 1 hour to allow thorough mixing before withdrawing the sample from the heat zone at a rate of 4mm/hr. The as-grown crystal was oriented by back-reflection Laue X-ray diffraction and the crystallographic directions assigned using x-ray diffraction two-theta scans of the single crystal. The sample was cut by spark cutting and the faces were polished using standard metallographic techniques.
The thermal expansion measurements were conducted using the strain-gauge method in a Janis Research 2-stage closed cycle helium refrigeration system with temperature in the range 10K – 325K. The strain gauge was mounted on the sample surface oriented along the a-axis using Permabond 910 glue which was cured at room temperature. The sample was cooled down from ambient (room) temperature through the transition, and then was heated back up through the transition. The linear thermal expansion was measured during both cooling and heating. The temperature change was under computer control using a control and data logging program written in LabView.

The dc magnetic field was produced by a standard electromagnet with full range of ± 2.5 Tesla. Thermal expansion measurements were carried out initially without applying a magnetic field. Then, a series of thermal expansion measurements were made for different constant applied magnetic field strengths along the a-axis. The magnetic field was maintained constant throughout the measurement cycle. The values of the field strength used were: 0, 1.0, 1.5, 2.0, 2.5 Tesla. The location of the steepest point of the strain versus temperature curve was taken to be the transition temperature.

RESULTS AND DISCUSSION

Figure 1 shows the linear thermal expansion measured along the a-axis in zero applied magnetic field. The strain $\lambda$ (\(\lambda = \Delta l / l_0\), where $l_0$ denotes the original length) showed an abrupt change during the cooling and heating processes due to the phase
transformation. The transformation is also manifested as a sharp peak in the plot of the differential thermal expansion against temperature as shown in Figure 2. On cooling, there are two transformations that happen simultaneously at 267 K. One is the crystalline structural transition: monoclinic → orthorhombic. The other is the magnetic transition: paramagnetic → ferromagnetic. An ordinary magnetic transition between paramagnetic state and ferromagnetic state is an order-disorder transition which is not accompanied by a simultaneous crystallographic transformation.

![Graph showing thermal expansion](image)

*Fig 1. Thermal expansion of Gd₅(Si₁.₉₅Ge₂.₀₅) along the a-axis under zero field. Tc is 267 K on cooling and 269 K on heating.*

In this material it was found that on heating the transition occurs at a higher temperature of 269 K. The temperature hysteresis is therefore 2 K. One of the features of a first-order phase transformation is the presence of hysteresis in the transition temperature which is due to the latent heat at the transition temperature for a first order transition. Therefore the thermal expansion data confirm that the transformation in this material is an unusual...
simultaneous first order magnetic-structural phase transformation that is magnetically an order-disorder transition, but structurally an order-order transition. In these materials the structural or crystalline phase transition can be caused either by change in temperature or change in magnetic field. Therefore the structural transition can be induced by the presence of a magnetic field at temperatures above the normal transition temperature. An example is given in Figure 3, which shows that the thermal expansion of Gd$_5$(Si$_{1.95}$Ge$_{2.05}$) under an applied field of 2 Tesla. The transition temperatures were found to be 276K on cooling and 279K on heating which are higher than the corresponding transition temperatures measured without any applied field. The dependence of the transition temperature of single crystal Gd$_5$(Si$_{1.95}$Ge$_{2.05}$) on the magnetic field along the $a$-axis is shown in Figure 4. On either cooling or heating the transition temperature increases

![Graph](image.png)

Fig 2 Dependence of the differential thermal expansion coefficient $\frac{dl}{dT} \cdot \frac{1}{l_0}$ on temperature while cooling down the sample.
linearly with magnetic field at a rate of 4.9 K/Tesla (the average value of the slopes of the plots is shown in Figure 4).

The magnetic structure of $Gd_3(Si_xGe_{1-x})_4$ is determined by two competing factors: the exchange interaction between Gd atoms which tends to order the magnetic moments, and the thermal energy which tends to disorder the magnetic moments. When the former is greater the material is ferromagnetic. At the transition temperature they are equal. Above the transition temperature the thermal energy is greater and the material is magnetically disordered. Since the magnetic field is applied along one direction, in this case the $a$-axis, we assume that the magnetic field suppresses the vibration of Gd atoms. Therefore in order to disrupt the magnetic order in the presence of a magnetic field, additional thermal energy is required. The result is that the transition temperature is shifted toward a higher temperature when a magnetic field is applied.
Fig 4. The dependence of transition temperature on the magnetic field applied along the a-axis.

The extra thermal energy $\Delta E$ for each atom of Gd required to disorder the magnetic moments is equal to the magnetic energy $E_H$ exerted by the external magnetic field:

$$\Delta E = \frac{n}{2} k_B \Delta T$$  \hspace{1cm} (1)$$

$$E_H = m \Delta B$$  \hspace{1cm} (2)$$

where $n$ is the number of degrees of freedom, $k_B$ is the Boltzmann's constant ($1.38 \times 10^{-23}$ J·K$^{-1}$), $m$ is the magnetic moment of Gd atom ($7.9 \mu_B = 7.3 \times 10^{-23}$ A·m$^2$). Based on this assumption the expected rate of change of transition temperature with field is

$$\frac{\Delta T}{\Delta B} = \frac{2m}{nk_B} \approx \frac{10}{n} \frac{6}{K \cdot T^{-1}}$$  \hspace{1cm} (3)$$

The measured rate of change of transition temperature with field ($\Delta T/\Delta B_{\text{meas}}$) is 4.9 K/Tesla. So, in order to agree with the experimental data, the number of degrees of freedom appears to be
According to equation (3) \( n = 2 \) would give the expected rate of change of transition temperature with field to be 5.3 K/Tesla, which is very close to the measured value of 4.9 K/Tesla. This suggests that the thermal energy required to overcome the effect of the applied field is equivalent to a system with only 2 degrees of freedom.

CONCLUSIONS

The linear thermal expansion along the \( a \)-axis of single crystal Gd\(_5\)(Si\(_{1.95}\)Ge\(_{2.05}\)) was measured for the first time. The results showed that the sudden change in strain is due to simultaneous magnetic and martensitic phase transformations. Both temperature and magnetic field influence the phase transformation. The sudden change in strain occurs at different temperatures depending on whether the temperature is being increased or decreased. This hysteresis in temperature is characteristic of a first order phase transformation. The temperature of the transition can also be increased by the presence of a magnetic field. An applied field shifts the transformation temperature by about 4.9 K/Tesla. It appears therefore that the magnetic field suppresses the vibration of the Gd atoms so that the magnetic and structural phase transitions are moved to higher temperature.
REFERENCES


CHAPTER 5 THERMAL EXPANSION STUDIES ON THE
UNUSUAL FIRST ORDER TRANSITION OF Gd₅(Si₂₀₉Ge₁₉₁):
EFFECTS OF PURITY OF Gd

A paper to be published in the Journal of Applied Physics, April 2003

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ABSTRACT

Two polycrystalline samples were made by using high purity Gd and commercial Gd respectively but with Si and Ge starting materials of the same purity in both cases. Thermal expansion results showed that both samples exhibited a first order phase transformation, with a discontinuity in thermally-induced strain and with hysteresis in the Curie temperature. Magnetic force microscopy has been used to demonstrate the magnetic phase transformation process from paramagnetic to ferromagnetic upon cooling. It was found that the Curie temperature was lower and the thermally-induced strain higher, in the sample made from lower purity level Gd starting materials compared with the sample made from high purity Gd metal. These results indicate that the impurities (mainly C, O, N and F) in the Gd starting material can significantly alter the strain and Curie temperature of Gd₅(Si₂Ge₁-x)₄ alloys.
INTRODUCTION

The properties of Gd$_5$(Si$_x$Ge$_{1-x}$)$_4$ were first studied in 1967 [1]. In recent years, this material has attracted much attention due to its unusual giant magnetocaloric effect (MCE) [2], giant magnetoresistance (GMR) and colossal magnetostriction (CMS)[3]. It is very unusual for a single material to possess these three effects together. The magnetocaloric effect is a phenomenon in which the alignment of randomly oriented magnetic moments caused by application of an external magnetic field results in heating, while randomizing the magnetic moments by removing the magnetic field results in cooling. Present results indicate that the impurities in starting Gd material play a critical role in determining the magnitude of the giant MCE in the final material [4]. In this study, the effect of impurities on the magnetoelastic properties of Gd$_5$(Si$_x$Ge$_{1-x}$)$_4$ system is also reported through the measurement of thermal expansion. The results show that the strain amplitude is higher in the material made from lower purity Gd.

EXPERIMENTAL DETAILS

Two polycrystalline Gd$_5$(Si$_{2.99}$Ge$_{1.91}$) samples were prepared by arc-melting a stoichiometric mixture of pure components in an argon atmosphere under normal pressure. The two samples used the same purity Si and Ge starting materials (both >99.99 at.%). One of the samples was prepared using Ames Laboratory (AL) Gd (99.8% pure), the major impurities (in atomic ppm) of which were: 440-O, 200-C, 160-H. Sample 2 was fabricated by using commercial purity Gd (96.9 at.% pure) which contained 18300-O, 4300-C, 4300-N and 3700-F (in atomic ppm). Mass losses after arc-melting were less
than 0.5 wt%, so the alloy chemical compositions were assumed to be to a first approximation unchanged in the final product. The thermal expansion measurements were conducted using the strain-gauge method in a Janis Research 2-stage closed cycle helium refrigeration system. The sample was cooled down from room temperature through the Curie point transition, and then later was heated up through the Curie point transition. The linear thermal expansion was measured during both cooling and heating. The Curie temperature were determined by differentiating the cooling and heating curves and finding the maximum derivative of the strain with respect to temperature. In addition, a magnetic field of $B=1$ T was applied along the measurement direction to study the effect of magnetic field on the magnetoelastic properties. *In-situ* magnetic force microscopy (MFM) was used to observe the phase transformation. This was carried out by using an MFM equipped with a heating-cooling stage.

**RESULTS AND DISCUSSION**

Thermal expansion measurement results are shown in Figure 1 for the sample Gd$_5$(Si$_{2.09}$Ge$_{1.91}$) made from Ames Laboratory high purity Gd at $B=0$ and 1 Tesla. An abrupt change in strain was observed at 283K on cooling and 288K on heating for $B=0$T; and at 287.5K on cooling and 298K on heating for $B=1$T. A discontinuity in thermal strain and thermal hysteresis are signatures of a first-order phase transition. Above the transition temperature, the sample is paramagnetic and monoclinic. Below the transition temperature, it is ferromagnetic and orthorhombic. Previous references have indicated that this first order coupled magnetic-crystallographic transition only occurs within the
composition range \([5] 0.24 \leq x \leq 0.5\). Recently, a more complete magnetic and crystallographic phase diagram has been established for the \(\text{Gd}_5(\text{Si}_{x}\text{Ge}_{1-x})_4\) system\(^6\), where a two-phase region \((0.503 < x < 0.575)\) is added between two regions that show a single phase around room temperature.

![Graph](image)

*Figure 1* Linear thermal strain (under fields of 0 and 1 T) of polycrystalline \(\text{Gd}_5\text{Si}_{2.09}\text{Ge}_{1.91}\) made from Ames Laboratory high purity gadolinium.

The composition of the present samples \((x=0.5225)\) falls into this so-called two-phase region. For this composition the two crystallographic structures that can exist around room temperature are: monoclinic \(\text{Gd}_5\text{Si}_2\text{Ge}_2\)-type paramagnetic state (the \(\beta\) phase) which is formed above 1200K and can be retained at room temperature, and orthorhombic \(\text{Gd}_5\text{Si}_4\)-type paramagnetic state (the \(\gamma\) phase) which is formed on heat treating the \(\beta\) phase above 690K but below 1200K and which appears to be stable at room temperature. When the paramagnetic \(\beta\) phase is cooled down below its Curie temperature, a coupled first-order magnetic-crystallographic phase transition occurs, and the ferromagnetically
ordered Gd$_5$Si$_4$-type structure ($\alpha$ phase) is formed. This transformation is reversible. When the paramagnetic orthorhombic Gd$_5$Si$_4$-type $\gamma$-phase is cooled, it undergoes only an ordinary second-order transition from paramagnetic to ferromagnetic with no associated crystallographic change. This transition is also reversible. In the two-phase region, one can get either or both of $\beta$ or $\gamma$ phase to exist at room temperature, depending on heat treatment.

![MFM images showing the magnetic phase transformation process for the sample made with high purity Ames Laboratory gadolinium. The leftmost image shows the sample in the paramagnetic state, the middle and the rightmost images show the ferromagnetic state with increasing domain size.](image_url)

The present samples had already been heat treated to ensure single phase before they are used for thermal expansion measurement. In Figure 2, the MFM images show the transition from paramagnetic state to ferromagnetic state upon cooling. Figure 1 shows a discontinuity in thermal strain at transition temperature of 283K on cooling and at 288K on heating, and hysteresis in the Curie temperature. These are both indicative of a first order phase transition. Thus taken together, they appear to indicate a first-order
simultaneous magnetic-crystallographic phase transition. The $\gamma$ phase of Gd$_3$Si$_4$ is expected to be ferromagnetic at room temperature and therefore not subject to a phase transformation upon cooling. Therefore on the basis of these results, it is believed that at room temperature, these samples adopted the crystal structure of the $\beta$ phase. In addition, as shown in Figure 1, the magnetic field can shift the Curie point to higher temperatures which also demonstrate that this first order transformation can be triggered by either temperature or applied magnetic field. In Figure 1, the linear thermal expansion ($\Delta l/l$) of 0.26%, corresponds to a volume expansion of ($\Delta V/V=3 \Delta l/l$) about 0.78% assuming minimal texturing. The thermal expansion results for sample 2 made from commercial Gd are shown in Figure 3. On cooling $T_c=270K$, on heating $T_c=275K$. Thus the higher levels of impurities in the commercial Gd appear to have the effect of decreasing the

![Figure 3 Linear thermal strain in zero applied field of polycrystalline Gd$_3$Si$_2$Ge$_{1.91}$ made from commercial quality gadolinium.](image)
transition temperature by $\Delta T_c = 13K$ (on either cooling or heating). The linear thermal expansion was 0.85%, corresponding to volume expansion of 2.55%, assuming minimal texturing. These values are considerably higher than those obtained in the sample made with high-purity Gd.

ACKNOWLEDGEMENTS

The Ames Laboratory is operated by Iowa State University for the U. S. Department of Energy under Contract No.W-7405-ENG-82. This work was supported by the Office of Basic Energy Sciences, Materials Sciences Division of the U. S. Department of Energy.

REFERENCES


APPENDIX

1. STRAIN GAUGE AND SAMPLE INSTALLATION

1.1 STRAIN GAGE MOUNTING PROCEDURES

Sample preparation for strain gage measurements

1. Decide what type of strain gage to be used.

2. Cut the sample to have two flat faces perpendicular to each other.
   2.1 One is for sticking to the strain gage, which should have an area a little larger than
       the gage surface.
   2.2 The other is for the bonding between the sample and the sample holder, which
       should be perpendicular to the strain direction to be measured. (As shown in the
       figure 1)

3. Polish the two flat faces with abrasive paper, first with grit 400 then with grit 600.

   ![Figure 1 showing how to mount the sample on the sample holder](image)

1.2 BONDING THE STRAIN GAUGE TO SAMPLE

1. Polish surface or abrade surface of material with fine emery cloth (e.g. 600 grit).

2. Clean material surface with Micro-Measurements acid solution (HCl).


4. Wipe surface with isopropyl alcohol to remove grease.
5. Lay gauge on “removable” scotch tape.

6. Put one end of tape down on sample and align gauge in desired direction.

7. When tape and gauge are correctly aligned, keeping one end of tape attached to the specimen, place a thin layer of adhesive on the surface of the gauge.

8. Run your finger along the tape beginning from the attached end to stick down the gauge and tape on to the specimen.

9. Cover the tape with non-adhesive material such as PTFE (Teflon) to apply continual pressure while adhesive sets.

10. Where necessary bake the sample and gauge or wait for about 24 hours to "cure" the bond.

1.3 CONNECTING THE STRAIN GAGE TO THE LEAD WIRES

We typically use a quarter bridge configurations. Three wires of different colors, i.e., white, red and black, are used for connecting the strain gage to the pin by soldering

1. One lead wire is soldered to the two bare leads on one side of the gage.

2. The other two lead wires are each connected to two separate leads on the other side of the gage.

The wires outside the system are connected to the wires inside by:
<table>
<thead>
<tr>
<th>In</th>
<th>Out (connected with strain indicator)</th>
</tr>
</thead>
<tbody>
<tr>
<td>White</td>
<td>White</td>
</tr>
<tr>
<td>Red</td>
<td>Red</td>
</tr>
<tr>
<td>Black</td>
<td>Black</td>
</tr>
</tbody>
</table>

3. Wrap the bare wires with electrical-insulator such as Teflon tape.

4. Check the resistance between the wires outside the system to make sure that the electrical connection is correct and not shorted. (Typically it is 120 $\Omega$ or 350$\Omega$.)

1.4 BONDING THE SAMPLE TO THE SAMPLE HOLDER

1. It is recommended to check the resistance between the wires outside the system before bonding.

2. To avoid stretching the strain gage during the bonding, use removable tape to hold the sample near the sample holder.

3. Clean the surface of the sample holder and the face of the sample to be adhered to the sample holder, first with Acetone, then with Isopropanol.

4. Be careful not to get any chemicals on the Cernox sensor.

5. GE7031 is used to bond the sample and the sample holder. Shake the bottle well before use.

6. Apply a very thin layer of adhesive to the sample holder (The wooden stick of a Q-tip can be used to do this).

7. Place the sample on it.

8. Hold the sample for a few minutes for it to stick to the sample holder.
9. Where necessary, non-adhesive materials such as removable tape or PTFE can be used to wrap the sample and sample holder together. (Remember to take the wrap off before closing the system)

10. To cure the bond faster, bake the sample and sample holder to no more than 52°C, otherwise, wait for about 24 hours to cure the bond.

2 STRAIN GAGE INDICATOR

1. Connection: The connection for the Quarter Bridge Configuration is shown in figure 2. For other connections, refer to the Strain Indicator Instruction Manual.

2. Turn on the Indicator.

3. Depress the AMP ZERO button; adjust the AMP ZERO potentiometer for a display reading of ±0000.

4. Select the desired bridge configuration FULL or 1/2-1/4 button. (for the quarter bridge, choose the 1/2-1/4).

5. Set the EXCITATION to 5, RANGE to 10%.
6. Depress the SET button, set the GAGE FACTOR switch to the required gage factor, which is given on the engineering data sheet with the strain gage.

7. Calibration. Depress the CAL button, calculate the calibration number with the following expression:

\[
5000 \times \frac{2.000}{GF} = \text{Calibration Number}
\]

Adjust the GAGE FACTOR potentiometer to give a reading equal to the calibration number. Lock the potentiometer in place.

8. Depress the RUN button. In this mode the strain indicator is reading the strain of the gage.

9. Set the COARSE BALANCE switch to 0. Adjust FINE BALANCE potentiometer for a display of ±0000. If the balance (±0000) cannot be reached, rotate the COARSE BALANCE switch to reduce the reading to near zero, and then complete balance with the FINE BALANCE potentiometer.

3 STRAIN GAGE INDICATOR ANALOG OUTPUT

Strain Gage Indicator Analog Output is available from the rear panel BNC connector.

The output is linear, with ±10.00 Volts maximum. It is adjustable over 11:1 range by a ten-turn potentiometer mounted on the rear panel. To calibrate the strain gage output

1. Attach the output to a voltmeter.

2. Set the voltmeter to display mV
3. Turn the Coarse Balance knob to one of the extreme positive or negative values.

4. Check to see if the strain gage display matches the mV output.

5. If the output differs, adjust the potentiometer on the back of the strain gage indicator so the values match.

6. Change the Course Balance knob to the extreme value.

7. Verify the Strain gage indicator display and output match.

8. Set the Course Balance knob to its original position.
4 DATA ACQUISITION SYSTEM

Figure 3 Data Acquisition System Interface developed by LabView language
1. Connect the analog outputs of the temperature controller and the strain indicator to the Data Acquisition System.

2. Run program Cryostat Controller, which is developed using LabView.

3. In the pop-up window, carefully set “Strain interval” as 30ppm and temperature interval as 1.00K, which means that either the strain changes by 30ppm or temperature changes by 1K, the system will read in a data;

4. Carefully set the upper temperature and lower temperature which defines the temperature range for the measurement.

5. Set “Direct Output Convert to Strain” as ppm;

6. Carefully set the “Gain” as 100, Gage factor as 2.04 (depending on which type strain gauge you used), set “Excitation Voltage” as 5.00;

7. There are two heater controlling buttons, if you want to use the heater, just enable ON button, at the meanwhile, set temperature Ramp rate (Degree/Minute) as you want.

8. Before you start to run the program, be sure you have selected Channel A, Channel A is used to indicate the temperature on the sample holder C.

9. When the environment parameters in the interface are carefully set, start the program by pressing and holding the Run button, then release it. Then the Data Acquisition System begin to take data and process them automatically.
10. If something found wrong, press “Pause Data Recording” button to pause it. When you have fixed the problem, press it again, it will resume to work.

11. Be sure not to press “Stop” button to pause the program. If you do so, the program will start a new project and you can not resume the previous data acquisition.
ACKNOWLEDGEMENTS

First of all, I would like to express my sincerest appreciation to my major professor, Dr. David C. Jiles, who gave me such a wonderful opportunity to join the magnetic group in Ames Laboratory and opened such an exciting research area for me. I cannot be more grateful for all his guidance and encouragement throughout all my research work and study.

Ames Laboratory is well-known for its research on rare earth elements in the world, especially in recently years its leading research on room temperature magnetic refrigeration using the colossal magnetic caloric effect of Gd₅(SiₓGe₁₋ₓ)₄. I feel very lucky and proud to be one of the members in the Complex Materials Group, Metal & Ceramics Sciences Division. I am also grateful for their financial support to my research.

I would like to take this opportunity to thank various friends and colleagues in Magnetic Group. I greatly appreciate their assistance in my experiments, helpful discussion. Particularly, I would like to thank Dr. John. E. Snyder, Dr. Chester C. H. Lo, Dr. Seong-Jae Lee and undergraduate students Jeff. S. Leib and Jason. A. Paulsen.

Finally, I would like to thank my parents, brothers and sister, and my girlfriend for their love, sacrifice, encouragement and support.