Superconductivity in ternary rare earth transition metal silicides and germanides with the Sc$_5$Co$_4$Si$_{10}$-type structure

Linda Sue Berg
Iowa State University

Follow this and additional works at: https://lib.dr.iastate.edu/rtd
Part of the Condensed Matter Physics Commons

Recommended Citation
Berg, Linda Sue, "Superconductivity in ternary rare earth transition metal silicides and germanides with the Sc$_5$Co$_4$Si$_{10}$-type structure " (1986). Retrospective Theses and Dissertations. 8056.
https://lib.dr.iastate.edu/rtd/8056

This Dissertation is brought to you for free and open access by the Iowa State University Capstones, Theses and Dissertations at Iowa State University Digital Repository. It has been accepted for inclusion in Retrospective Theses and Dissertations by an authorized administrator of Iowa State University Digital Repository. For more information, please contact digirep@iastate.edu.
INFORMATION TO USERS

This reproduction was made from a copy of a manuscript sent to us for publication and microfilming. While the most advanced technology has been used to photograph and reproduce this manuscript, the quality of the reproduction is heavily dependent upon the quality of the material submitted. Pages in any manuscript may have indistinct print. In all cases the best available copy has been filmed.

The following explanation of techniques is provided to help clarify notations which may appear on this reproduction.

1. Manuscripts may not always be complete. When it is not possible to obtain missing pages, a note appears to indicate this.

2. When copyrighted materials are removed from the manuscript, a note appears to indicate this.

3. Oversize materials (maps, drawings, and charts) are photographed by sectioning the original, beginning at the upper left hand corner and continuing from left to right in equal sections with small overlaps. Each oversize page is also filmed as one exposure and is available, for an additional charge, as a standard 35mm slide or in black and white paper format.*

4. Most photographs reproduce acceptably on positive microfilm or microfiche but lack clarity on xerographic copies made from the microfilm. For an additional charge, all photographs are available in black and white standard 35mm slide format.*

*For more information about black and white slides or enlarged paper reproductions, please contact the Dissertations Customer Services Department.

U-MI Dissertation Information Service
University Microfilms International
A Bell & Howell Information Company
300 N. Zeeb Road, Ann Arbor, Michigan 48106
Berg, Linda Sue

SUPERCONDUCTIVITY IN TERNARY RARE EARTH TRANSITION METAL SILICIDES AND GERMANIDES WITH THE SCANDIUM(5) COBALT(4) SILICON(10)-TYPE STRUCTURE

Iowa State University

University Microfilms International 300 N. Zeeb Road, Ann Arbor, MI 48106
Superconductivity in ternary rare earth transition metal silicides and germanides with the $\text{Sc}_5\text{Co}_6\text{Si}_{10}$-type structure

by

Linda Sue Berg

A Dissertation Submitted to the Graduate Faculty in Partial Fulfillment of the Requirements for the Degree of

DOCTOR OF PHILOSOPHY

Department: Physics
Major: Solid State Physics

Approved:

Signature was redacted for privacy.

In Charge of Major Work

Signature was redacted for privacy.

For the Major Department

Signature was redacted for privacy.

For the Graduate College

Iowa State University
Ames, Iowa

1986
TABLE OF CONTENTS

DEDICATION iv

I. INTRODUCTION 1
   A. Historical Background of Superconductivity 1
   B. Ternary Superconductors 4

II. Sc$_5$Co$_4$Si$_{10}$-TYPE CRYSTAL STRUCTURE 8

III. EXPERIMENTAL DETAILS 14
   A. Sample Preparation 14
   B. Sample Characterization 14
   C. Heat Capacity Measurements 17
   D. Sample Property Measurement System 20
   E. DC Electrical Resistivity Measurements 22
   F. Static Magnetic Susceptibility Measurements 23
   G. Upper Critical Magnetic Field Measurements 23

IV. RESULTS AND DISCUSSION 25
   A. Heat Capacity Measurements 25
      1. Introduction 25
      2. Results 29
         a. Sc$_5$Co$_4$Si$_{10}$ 30
         b. Sc$_5$Rh$_4$Si$_{10}$ 35
         c. Sc$_5$Ir$_4$Si$_{10}$ 35
         d. Y$_5$Ir$_4$Si$_{10}$ 40
         e. Lu$_5$Rh$_4$Si$_{10}$ 40
         f. Lu$_5$Ir$_4$Si$_{10}$ 40
         g. Y$_5$Rh$_4$Ge$_{10}$ 40
DEDICATION

to my father
I. INTRODUCTION

A. Historical Background of Superconductivity

Since its startling discovery by the Dutch physicist Kamerlingh Onnes\(^1\)-\(^4\) in 1911, the phenomenon of superconductivity has been a subject of intense interest. Our present understanding of this unique property of many solids, has taken many years to develop. However, though we have learned much about the mechanisms of superconductivity, the continual discovery of additional compounds exhibiting this property has required reevaluation of existing theories and development of new explanations. A brief historical evolution of our grasp of the basics of superconductivity presented in the following paragraphs, will hopefully provide the reader with some perspective of the phenomenon as a whole.

While performing electrical conductivity experiments on metals at low temperatures in 1911, Onnes observed the first traditional hallmark of superconductivity, namely, perfect conductivity. He noticed that as mercury was cooled its resistance disappeared abruptly at about 4.2 K. The temperature at which the resistance drops to zero is characteristic of the materials and is called the critical temperature, \(T_c\).

Meissner and Ochsenfeld discovered the second hallmark of superconductivity, perfect diamagnetism\(^5\) (Meissner effect), in 1933. They noticed that in an applied magnetic field an originally normal,
high quality sample cooled through the superconducting transition temperature, suddenly and completely expels the magnetic flux.\(^a\)

Following the discovery of the aforementioned hallmarks of superconductivity, scientists began to develop theories in an attempt to explain the observations of this fascinating phenomenon thus far. The two basic electrodynamic properties were well-described in a theory put forward in 1935 by the brothers F. and H. London,\(^6\) with two equations governing the microscopic electric and magnetic fields. Concentrating completely on the superconducting electrons instead of excitations, V. L. Ginzburg and L. D. Landau\(^7\) presented their phenomenological theory of superconductivity in 1950. The main feature of this theory was the characterization of the superconducting state by a complex "order parameter", \(\psi(r)\). The magnitude of \(\psi(r)\) below \(T_c\) is a measure of the degree of superconducting order at position \(r\); above \(T_c\), \(\psi(r)\) vanishes.

In 1953, A.B. Pippard introduced the coherence length while proposing a nonlocal generalization of the London equation.\(^8\) The precise measurements of the electronic specific heat of superconductors by Corak et al.\(^9-10\) in 1954 and 1956 and the measurements by Glover and Tinkham\(^11-12\) of electromagnetic absorption on thin lead and tin films at temperatures below \(T_c\) in 1957, established the existence of an energy gap in the energy spectrum of the superconductor.\(^b\) Lastly, an important

\(^a\)Perfect diamagnetism is only true in bulk samples and type I superconductors. For type II superconductors the magnetic flux does penetrate a finite distance, \(\lambda\) (the penetration depth), into the sample.

\(^b\)The concept of an energy gap had been suggested earlier by J. G. Daunt and K. Mendelssohn (Ref. 13).
discovery by A.A. Abrikosov\textsuperscript{14} was almost overlooked in 1957. Beginning with the Ginzburg-Landau theory, Abrikosov showed that superconducting materials can be classified as either "type I" or "type II." This classification was based on the ratio of the penetration depth and coherence length, namely, the Ginzburg-Landau parameter, $\kappa = \lambda / \xi$. Today we know most superconducting elements are type I and most superconducting compounds are type II.

All of the mentioned advancements have added much to our current understanding of superconductivity. However, the major breakthrough in our understanding of this phenomenon came with what is now hailed as the modern microscopic theory of superconductivity. This theory was put forth by Bardeen, Cooper, and Schrieffer (BCS theory)\textsuperscript{15} in 1957 and is now accepted universally. The main aspects of this theory are as follows. 1) Resulting from an electron-lattice interaction, two electrons, with opposite momenta and spins, very close to the Fermi surface, attract one another and form a bound state; these two electrons are called a Cooper pair. This attractive interaction between electrons can lead to a ground state of the entire electronic system that is separated from the excited states by an energy gap. 2) The penetration depth, $\lambda$, and the coherence length, $\xi$, emerge naturally from the BCS theory. 3) The criterion for the occurrence of superconductivity and for the magnitude of the transition temperature in an element or alloys involves the electron density of states at the Fermi level and the electron-phonon interaction. 4) The magnetic flux through a superconducting ring is quantized and the effective unit of charge is $2e$ rather than $e$. 
The above gives the reader a very brief overview of the evolution of our understanding of superconductivity. Scientists' efforts to explain this unique and interesting phenomenon have contributed greatly to our present understanding of superconductivity as well as of solids at low temperatures.

B. Ternary Superconductors

Since the first observation of superconductivity, scientists have devoted a great deal of time and energy in the search for new superconducting materials. The elements were, of course, the first to be looked at; many basic solid state texts and review papers on superconductivity include a periodic table or list indicating those superconducting elements. The investigation of alloys and binary compounds was the next step in this search. Some noted superconducting binary systems include 1) the cubic NaCl type (B1), the cubic MgCu₂ type (C15 or Laves phases), and 3) the β-W type (A15) systems. For the past thirty years, A15 compounds have dominated the class of high temperature superconductors. This system includes the compound with the highest $T_c$ to date: Nb₃Ge ($T_c = 23$ K).

Superconductivity at even higher temperatures, (including room temperature), has been a goal of scientists for many years. Unfortunately, the binary and pseudobinary compounds investigated yielded no new high $T_c$ superconductors; hence, the attention began to focus on ternary compounds as a new possible source. The fact that
ternary compounds offer an extra chemical "degree of freedom" available through substitution on the third site was one main motivation for this focus. Before continuing, it is perhaps useful to distinguish between a ternary and a pseudobinary compound: each of the three elements constituting the former has a distinct crystallographic site, whereas, in the latter, only two unique crystallographic sublattices exist, the third element being substituted for one of the other two.

To date over thirty different structures are known to contain ternary superconductors. Matthias and coworkers reported the first, Zr_{0.6}Rh_{0.285}Os_{0.105}, in 1935. Until the discovery of superconductivity in the molybdenum sulfides in 1972, ternary compounds were not the subject of intense research, although six new superconducting ternary systems had been reported up till then. The $\text{M}_x\text{Mo}_6\text{S}_8$ compounds sparked a renewed interest in ternary superconductors. Several reasons contributed to this revival of attention. Some of these compounds exhibited extremely high upper critical magnetic fields, the highest being about 600 kOe for $\text{PbMo}_6\text{S}_8$. Also, in many cases, it was found that magnetic rare earth elements could be put into the third atom "M" position in the $\text{MMo}_6\text{S}_8$ compounds without destroying the superconductivity of the ternary. The rhodium and ruthenium borides systems, $\text{MRh}_4\text{B}_4$, discovered in 1977, kept the intense interest in ternary superconductors alive. These compounds exhibited some of the fascinating properties shown by the molybdenum chalcogenides (Chevrel phases). Here too, magnetic rare earth elements could be incorporated
on the third atom "M" position of some ternary borides without disturbing the superconductivity; the best known is the reentrant superconductor ErRh$_4$B$_4$. The idea that one could have a regular sublattice of magnetic atoms and still have superconductivity was certainly novel.

Another very interesting property displayed by the Chevrel phases and the borides is the presence of transition metal clusters. In the Chevrel phases, the molybdenum atoms form slightly distorted octahedral clusters; in the borides we have either Rh$_4$ or Ru$_4$ tetrahedral clusters. The rare earth molybdenum chalcogenides and some of the ternary borides have become model systems for studying the interplay between superconductivity and long-range magnetic order.

Until recently, the interest in ternary superconductors has focused on the Chevrel phases and rhodium borides. However, the discovery of the coexistence of superconductivity and a regular sublattice of magnetic rare earth atoms has prompted the search for more ternary systems with this property. Eleven new superconducting structure types were reported in 1980 alone. The discovery of two of these new ternary systems, M$_2$Fe$_3$Si$_5$ and M$_5$Co$_4$Si$_{10}$, presented scientists with a new property. In two separate silicide phases, Lu$_2$Fe$_3$Si$_5$ and Sc$_5$Co$_4$Si$_{10}$, superconductivity still exists ($T_C = 4.7$ K or greater) in the presence of a significant amount of a magnetic 3d transition metal; 30% in the former and 21% in the latter. However, neither the Fe nor Co atom was reported to exhibit a magnetic moment in these compounds.
It is apparent that the superconducting ternary systems discovered thus far have provided scientists with many novel phenomena to explain and have caused questioning of the validity of some time-held beliefs. The extraordinary data on these systems gathered to this date will certainly challenge scientists for years to come.

For this work, the relatively new ternary system, $\text{RE}_{5}\text{T}_{4}\text{X}_{10}$, has been chosen. The results from a systematic measurement of a variety of low temperature properties such as specific heat, DC electrical resistivity, static magnetic susceptibility, and upper critical magnetic field, will be used to better characterize the superconducting compounds in this system. These experiments and the analysis thereof should clarify the origins of superconductivity in this complex family of materials. Hopefully the results will give interested scientists a better insight into ternary superconductors and the mechanisms that cause various sample behaviors.
II. $\text{Sc}_5\text{Co}_4\text{Si}_{10}$-TYPE CRYSTAL STRUCTURE

The many novel electronic and low temperature properties of the first ternary superconducting compounds$^{26-28}$ have motivated the search for additional ternary systems. The $\text{RE}_5\text{T}_4\text{X}_{10}$ series,$^{49-50}$ first reported in 1980, is one successful example of such a search. This new class of superconducting and magnetic compounds is constituted as follows: $\text{RE} =$ rare earth, including Sc and Y, $\text{T} =$ Co, Rh, Ir, or Os, and $\text{X} =$ Si or Ge. The system crystallizes in the $\text{Sc}_5\text{Co}_4\text{Si}_{10}$-type structure which is primitive tetragonal, space group $\text{P4/mbm}$, and has 38 atoms per unit cell. The crystallographic data for the $\text{Sc}_5\text{Co}_4\text{Si}_{10}$-type structure are summarized in Tables 1 and 2. Note that both the RE and X atoms occupy three crystallographically distinct sites.

The structure type may be described in two ways. 1) The projection of the $\text{Sc}_5\text{Co}_4\text{Si}_{10}$ structure along the c-axis yields Co and Si atoms in planar nets of pentagons and hexagons stacked parallel to the basal plane and connected along the c-axis by Co-Si-Co zigzag chains. The pentagon-hexagon layers are separated by layers of Sc. 2) Two distinct building blocks, namely, a trigonal prism and a tetragonal antiprism are stacked. The trigonal prism is formed by six scandium atoms centered by silicon. The tetragonal antiprism has the formula CoSc$_4$Si$_4$ and is Co-centered. It is comprised of four Sc atoms forming a rectangular face of the Sc double prism and four Si atoms having a near square planar configuration. A fifth Si atom, at the center of the Sc prism, completes these antiprisms to give CoSc$_4$Si$_5$ units. These two
Table 1. Positional (x10^4) and equivalent isotropic thermal (x10^2) parameters for Sc\textsubscript{5}Co\textsubscript{4}Si\textsubscript{10}\textsuperscript{a}

<table>
<thead>
<tr>
<th>Atom</th>
<th>Position</th>
<th>x</th>
<th>y</th>
<th>z</th>
<th>U\textsubscript{eq}(\text{Å}^2)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sc(1)</td>
<td>2(a)</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0.86(4)</td>
</tr>
<tr>
<td>Sc(2)</td>
<td>4(h)</td>
<td>1756(1)</td>
<td>6756(1)</td>
<td>1/2</td>
<td>1.06(4)</td>
</tr>
<tr>
<td>Sc(3)</td>
<td>4(h)</td>
<td>3882(1)</td>
<td>8882(1)</td>
<td>1/2</td>
<td>1.18(4)</td>
</tr>
<tr>
<td>Co</td>
<td>8(i)</td>
<td>2540(1)</td>
<td>5240(1)</td>
<td>0</td>
<td>0.86(4)</td>
</tr>
<tr>
<td>Si(1)</td>
<td>4(g)</td>
<td>679(1)</td>
<td>5679(1)</td>
<td>0</td>
<td>0.89(5)</td>
</tr>
<tr>
<td>Si(2)</td>
<td>8(i)</td>
<td>1575(1)</td>
<td>1985(1)</td>
<td>0</td>
<td>1.26(5)</td>
</tr>
<tr>
<td>Si(3)</td>
<td>8(j)</td>
<td>1638(1)</td>
<td>31(1)</td>
<td>1/2</td>
<td>1.38(5)</td>
</tr>
</tbody>
</table>

\textsuperscript{a}E.s.d.s in units of the least significant figure are given in parentheses.

Table 2. Selected bond distances (Å) in Sc\textsubscript{5}Co\textsubscript{4}Si\textsubscript{10}\textsuperscript{a}

<table>
<thead>
<tr>
<th>Bond</th>
<th>Distance</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sc(1)-Si(2)</td>
<td>4 x 3.043(2)</td>
</tr>
<tr>
<td>Si(3)-Co</td>
<td>4 x 2.968(2)</td>
</tr>
<tr>
<td>Co-Si(2)</td>
<td>4 x 2.823(2)</td>
</tr>
<tr>
<td>Sc(2)-Si(3)</td>
<td>2 x 2.783(2)</td>
</tr>
<tr>
<td>Si(1)-Sc(2)</td>
<td>2 x 2.783(2)</td>
</tr>
<tr>
<td>Si(3)-Sc(2)</td>
<td>2 x 2.831(2)</td>
</tr>
<tr>
<td>Co-Si(3)</td>
<td>2 x 2.832(2)</td>
</tr>
<tr>
<td>Sc(3)-Si(2)</td>
<td>4 x 3.060(2)</td>
</tr>
<tr>
<td>Si(1)-Sc(3)</td>
<td>4 x 2.968(2)</td>
</tr>
<tr>
<td>Si(3)-Sc(3)</td>
<td>4 x 3.028(3)</td>
</tr>
<tr>
<td>Co-Si(3)</td>
<td>4 x 3.074(2)</td>
</tr>
<tr>
<td>Sc(1)-Co</td>
<td>1 x 2.969(3)</td>
</tr>
<tr>
<td>Sc(2)-Co</td>
<td>2 x 2.842(2)</td>
</tr>
<tr>
<td>Sc(3)-Co</td>
<td>2 x 3.074(2)</td>
</tr>
<tr>
<td>Si(1)-Co</td>
<td>2 x 2.969(3)</td>
</tr>
<tr>
<td>Si(3)-Co</td>
<td>2 x 2.842(2)</td>
</tr>
<tr>
<td>Si(3)-Co</td>
<td>2 x 3.074(2)</td>
</tr>
</tbody>
</table>

\textsuperscript{a}E.s.d.s are in parentheses.
building blocks are fairly common to rare earth and transition metal binary or ternary silicides. Figure 1 indicates the structure of Sc$_5$Co$_4$Si$_{10}$ viewed approximately along the c-axis. Figure 2 shows the two basic building blocks comprising this structure.

One interesting feature of this structure is the absence of transition metal-transition metal bonds. This is quite different from what is found in the molybdenum chalcogenides$^{57}$ and rhodium borides$^{58}$ both well studied ternary systems, in which the transition metal atoms form clusters. In these two systems, the intracluster T-T distances are shorter than in the metal, whereas, in the Sc$_5$Co$_4$Si$_{10}$ structure, the shortest T-T distances are approximately 4 Å.

A couple of other facts about this class of compounds worth mentioning, are 1) the existence of quite short Co-Si distances, about 2.3 Å; these Co-Si bonds form a three-dimensional network in which each Co atom has five Si neighbors at a distance equal to the sum of their covalent radii, and 2) Sc$_5$Co$_4$Si$_{10}$ has one of the highest transition temperatures known for Co compounds.

To this date there are 15 compounds that are either superconducting or magnetic in this new ternary system. Tables 3 and 4 list all the Sc$_5$Co$_4$Si$_{10}$-type compounds with the reported critical temperatures and the year first reported.
Figure 1. Sc$_5$Co$_4$Si$_{10}$-type crystal structure looking approximately along the c-axis
Figure 2. The two basic building blocks in the Sc$_5$Co$_4$Si$_{10}$-type structure
Table 3. Superconducting compounds in the $\text{RE}_5\text{T}_4\text{X}_{10}$ system

<table>
<thead>
<tr>
<th>Compound</th>
<th>Reported $T_c$(K)</th>
<th>Year Reported</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{Sc}_5\text{Co}<em>4\text{Si}</em>{10}$</td>
<td>5.00-4.80</td>
<td>1980</td>
<td>49</td>
</tr>
<tr>
<td>$\text{Sc}_5\text{Rh}<em>4\text{Si}</em>{10}$</td>
<td>8.54-8.45</td>
<td>1980</td>
<td>49</td>
</tr>
<tr>
<td>$\text{Sc}_5\text{Ir}<em>4\text{Si}</em>{10}$</td>
<td>8.46-8.38</td>
<td>1980</td>
<td>49</td>
</tr>
<tr>
<td>$\text{Y}_5\text{Ir}<em>4\text{Ge}</em>{10}$</td>
<td>2.62-2.58</td>
<td>1980</td>
<td>49</td>
</tr>
<tr>
<td>$\text{Y}_5\text{Os}<em>4\text{Ge}</em>{10}$</td>
<td>8.68-8.41</td>
<td>1980</td>
<td>49</td>
</tr>
<tr>
<td>$\text{Y}_5\text{Ir}<em>4\text{Si}</em>{10}$</td>
<td>3.00-2.30</td>
<td>1981</td>
<td>56</td>
</tr>
<tr>
<td>$\text{Lu}_5\text{Ir}<em>4\text{Si}</em>{10}$</td>
<td>3.76-3.72</td>
<td>1981</td>
<td>56</td>
</tr>
<tr>
<td>$\text{Lu}_5\text{Rh}<em>4\text{Ge}</em>{10}$</td>
<td>2.20-1.60</td>
<td>1984</td>
<td>59</td>
</tr>
<tr>
<td>$\text{Lu}_5\text{Ir}<em>4\text{Ge}</em>{10}$</td>
<td>2.01-1.94</td>
<td>1984</td>
<td>59</td>
</tr>
<tr>
<td>$\text{Y}_5\text{Rh}<em>4\text{Ge}</em>{10}$</td>
<td>1.35-1.34$^a$</td>
<td>1984</td>
<td>59</td>
</tr>
<tr>
<td>$\text{Lu}_5\text{Rh}<em>4\text{Si}</em>{10}$</td>
<td>3.95-3.87</td>
<td>1985</td>
<td>60</td>
</tr>
</tbody>
</table>

$^a$The existence of this phase was reported in reference 59; however, the $T_c$ was not given. The $T_c$ was first reported in reference 60.

Table 4. Magnetic Compounds in the $\text{RE}_5\text{T}_4\text{X}_{10}$ system

<table>
<thead>
<tr>
<th>Compound</th>
<th>Reported $T_H$(K)</th>
<th>Year Reported</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{Tm}_5\text{Ir}<em>4\text{Si}</em>{10}$</td>
<td>1.0</td>
<td>1981</td>
<td>56</td>
</tr>
<tr>
<td>$\text{Er}_5\text{Ir}<em>4\text{Si}</em>{10}$</td>
<td>2.3</td>
<td>1981</td>
<td>56</td>
</tr>
<tr>
<td>$\text{Ho}_5\text{Ir}<em>4\text{Si}</em>{10}$</td>
<td>1.5</td>
<td>1981</td>
<td>56</td>
</tr>
<tr>
<td>$\text{Dy}_5\text{Ir}<em>4\text{Si}</em>{10}$</td>
<td>5.0</td>
<td>1981</td>
<td>56</td>
</tr>
</tbody>
</table>
III. EXPERIMENTAL DETAILS

A. Sample Preparation

All eleven superconducting samples investigated for this work were prepared from high-purity (at least 99.9%) elements by arc-melting stoichiometric amounts in a Zr-gettered argon atmosphere. The sources and purities of the starting materials are listed in the appendix. The resulting ingots were turned over and remelted two to three times, holding the arc on the sample for at least thirty seconds, to promote homogeneity. It was found that this method of synthesizing an as-cast sample worked best as trying to remelt the ingots more than three times resulted in the sample breaking apart. Mass losses were typically less than 0.4%, often much less. The samples were then sealed in quartz ampoules under 150 torr of argon and subjected to a heat treatment of 18 days at 1050°C, followed by a water quench. The resulting ingots were dull and quite brittle with fine cracks throughout the bulk of the sample. Some ingots showed a needle like structure on top, whereas others were relatively smooth.

B. Sample Characterization

Two measurements were used to characterize the samples. The first was powder X-ray diffraction work carried out on a microcomputer-controlled Rigaku powder diffractometer. The program FINAX$^6$ was used
to generate a theoretical powder diffraction pattern given the crystallographic space group, the positions of the atoms in the unit cell, and estimations of the lattice parameters. The measured X-ray patterns were then compared to the FINAX output which consists of the calculated peaks and their intensities. In most cases the agreement was quite good; however, several samples did have a few peaks unindexable to the Sc$_5$Co$_4$Si$_{10}$-type structure. The lattice parameters of each sample studied for this work were then determined by the method of least squares using 20–24 reflections including an internal silicon standard ($a = 5.43083$ Å). These are in good agreement with those reported by Braun et al.$^{56}$ and Venturini et al.$^{59}$

The ambient pressure superconducting transition temperatures ($T_c$) of the samples were determined from low frequency (about 25 Hz) ac susceptibility measurements from 1.2 K to 20 K. All samples were measured in powdered form in order to eliminate the possibility of screening effects. In most cases, the transitions were fairly sharp ($\Delta T_c$ not more than 0.2 K); however, $\Delta T_c = 0.34$ K for Y$_5$Os$_4$Ge$_{10}$. The midpoint of the transition is defined as $T_c$, whereas the 10% and 90% values were used to define the transition width. The lattice parameters, cell volume, and transition temperatures (reporting the values at 10% and 90% of the transition) of the samples studied are listed in Table 5.

---

$^c$A second superconducting phase was found in the Y$_5$Os$_4$Ge$_{10}$ sample; the transition temperature is 1.47 K. At this point however, the structure has not been determined.
Table 5. Lattice parameters for $\text{RE}_5\text{T}_4\text{X}_{10}^a$

<table>
<thead>
<tr>
<th>Compound</th>
<th>$a(\text{Å})$</th>
<th>$c(\text{Å})$</th>
<th>$a/c$</th>
<th>$V(\text{Å}^3)$</th>
<th>$T_c(\text{K})$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{Sc}_5\text{Co}<em>4\text{Si}</em>{10}$</td>
<td>3.013(2)</td>
<td>3.936(1)</td>
<td>3.052</td>
<td>568.1</td>
<td>4.82-4.67</td>
</tr>
<tr>
<td>$\text{Sc}_5\text{Rh}<em>4\text{Si}</em>{10}$</td>
<td>12.344(2)</td>
<td>4.039(1)</td>
<td>3.056</td>
<td>615.5</td>
<td>8.31-8.13</td>
</tr>
<tr>
<td>$\text{Sc}_5\text{Ir}<em>4\text{Si}</em>{10}$</td>
<td>12.335(1)</td>
<td>4.083(1)</td>
<td>3.021</td>
<td>621.2</td>
<td>8.51-8.38</td>
</tr>
<tr>
<td>$\text{Y}_5\text{Ir}<em>4\text{Si}</em>{10}$</td>
<td>12.586(4)</td>
<td>4.239(3)</td>
<td>2.969</td>
<td>671.4</td>
<td>2.25-2.17</td>
</tr>
<tr>
<td>$\text{Lu}_5\text{Rh}<em>4\text{Si}</em>{10}$</td>
<td>12.506(2)</td>
<td>4.139(2)</td>
<td>3.022</td>
<td>627.3</td>
<td>3.41-3.24</td>
</tr>
<tr>
<td>$\text{Lu}_5\text{Ir}<em>4\text{Si}</em>{10}$</td>
<td>12.475(3)</td>
<td>4.173(1)</td>
<td>2.990</td>
<td>649.4</td>
<td>3.75-3.63</td>
</tr>
<tr>
<td>$\text{Y}_5\text{Rh}<em>4\text{Ge}</em>{10}$</td>
<td>12.952(5)</td>
<td>4.274(4)</td>
<td>3.030</td>
<td>717.0</td>
<td>1.27-1.23</td>
</tr>
<tr>
<td>$\text{Y}_5\text{Ir}<em>4\text{Ge}</em>{10}$</td>
<td>12.917(3)</td>
<td>4.304(2)</td>
<td>3.001</td>
<td>718.2</td>
<td>2.77-2.57</td>
</tr>
<tr>
<td>$\text{Y}_5\text{Os}<em>4\text{Ge}</em>{10}$</td>
<td>12.983(8)</td>
<td>4.284(6)</td>
<td>3.031</td>
<td>722.1</td>
<td>9.02-8.68</td>
</tr>
<tr>
<td>$\text{Lu}_5\text{Rh}<em>4\text{Ge}</em>{10}$</td>
<td>12.848(2)</td>
<td>4.216(1)</td>
<td>3.047</td>
<td>695.9</td>
<td>2.78-2.64</td>
</tr>
<tr>
<td>$\text{Lu}_5\text{Ir}<em>4\text{Ge}</em>{10}$</td>
<td>12.823(1)</td>
<td>4.248(1)</td>
<td>3.019</td>
<td>699.1</td>
<td>2.51-2.32</td>
</tr>
</tbody>
</table>

$^a$Estimated standard deviation in parentheses.
C. Heat Capacity Measurements

Heat capacity measurements were carried out at temperatures ranging from 0.5 K to 30 K in a heat pulse-type semi-adiabatic calorimeter; details are given elsewhere. Two features of the calorimeter are (1) a \( ^3\text{He} \) pot/bellows together with a mechanical heat switch serving to cool the sample without exchange gas, and (2) a continuously operating \( ^4\text{He} \) cold plate. The cryostat is designed as an insert to existing helium dewar and gas handling systems.

As Figure 3 indicates, the calorimeter is comprised of the vacuum, \( ^3\text{He} \), and \( ^4\text{He} \) systems. The vacuum can is pumped overnight and typically achieves a vacuum around 5 x 10^{-6} \text{ torr}. The \( ^4\text{He} \) system has an opening on top of the flange to allow \( ^4\text{He} \) to flow through a capillary, with a wire inserted, to a copper block partially filled with sintered copper. The \( ^4\text{He} \) system is pumped throughout the entire experiment thus providing a continuous circulation of \( ^4\text{He} \) as long as the liquid \( ^4\text{He} \) covers the flange. The temperature of the \( ^3\text{He} \) condenser / \( ^4\text{He} \) evaporator (coneva) is thus maintained at about 1.2 K. The \( ^3\text{He} \) system operates as follows: \( ^3\text{He} \) gas enters the calorimeter through the top; upon reaching the coneva it condenses. Via another capillary, it then flows to the \( ^3\text{He} \) pot/bellows where it collects. When it is necessary to achieve temperatures below about 1.2 K, the \( ^3\text{He} \) system is pumped, thereby providing a continuous circulation of \( ^3\text{He} \) enabling the \( ^3\text{He} \) pot/bellows (and hence the sample) to cool down to about 0.5 K.
1. Flanges
2. Indium O-ring
3. Vacuum can
4. Vacuum can pumping line
5. Coneva
   A. He\textsuperscript{3} condenser
   B. He\textsuperscript{4} evaporator
6. He\textsuperscript{3} precooler (partially shown)/He\textsuperscript{3} return line
7. He\textsuperscript{3} inlet
8. He\textsuperscript{3} pot
9. He\textsuperscript{3} pumping line
10. He\textsuperscript{4} inlet (partially shown)
11. He pumping line
12. Mechanical heat switch actuator rod
13. Radiation shield support
14. Radiation shield
15. Nylon addenda support
16. Gold plated heat switch
17. Gold plated addenda
   A. Upper half
   B. Lower half

Figure 3. Lower portion of heat capacity cryostat
Details relating to the heat capacity measurements are as follows. The masses of the superconducting samples investigated ranged between 2.1 and 3.3 g. The sample is clamped between the two halves of the gold-plated Cu addenda. This arrangement provides good thermal and mechanical contact. The sample holder (addenda) is then supported by a rigid nylon support which has a low thermal conductivity. Ambient temperature control is provided by a radiation shield with a heater, slipped over the sample area, and a mechanical heat switch. A four probe method is used to simultaneously measure the current and voltage during each heat pulse of a 1000 Ω Pt-W heater wound on the bottom half of the sample holder. A commercial digital timer measures the duration of the heat pulse.

The thermometry consists of the sample thermometer which is a germanium resistance thermometer (GRT), the He³ pot thermometer (GRT), the He⁴ pot thermometer (Pt), and a commercially available potentiometric conductance bridge. The temperature change of the sample during a heat pulse is determined by monitoring the sample's GRT conductance on a strip chart recorder. The main source of error in determining the heat capacity of the sample is believed to lie in this graphical procedure.

The thermometer calibrations are incorporated in a program written for a HP-97 calculator. This program calculates the total heat capacity (heat capacity of the addenda plus the sample) utilizing the values of the parameters obtained for each data point; these parameters include the duration of the heat pulse, the voltage across the sample, the
voltage across a standard 1000 Ω resistor, and the temperature change of the sample during a heat pulse. The total heat capacity is later used in a general heat capacity program to determine and analyze the specific heat of the sample.

D. Sample Property Measurement System

The DC electrical resistivity, static magnetic susceptibility, and upper critical magnetic field measurements were performed on a fully automated sample property measurement system (Figure 4) from Quantum Design Inc. This versatile measurement system is centered around a basic, temperature-controlled module, allowing the user to utilize different detection systems with the same Temperature Control Module (TCM). Detectors to study magnetic, electrical, or resonance properties of the sample are a few examples.

The model in our laboratory includes a specific design for a magnetic detection system. In order to study the magnetic properties of small samples, a SQUID detector is incorporated into the TCM. The magnetic property measurement system (MPMS) combines seven major control systems:

1) The Temperature Control Module enabling the user to measure at temperatures ranging from 2.1 K to 400 K.
2) Superconducting Magnet System allowing one to achieve a maximum magnetic field of ± 20 kG.
3) SQUID Detector System.
4) Sample Handling System allowing the user to
Figure 4. Interior of the sample property measurement system
automatically manipulate any inserted sample.

5) Gas Handling System providing gas flow control during all phases of temperature control.

6) Liquid Helium System providing cooling for the SQUID, magnet and operation below room temperature.

7) Controlling computer HP-85.

E. DC Electrical Resistivity Measurements

Excluding Y_{50}Os_{4}Ge_{10}, all samples used for this measurement were rectangular parallelepiped having approximate dimensions (1.5-4.9) x (1.6-2.6) x (1.0-2.8) mm$^3$. The Y_{50}Os_{4}Ge_{10} sample used was an irregular piece with an average height of 2.6 mm. These measurements were made using a vernier caliper and a microscope.

The static electrical resistivity data were taken using a standard four-probe technique with temperature control provided by the sample property measurement system discussed previously. Four leads were spot welded onto all samples. The method of van der Pauw$^{63}$ was used to calculate the resistivity at room temperature for Y_{50}Os_{4}Ge_{10}. Using a constant current source, a current was first sent through two wires in one direction and the voltage drop, $V_+$, was measured across the remaining two wires. The current direction was then reversed and $V_-$ was determined. The voltage used was the average of $V_+$ and $V_-$. Since the sample current was essentially constant over the entire temperature range, $\rho(T)/\rho(300 \text{ K}) = V(T)/ V(300 \text{ K}) = R(T)/ R(300 \text{ K})$. One note: the
resistivity data for Sc$_5$Co$_4$Si$_{10}$, Sc$_5$Rh$_4$Si$_{10}$, Sc$_5$Ir$_4$Si$_{10}$, and Y$_5$Os$_4$Ge$_{10}$ were taken interactively (manually) for each temperature; however, a sequence was available to determine the resistivity data of the remaining samples automatically. In these cases, the output generated by the HP-85 resulted in a value for the resistance of the sample.

F. Static Magnetic Susceptibility Measurements

The static magnetic susceptibility measurements were performed on the sample property measurement system described already. The samples used were irregular pieces and had a mass on the order of 100 mg. The samples were suspended from the bottom of the cryostat by a piece of dental floss. The cryostat was then inserted into the susceptometer and a sequence was activated to begin measuring the magnetic susceptibility of the sample automatically in an applied magnetic field of 5000 Oe. The temperature region investigated ranged from 2.6 K to 380 K.

G. Upper Critical Magnetic Field Measurements

The samples used for low temperature upper critical magnetic field measurements were roughly rectangular in shape with lengths approximately 5 mm, cross sectional areas around 1.5 mm$^2$, and masses between 10 and 70 mg. The rectangles were then placed in the center of a nylon sleeving. Dental floss was used to insure the sample would not slip within the sleeving by tying a piece just above and below the
sample. Both the sleeving and dental floss have been shown to have a negligible magnetic signal.

The nylon sleeving was attached to the bottom of a cryostat which was then inserted into the susceptometer; a sequence was activated to begin the measurement. Temperature control was provided by the sample property measurement system outlined earlier. For a set temperature below $T_c$ of the sample, the sequence enabled the magnetization of the sample for various applied magnetic fields (up to 20 kOe) to be measured automatically. For each new set temperature the sequence had to be restarted.

The result of these measurements for each compound studied was a set of magnetization versus applied magnetic field curves. The upper critical field for each temperature was established by determining where each $M$ vs. $H$ curve crossed the $H$-axis (where $M = 0$).
IV. RESULTS AND DISCUSSION

A. Heat Capacity Measurements

1. Introduction

Knowledge of the low temperature heat capacity is exceptionally valuable in the study of many materials. It provides important information in numerous areas, such as lattice vibrations, electronic distributions, energy levels in magnetic materials, and order-disorder phenomena in molecules. In the case of superconductors, the specific heat is an excellent confirmation of the bulk nature of the superconducting state. Many theories have been proposed in an attempt to explain the behaviors exhibited by the heat capacity of many substances. One of the earliest empirical generalizations concerning the specific heats of solids was put forth by Dulong and Petit (cited in Ref. 16) in 1819 with the theoretical justification advanced by Boltzmann (cited in Ref. 16) in 1871. Unfortunately, this theory failed at low temperatures. In 1907 Einstein showed why this was the case by applying quantum theory to the thermal vibrations of atoms. He considered a very simple model of lattice vibrations, in which all the atoms vibrate independently of one another with the same frequency, \( \nu_0 \). The qualitative aspects of Einstein's theory were confirmed quite well by systematic calorimetric measurements undertaken at low temperatures at

\[ \text{The theoretical justification was based on the theorem of equipartition of energy developed by Boltzmann.} \]
that time. However, the quantitative agreement was not satisfactory. His theory predicted that at low temperatures the specific heat should decrease more rapidly than was actually found experimentally. In essence, Einstein's model was too simplified.

Utilizing Einstein's fundamental approach of applying quantum ideas to thermal vibrations in atoms as a stepping stone, Debye arrived at a better description of lattice vibrational frequencies. At low temperatures, the quantization of vibrational energy indicates that only the low frequency modes of the lattice vibrations will be measurably excited; these usually correspond to the acoustic modes of a solid. Debye thus calculated the distribution of frequencies $g(v)$ which results from the propagation of acoustic waves of permitted wavelengths in a continuous isotropic solid and assumed the same distribution to be valid in a crystal. He then proceeded to calculate the heat capacity at constant volume, $C_v$. At very low temperatures ($T < \Theta_D/10$), the expression for $C_v$ derived by Debye results in a very simple form

$$C_v = \frac{12\pi^4 N r k_B T^3}{5 \Theta_D^3}$$

(1)

where $\Theta_D$ is the Debye temperature, $N$ is Avogadro's number, $r$ is the number of atoms per molecule, and $k_B$ is Boltzmann's constant. Thus the

---

*Born and Von Karman also arrived at a better description; however, Debye’s model is simpler.*

*${\Theta}_D = h\nu/k_B$; $\nu_D$ is an upper limit to the frequency of the lattice vibrations; this is obtained from the normalizing condition that the total number of modes is equal to $3rN$ per mole.*
above equation gives one an approximation at low temperatures for the specific heat due to the lattice. At high temperatures, \( T >> \Theta_D \), the specific heat approaches the value found by Dulong and Petit. At intermediate temperatures, however, the Debye function must be evaluated numerically.

The conduction electrons also contribute to the total specific heat of a solid. In comparison to the lattice contribution, the electronic contribution to the heat capacity of a metal at room temperature is negligible; however, at low temperatures the situation is very different. Initially, the methods used in the classical kinetic theory of gases were applied by Drude, Lorentz, and others (cited in Ref. 16) to explain how the conduction electrons were responsible for the high thermal and electrical conductivities found in metals. However, using the equipartition theorem, the calculated total specific heat of a metal at room temperature was found to be larger than the experimental value. This measured value was totally accounted for by the lattice contribution. As in the case of the lattice, the use of quantum theory provided an answer to the dilemma. In 1928, after Sommerfeld applied quantum statistics to free electrons in a metal, the reason for the small electronic specific heat become evident. Thus the application of Fermi-Dirac statistics to the conduction electrons results in the following expression for the electronic specific heat at low temperatures (i.e. \( T << T_F \)).

\( \varepsilon_{T_F} \) is called the Fermi temperature; \( T_F = \varepsilon_F / k_B \) where \( \varepsilon_F \) is the Fermi energy.
\[ C_e = \frac{2\pi^2 N r k_B^2 N(0) T}{3} = \gamma T \]  

where \( N(0) \) is the enhanced electronic density of states per spin at the Fermi surface. At higher temperatures, the calculations are quite involved.

One must realize, however, that the expressions given above for the lattice and electronic heat capacities at low temperatures are certainly simplified and a relatively crude approximation to the actual behavior in real solids. As the material investigated becomes more complicated (more complex phonon spectrum, several types of atoms, etc.) the less these expressions fit the true specific heat and the greater the need for a more complete treatment of the problem.

Just a few words about the heat capacity of superconductors and then the specific heat data of the \( \text{Sc}_5\text{Co}_4\text{Si}_{10} \)-type compounds will be presented. Shortly after the discovery of superconductivity, specific heat measurements made on these new superconductors showed no difference between the heat capacity in the normal state, \( C_n \), and the heat capacity in the superconducting state, \( C_s \). With improvements in thermometry, Keesom and van Laer\(^\text{64}\) discovered the discontinuity (a jump) in the specific heat of tin at the transition temperature. This feature is now found in all specific heat measurements of bulk superconductors. Also, according to early specific heat measurements\(^9\text{--}^{10}\) and the predictions of the BCS theory,\(^15\) the electronic contribution to \( C_s \), \( C_{es} \), goes approximately as \( a \exp(-b/T) \) where \( a \) and \( b \) are positive constants (the lattice contribution is assumed to remain the same below \( T_C \) as above).
This expression implies the existence of an energy gap in the superconducting state. As more complicated compounds are investigated, however, the behavior of $C_{es}$ can deviate substantially from the BCS predictions.

2. Results

The heat capacity data for the superconducting compounds belonging to the ternary system $RE_5T_4X_{10}$ ($RE = Sc, Y, or Lu, T = Co, Rh, Ir, or Os, and X = Si or Ge$) are presented in Figures 5 through 26. For each of the eleven samples studied there are two graphs: 1) $C$ vs. $T$ over the entire temperature range investigated with an inset of $C$ vs. $T$ focusing on the specific heat jump at the transition temperature and 2) $C/T$ vs. $T^2$ over the entire temperature range investigated with an inset of $C/T$ vs. $T^2$ emphasizing the superconducting transition. We will first discuss the low temperature heat capacity results for the samples individually and then point out any systematic trends discovered. The method of taking the heat capacity data has been treated in detail in Chapter III. For each compound, the total heat capacity, after correcting for the addenda, was expressed as

$$C = C_e + C_l$$

(3)

where $C_e$ is the usual electronic contribution and $C_l$ is the lattice contribution. The heat capacity data from above $T_c$ to 16 K were then fitted to an equation of the form

$$C_n = \gamma_n T + \beta_n T^3 + \alpha_n T^5$$

(4)
where \( \gamma_n \) is the electronic specific heat coefficient in the normal state, \( \beta_n \) is the lattice specific heat coefficient in the normal state, and \( \alpha_n \) is a term to account for the anharmonicity of the lattice. Using these coefficients, we calculated \( N(0) \), the enhanced density of electronic states per spin at the Fermi level,

\[
N(0) = \frac{3\gamma_n}{2\pi^2\hbar^2k_B^2}
\]

as well as the Debye temperature \( (T < \Theta_D/10) \),

\[
\Theta_D^3 = \frac{12\pi^4Nrk_B}{5\beta_n}
\]

for each compound. In the above equations, \( N \) is Avogadro's number, \( r \) is the number of atoms per formula unit, and \( k_B \) is Boltzmann's constant.

In order to calculate \( \lambda \), the electron-phonon coupling constant for each sample, McMillan's formula\(^ {65} \) with \( \mu^* = 0.1 \) was used (\( \mu^* \) is the Coulomb pseudopotential of Morel and Anderson\(^ {66} \), i.e. the Coulomb coupling constant):

\[
\lambda = \frac{1.04 + \mu^* \ln(\Theta_D/1.45T_C)}{(1 - 0.62\mu^*\ln(\Theta_D/1.45T_C)) - 1.04}
\]

The data for all samples are tabulated in Tables 6 and 7.

a. Sc\(_5\)Co\(_4\)Si\(_{10}\) The low temperature heat capacity data for Sc\(_5\)Co\(_4\)Si\(_{10}\) (from 1.6 K to 29 K) are presented in Figures 5 and 6. The inset of the C vs. T graph clearly indicates that the calorimetric \( T_C \) is
Table 6. Superconducting and normal state properties of the RE$_5$T$_4$X$_{10}$ compounds

<table>
<thead>
<tr>
<th>Compound</th>
<th>MW (g/mole)</th>
<th>Tc (K)</th>
<th>ΔC (mJ/mol-K)</th>
<th>γn (mJ/mol-K$^2$)</th>
<th>βn (mJ/mol-K$^4$)</th>
<th>αn (mJ/mol-K$^6$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sc$_5$Co$<em>4$Si$</em>{10}$</td>
<td>741.4</td>
<td>4.89</td>
<td>160</td>
<td>30.9</td>
<td>0.182</td>
<td>4.14x10$^{-4}$</td>
</tr>
<tr>
<td>Sc$_5$Rh$<em>4$Si$</em>{10}$</td>
<td>917.3</td>
<td>8.43</td>
<td>400</td>
<td>17.1</td>
<td>0.412</td>
<td>5.17x10$^{-4}$</td>
</tr>
<tr>
<td>Sc$_5$Ir$<em>4$Si$</em>{10}$</td>
<td>1274.5</td>
<td>8.58</td>
<td>250</td>
<td>9.93</td>
<td>0.571</td>
<td>6.67x10$^{-4}$</td>
</tr>
<tr>
<td>Y$_5$Ir$<em>4$Si$</em>{10}$</td>
<td>1494.3</td>
<td>2.29</td>
<td>55</td>
<td>23.1</td>
<td>0.627</td>
<td>1.17x10$^{-3}$</td>
</tr>
<tr>
<td>Lu$_5$Rh$<em>4$Si$</em>{10}$</td>
<td>1567.3</td>
<td>3.45</td>
<td>112</td>
<td>23.6</td>
<td>1.10</td>
<td>2.04x10$^{-3}$</td>
</tr>
<tr>
<td>Lu$_5$Ir$<em>4$Si$</em>{10}$</td>
<td>1924.6</td>
<td>3.77</td>
<td>124</td>
<td>23.4</td>
<td>0.752</td>
<td>3.95x10$^{-3}$</td>
</tr>
<tr>
<td>Y$_5$Rh$<em>4$Ge$</em>{10}$</td>
<td>1582.1</td>
<td>1.25</td>
<td>34</td>
<td>21.2</td>
<td>0.738</td>
<td>6.37x10$^{-3}$</td>
</tr>
<tr>
<td>Y$_5$Ir$<em>4$Ge$</em>{10}$</td>
<td>1939.3</td>
<td>2.75</td>
<td>85</td>
<td>25.4</td>
<td>0.824</td>
<td>6.27x10$^{-3}$</td>
</tr>
<tr>
<td>Y$_5$Os$<em>4$Ge$</em>{10}$</td>
<td>1931.1</td>
<td>9.10</td>
<td>570</td>
<td>12.9</td>
<td>1.84</td>
<td>3.48x10$^{-4}$</td>
</tr>
<tr>
<td>Lu$_5$Rh$<em>4$Ge$</em>{10}$</td>
<td>2012.4</td>
<td>2.74</td>
<td>99</td>
<td>24.6</td>
<td>1.15</td>
<td>1.13x10$^{-2}$</td>
</tr>
<tr>
<td>Lu$_5$Ir$<em>4$Ge$</em>{10}$</td>
<td>2369.6</td>
<td>2.54</td>
<td>77</td>
<td>20.0</td>
<td>1.43</td>
<td>1.06x10$^{-2}$</td>
</tr>
</tbody>
</table>
Table 7. Superconducting and normal state properties of the \( \text{Re}_5\text{T}_4\text{X}_{10} \) compounds

<table>
<thead>
<tr>
<th>Compound</th>
<th>( \Delta C )</th>
<th>( \gamma_{nTc} )</th>
<th>( N(0) )</th>
<th>( \Theta_D )</th>
<th>( \lambda )</th>
<th>rmsd&lt;sup&gt;a&lt;/sup&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{Sc}_5\text{Co}<em>4\text{Si}</em>{10} )</td>
<td>1.08</td>
<td>0.35</td>
<td>580</td>
<td>0.47</td>
<td>0.047</td>
<td></td>
</tr>
<tr>
<td>( \text{Sc}_5\text{Rh}<em>4\text{Si}</em>{10} )</td>
<td>2.82</td>
<td>0.19</td>
<td>450</td>
<td>0.60</td>
<td>0.019</td>
<td></td>
</tr>
<tr>
<td>( \text{Sc}_5\text{Ir}<em>4\text{Si}</em>{10} )</td>
<td>2.96</td>
<td>0.11</td>
<td>400</td>
<td>0.62</td>
<td>0.026</td>
<td></td>
</tr>
<tr>
<td>( \text{Y}_5\text{Ir}<em>4\text{Si}</em>{10} )</td>
<td>1.05</td>
<td>0.26</td>
<td>390</td>
<td>0.44</td>
<td>0.031</td>
<td></td>
</tr>
<tr>
<td>( \text{Lu}_5\text{Rh}<em>4\text{Si}</em>{10} )</td>
<td>1.38</td>
<td>0.26</td>
<td>320</td>
<td>0.50</td>
<td>0.036</td>
<td></td>
</tr>
<tr>
<td>( \text{Lu}_5\text{Ir}<em>4\text{Si}</em>{10} )</td>
<td>1.40</td>
<td>0.26</td>
<td>370</td>
<td>0.50</td>
<td>0.026</td>
<td></td>
</tr>
<tr>
<td>( \text{Y}_5\text{Rh}<em>4\text{Ge}</em>{10} )</td>
<td>1.28</td>
<td>0.24</td>
<td>370</td>
<td>0.40</td>
<td>0.036</td>
<td></td>
</tr>
<tr>
<td>( \text{Y}_5\text{Ir}<em>4\text{Ge}</em>{10} )</td>
<td>1.22</td>
<td>0.28</td>
<td>360</td>
<td>0.47</td>
<td>0.054</td>
<td></td>
</tr>
<tr>
<td>( \text{Y}_5\text{Os}<em>4\text{Ge}</em>{10} )</td>
<td>4.86</td>
<td>0.14</td>
<td>270</td>
<td>0.75</td>
<td>0.016</td>
<td></td>
</tr>
<tr>
<td>( \text{Lu}_5\text{Rh}<em>4\text{Ge}</em>{10} )</td>
<td>1.54</td>
<td>0.26</td>
<td>310</td>
<td>0.48</td>
<td>0.059</td>
<td></td>
</tr>
<tr>
<td>( \text{Lu}_5\text{Ir}<em>4\text{Ge}</em>{10} )</td>
<td>1.52</td>
<td>0.22</td>
<td>300</td>
<td>0.48</td>
<td>0.036</td>
<td></td>
</tr>
</tbody>
</table>

<sup>a</sup>This column gives the root mean square deviation of the fit to the heat capacity data.
Figure 5. Specific heat versus temperature for Sc$_5$Co$_4$Si$_{10}$. The inset focuses on the specific heat jump.
Figure 6. Specific heat divided by temperature $T$ versus $T^2$ for $\text{Sc}_5\text{Co}_4\text{Si}_{10}$. The inset focuses on the specific heat jump
4.89 K, whereas the heat capacity jump, $\Delta C$, is 160 mJ/mol-K. Analysis of the data yields a value for $\Delta C/\gamma_n T_c = 1.08$, somewhat reduced from the BCS value of 1.43, as well as a very high Debye temperature, $\Theta_D = 580$ K. The value of $\lambda$ indicates the sample is probably an intermediate-coupled superconductor.

b. Sc$_5$Rh$_4$Si$_{10}$ The low temperature heat capacity data (from 1.2 K to 30 K) for Sc$_5$Rh$_4$Si$_{10}$ are presented in Figures 7 and 8. The values of $T_c = 8.43$ K and $\Delta C = 400$ mJ/mol-K are evident from the graphs. Fitting the heat capacity data in the normal state with a modified Debye model yielded physically unreasonable results for the parameters $\gamma_n$ and $\beta_n$. However, attempting to fit the normal state entropy (from above $T_c$ to 28 K) to an equation of the form

$$S_n = \gamma_n T + \frac{1}{3} \beta_n T^3 + \frac{1}{5} \alpha_n T^5$$

yielded more reasonable values. As for Sc$_5$Co$_4$Si$_{10}$, the value of the Debye temperature for this sample, $\Theta_D = 450$ K, is quite large compared to most ternary superconducting compounds. A couple of interesting items to note are the values of 1) $\Delta C/\gamma_n T_c = 2.82$, which is much larger than the BCS value, and 2) $\lambda = 0.60$. The values of these two parameters indicate that Sc$_5$Rh$_4$Si$_{10}$ is a strong-coupled superconductor.

c. Sc$_5$Ir$_4$Si$_{10}$ The low temperature heat capacity data (0.5 K to 30 K) for Sc$_5$Ir$_4$Si$_{10}$ are presented Figures 9 and 10. The graphs clearly indicate values of $T_c = 8.57$ K and $\Delta C = 250$ mJ/mol-K. As for Sc$_5$Rh$_4$Si$_{10}$, the normal state entropy rather than the heat capacity data above $T_c$ for this compound had to be fit in order to arrive at
Figure 7. Specific heat versus temperature for Sc$_5$Rh$_4$Si$_{10}$. The inset focuses on the specific heat jump.
Figure 8. Specific heat divided by temperature $T$ versus $T^2$ for $\text{Sc}_5\text{Rh}_4\text{Si}_{10}$. The inset focuses on the specific heat jump.
Figure 9. Specific heat versus temperature for Sc$_5$Ir$_4$Si$_{10}$. The inset focuses on the specific heat jump.
Figure 10. Specific heat divided by temperature $T$ versus $T^2$ for $\text{Sc}_5\text{Ir}_4\text{Si}_{10}$. The inset focuses on the specific heat jump.
reasonable values for the normal state parameters. The value of the Debye temperature, $\Theta_D = 400$ K, though not as large as the previous two samples, is still high. However, the data for Sc$_5$Ir$_4$Si$_{10}$ yield even higher values for $\Delta C/\gamma T_c = 2.96$ and $\lambda = 0.62$ than for Sc$_5$Rh$_4$Si$_{10}$. Again, one may draw the same conclusion: Sc$_5$Ir$_4$Si$_{10}$ is a strong-coupled superconductor.

d. Y$_5$Ir$_4$Si$_{10}$ The low temperature heat capacity data (from 0.6 K to 30 K) for Y$_5$Ir$_4$Si$_{10}$ are presented in Figures 11 and 12. From the graphs one notices $T_c = 2.29$ K and $\Delta C = 55$ mJ/mol-K. The ratio $\Delta C/\gamma T_c = 1.05$ for this compound is less than the BCS value. The Debye temperature is close to that of Sc$_5$Ir$_4$Si$_{10}$ having a value of 390 K.

e. Lu$_5$Rh$_4$Si$_{10}$ The low temperature heat capacity data (from 0.8 K to 29 K) for Lu$_5$Rh$_4$Si$_{10}$ are presented in Figures 13 and 14. Figure 13 clearly indicates that $T_c = 3.45$ K and $\Delta C = 112$ mJ/mol-K. The ratio $\Delta C/\gamma T_c = 1.38$ is quite close to the BCS value. Fitting the heat capacity data above $T_c$ yields a relatively large value for $\gamma_n = 1.10$ mJ/mol-K$^2$ and a Debye temperature of 320 K.

f. Lu$_5$Ir$_4$Si$_{10}$ The low temperature heat capacity data (from 0.7 K to 29 K) for Lu$_5$Ir$_4$Si$_{10}$ are presented in Figures 15 and 16. The values of $T_c = 3.77$ K and $\Delta C = 124$ mJ/mol-K are evident from the graphs. Compared to the BCS value of 1.43, the value of $\Delta C/\gamma T_c = 1.40$ for this compound is quite close. A value of $\Theta_D = 370$ K is obtained from the fit of the normal state data.

g. Y$_5$Rh$_4$Ge$_{10}$ The low temperature heat capacity data (from 0.6 K to 30 K) for Y$_5$Rh$_4$Ge$_{10}$ are presented in Figures 17 and 18. These
Figure 11. Specific heat versus temperature for $Y_5\text{Ir}_4\text{Si}_{10}$. The inset focuses on the specific heat jump.
Figure 12. Specific heat divided by temperature $T$ versus $T^2$ for $Y_5\text{Ir}_4\text{Si}_{10}$. The inset focuses on the specific heat jump.
Figure 13. Specific heat versus temperature for Lu$_5$Rh$_4$Si$_{10}$. The inset focuses on the specific heat jump.
Figure 14. Specific heat divided by temperature $T$ versus $T^2$ for Lu$_5$Rh$_4$Si$_{10}$. The inset focuses on the specific heat jump.
Figure 15. Specific heat versus temperature for Lu$_5$Ir$_4$Si$_{10}$. The inset focuses on the specific heat jump.
Figure 16. Specific heat divided by temperature $T$ versus $T^2$ for Lu$_5$Ir$_4$Si$_{10}$. The inset focuses on the specific heat jump.
Figure 17. Specific heat versus temperature for $Y_5 Rh_4 Ge_{10}$. The inset focuses on the specific heat jump.
Figure 18. Specific heat divided by temperature $T$ versus $T^2$ for $Y_5$Rh$_4$Ge$_{10}$. The inset focuses on the specific heat jump...
figures indicate that \( T_C = 1.25 \text{ K} \) and \( \Delta C = 34 \text{ mJ/mol-K} \). The calorimetric transition for this compound is quite sharp being about 0.05 K wide. The Debye temperature for this material has a value of 370 K.

h. \( \text{Y}_5\text{Ir}_4\text{Ge}_{10} \) The low temperature heat capacity data (from 0.6 K to 30 K) for \( \text{Y}_5\text{Ir}_4\text{Ge}_{10} \) are presented in Figures 19 and 20. It is evident from the graphs that \( T_C = 2.75 \text{ K} \) and \( \Delta C = 85 \text{ mJ/mol-K} \). Following \( \text{Sc}_5\text{Co}_4\text{Si}_{10} \), \( \text{Y}_5\text{Ir}_4\text{Ge}_{10} \) has the second highest value for \( \gamma_n = 25.4 \text{ mJ/mol-K}^2 \). The value of \( \beta_n = 0.824 \text{ mJ/mol-K}^4 \) obtained from fitting the normal state data yields a \( \Theta_D = 360 \text{ K} \).

i. \( \text{Y}_5\text{Os}_4\text{Ge}_{10} \) The low temperature heat capacity data (from 0.6 K to 30 K) are presented in Figures 21 and 22. One obtains values of \( T_C = 9.10 \text{ K} \) and \( \Delta C = 570 \text{ mJ/mol-K} \) from the graphs. As with the normal state specific heat data for \( \text{Sc}_5\text{Rh}_4\text{Si}_{10} \) and \( \text{Sc}_5\text{Ir}_4\text{Si}_{10} \), it was difficult to fit the heat capacity data above \( T_C \) and arrive at reasonable values for \( \gamma_n, \beta_n, \) and \( \alpha_n \). Once again, the normal state entropy data were fit instead. Utilizing the parameters from the fit yielded values of 4.86 for \( \Delta C/\gamma_n T_C \), quite large compared to the BCS value of 1.43, and 0.75 for \( \lambda \). Note also the relatively small values for \( \gamma_n = 9.93 \text{ mJ/mol-K} \) and \( \Theta_D = 270 \text{ K} \). The same conclusion may be drawn as for \( \text{Sc}_5\text{Rh}_4\text{Si}_{10} \) and \( \text{Sc}_5\text{Ir}_4\text{Si}_{10} \); \( \text{Y}_5\text{Os}_4\text{Ge}_{10} \) is a strong-coupled superconductor. One also notes the existence of a second superconducting phase in this sample, having a \( T_C = 1.47 \text{ K} \). The presence of a heat capacity jump at this temperature confirms the bulk nature of the superconductivity of this unknown phase. The phase is yet to be determined.
Figure 19. Specific heat versus temperature for $Y_5Ir_4Ge_{10}$. The inset focuses on the specific heat jump.
Figure 20. Specific heat divided by temperature T versus $T^2$ for $Y_5Ir_4Ge_{10}$. The inset focuses on the specific heat jump.
Figure 21. Specific heat versus temperature for Y$_5$Os$_4$Ge$_{10}$. The inset focuses on the specific heat jump.
Figure 22. Specific heat divided by temperature $T$ versus $T^2$ for $Y_5Os_4Ge_{10}$. The inset focuses on the specific heat jump.
j. **Lu$_5$Rh$_4$Ge$_{10}$** The low temperature heat capacity data (from 0.6 K to 29 K) for Lu$_5$Rh$_4$Ge$_{10}$ are presented in Figures 23 and 24. A $T_c = 2.74$ K and a $\Delta C = 105$ mJ/mol-K are evident from these figures. Fitting the heat capacity data above $T_c$ yields a large value for $\beta_n$ of 1.15 mJ/mol-K$^4$ and hence, a relatively small value of $\Theta_D = 310$ K. The value of $\alpha_n$ is extremely high giving a 44% contribution of the anharmonic term to the total heat capacity at 10 K.

k. **Lu$_5$Ir$_4$Ge$_{10}$** The low temperature heat capacity data (from 1 K to 29 K) for Lu$_5$Ir$_4$Ge$_{10}$ are presented in Figures 25 and 26. It is evident from these graphs that $T_c = 2.54$ K and $\Delta C = 77$ mJ/mol-K. Next to Y$_5$Os$_4$Ge$_{10}$, this sample has the second highest value of $\beta_n = 1.43$ mJ/mol-K$^2$ and hence, the second lowest value of $\Theta_D = 300$ K. Note the large value of $\alpha_n = 1.06 \times 10^{-2}$ mJ/mol-K$^6$. This yields a 39% contribution at 10 K to the total normal state heat capacity due to the anharmonic term.

3. Discussion

a. **Normal state** Having briefly presented the individual low temperature heat capacity of the superconducting compounds in the RE$_5$T$_4$X$_{10}$ system, we will now concentrate on any systematic trends observed in these data. Tables 6 and 7 present the normal state data for each compound studied.

One obvious trend is exhibited by the high $T_c$ materials, Sc$_5$Rh$_4$Si$_{10}$, Sc$_5$Ir$_4$Si$_{10}$, and Y$_5$Os$_4$Ge$_{10}$. As noted previously, for each of these compounds fitting the normal state heat capacity data with a
Figure 23. Specific heat versus temperature for Lu$_5$Rh$_4$Ge$_{10}$. The inset focuses on the specific heat jump.
Figure 24. Specific heat divided by temperature $T$ versus $T^2$ for Lu$_5$Rh$_4$Ge$_{10}$. The inset focuses on the specific heat jump.
Figure 25. Specific heat versus temperature for Lu$_5$Ir$_4$Ge$_{10}$. The inset focuses on the specific heat jump
Figure 26. Specific heat divided by temperature $T$ versus $T^2$ for Lu$_5$Ir$_4$Ge$_{10}$. The inset focuses on the specific heat jump.
modified Debye model yielded physically unrealistic results for the normal state parameters $\gamma_n$ and $\beta_n$. Because of the high transition temperatures of these samples, an extrapolation of the above fit below $T_C$ might not be reliable. However, although the normal state data of the low $T_C$ Sc$_2$Co$_4$Si$_{10}$-type compounds seem to be reasonably well described by the modified Debye model (the fits yield reasonable values for $\gamma_n$ and $\beta_n$), the fits were not as good (see Table 7) as for other superconducting samples fit in this manner.\textsuperscript{62} This indicates that the extrapolation from high temperatures is most likely not the main cause. Quenching the $T_C$'s by the application of a magnetic field would be useful in understanding the normal state behavior of these compounds.

A more probable reason evident from the inability to fit the normal state data to equation 4, is that the phonon spectrum of these structurally complex compounds is too complicated to be adequately described by the Debye model which utilizes just one characteristic temperature. This problem has already been noted in other ternary compounds as well as the high $T_C$ A-15 materials.\textsuperscript{67-70} The high $T_C$ materials investigated thus far seem to have an excess of phonon modes at the low frequencies.

In view of the technological importance of the A-15 compounds, much attention has been focused on obtaining a better model of the phonon density of states for these high $T_C$ materials thereby arriving at a physically more reasonable description of the lattice contribution to the heat capacity. Junod et al.\textsuperscript{68-70} have been active in this search for some years and met with success. Rather than fit the specific heat to a polynomial expression of the form
as is typically done, they present a qualitative model of the phonon spectrum to fit the phonon part of the specific heat. This is given by

\[ C = \gamma T + \sum_{k=1}^{N} C_{k} T^{2k+1} \quad (9) \]

Thus the expression for the total normal state heat capacity is of the form

\[ C_{\text{ph}} = \sum_{i=1}^{M} D_{i} C_{\text{D}} \left( \frac{T}{T_{i}} \right) \quad (10) \]

Thus the expression for the total normal state heat capacity is of the form

\[ C = \gamma T + \sum_{i=1}^{M} D_{i} C_{\text{D}} \left( \frac{T}{T_{i}} \right) \quad (11) \]

where \( \gamma T \) is the usual electronic contribution to the heat capacity, the function \( C_{\text{D}}(T/T_{i}) \) is the Debye specific heat function characterized by a partial Debye temperature, \( T_{i} \), and \( D_{i} \) represents the relative weight of the contribution to \( C \) of the Debye function with \( T_{i} \). The fitting procedure is subjected to three constraints: The normal state entropy has to be equal to the measured superconducting state entropy at \( T_{c} \); the initial curvature of the phonon spectrum is determined by the initial Debye temperature \( \Theta(T = 0 \, K) \); the phonon spectrum is normalized to unity i.e. \( C - \gamma T \to 3R \) when \( T \to \infty \).

In practice Junod et al. use 6 parameters (i.e. \( M = 3 \)) to yield a phonon spectrum with three characteristic temperatures \( T_{1}, T_{2}, \) and \( T_{3} \) with corresponding relative weights \( D_{1}, D_{2}, \) and \( D_{3} \). A smaller set of parameters, in their opinion, cannot give an adequate fit to the structure in the specific heat curve in the entire temperature range fit.
(up to about 50 K). Physically, the parametrized model for the phonon spectrum proposed is just a Debye model with an additional peak at lower frequencies representing the "soft modes" present in most high $T_c$ compounds. Fitting the normal state heat capacity data for the high $T_c$ Sc$_5$Co$_4$Si$_{10}$-type compounds with this model would probably improve our understanding of the behavior of their low temperature specific heats thereby lending a better feel for the superconducting phenomenon in these materials. To actually determine the detailed form of the phonon density of states, $P(\omega)$, inelastic neutron scattering experiments must be done on these samples. Tunneling is also a possible experiment to obtain the precise form of the electron-phonon spectral function, $\alpha^2F(\omega)$.

Another interesting trend evident in the high $T_c$ compounds studied is the extraordinarily large deviations of $\Delta C/\gamma_nT_c$ from the BCS value of 1.43. The values of the electron-phonon interaction parameter, $\lambda$, are also quite large. These two observations lead to the conclusion that Sc$_5$Rh$_4$Si$_{10}$, Sc$_5$Ir$_4$Si$_{10}$, and Y$_5$Os$_4$Ge$_{10}$ are exhibiting strong coupling in the superconducting state. The presence of the strong electron-phonon interaction in these and other high $T_c$ A-15's is one additional reason for the systematic deviations of the normal state lattice contribution from the Debye model. In that case, the BCS theory, which assumes weak coupling between the electrons and phonons, is no longer strictly valid in its application to these materials. A more complete treatment of this interaction, already handled by many scientists, 71-77 is then necessary to afford a better description of the various superconducting
and normal state behaviors exhibited by these strong-coupled superconductors.

A couple of other important observations are the following. The Debye temperatures of the silicides in this system are generally much higher than what is found in other ternary superconducting systems. This is most likely attributable to the fact that Si has a Debye temperature of 630 K and is a major constituent in these materials (Ge has a $\Theta_D = 370$ K). The relatively large contributions to the normal state heat capacity from the anharmonic term in the low $T_\text{c}$ compounds (especially Lu$_5$Rh$_4$Ge$_{10}$ and Lu$_5$Ir$_4$Ge$_{10}$) is probably due to the complex phonon structure of these materials.

b. **Superconducting state**  As mentioned briefly in the introduction of this section, the BCS theory predicts that the electronic contribution to the heat capacity well below $T_\text{c}$, $C_{es}$, should follow an exponential temperature dependence. The lattice contribution, $C_L$, remains essentially the same as in the normal state.

We thus attempted to fit our heat capacity data below $T_\text{c}$ to an equation of the form

$$C_s = a e^{-\Delta/k_B T} + b T^3$$

(12)

where $C_{es} = a e^{-\Delta/k_B T}$ implies the existence of an energy gap $E_g(0) = 2\Delta$ in the superconducting state. The BCS theory yields a relation between $E_g(0)$ and $T_\text{c}$ of the form

$$E_g(0) = 3.52 k_B T_\text{c}$$

(13)
One is therefore able to determine a value for the energy gap in the superconducting state and, with the value of the transition temperature, compare the ratio $E_g(0)/k_B T_C$ to the BCS prediction.

For those samples where it was possible to fit the heat capacity data below $T_C$ to equation (12), energy gaps ranging from about $2 \times 10^{-4}$ to $16 \times 10^{-4}$ ev were determined. Comparing the corresponding values of $E_g(0)/k_B T_C$ to the BCS value yielded fairly large deviations; the ratio ranged from 1 to 3.2. The root mean square deviations of the fits ranged from 0.02 to 0.2. One note must be made: the temperature range of data fit was not very large, sometimes only a couple of degrees; thus the above results are rather suspect.

The following conclusion can be stated. It is obvious that the BCS theory does not afford an adequate description of the superconducting state of these ternary silicides and germanides. The theory incorporates several simplifications regarding the electron-phonon interaction and the phonon density of states. The fact that these Sc$_5$Co$_4$Si$_{10}$-type compounds do not adhere to the predictions of this theory is most likely another experimental manifestation of the complex phonon structure inherent in these compounds. Thus, the numbers quoted above are to be viewed with some suspicion. However, though one cannot take these values as quantitatively correct, they do indicate that a more complete treatment of the superconducting state must be utilized in these materials.
B. DC Electrical Resistivity Measurements

1. Introduction

Generally, the variation of the resistivity with temperature of a metal behaves in a characteristic manner. Near $T = 0$ K, the resistivity has a small constant value; however, as $T$ increases, $\rho$ increases, quickly at first, but eventually changing linearly with $T$. The resistivity of a metal is given by

$$\rho = \frac{m^*}{Ne^2\tau}$$  \hspace{1cm} (14)

where $m^*$ is the effective mass of an electron in the material, $N$ is the concentration of conduction electrons, $e$ is the electronic charge, and $\tau$ is the time between scattering events. Thus $1/\tau$ is actually equal to the probability of an electron undergoing a scattering per unit time. The electron will suffer a collision only if the lattice is not regular. Two types of perfect lattice deviations are 1) lattice vibrations (phonons) and 2) impurities and crystal defects. The resistivity can then be expressed as the sum of two terms,

$$\rho = \rho_i + \rho_{ph}(T)$$  \hspace{1cm} (15)

where $\rho_i$ is due to the scattering by impurities (independent of $T$) and is called the residual resistivity, $\rho_{res}$, and $\rho_{ph}(T)$ is due to the scattering by phonons, and thus is temperature dependent; $\rho_{ph}$ is called the ideal resistivity. This is often referred to as the Matthiessen
At very low T, scattering by the phonons is negligible as the thermal excitation of the ions is small; hence \( \rho = \rho_1 \). Thus the ratio of \( \rho_1/\rho_{300} \) of one sample is a measure of the relative amounts of impurities and imperfections compared to other samples of the same compound: a lower value of \( \rho_1/\rho_{300} \) indicates fewer impurities and defects. As the temperature increases, the scattering by phonons begins to dominate until, at high enough temperatures, \( \rho = \rho_{ph}(T) \). The actual temperature dependence of the resistivity of a simple metal goes as \( T^5 \) at low temperatures and as \( T \) at high temperatures \( (T > \Theta_B) \). Many compounds investigated to this date, however, exhibit resistivity data that deviate in temperature dependence from that of a simple metal. To account for these differences other, more complex, theories have been proposed.

2. Results

The resistivity data for the eleven superconducting compounds discussed in this work are presented in Figures 27 through 29. For each sample the graph is of the resistivity, normalized to the resistivity value at 300 K, versus temperature. In Table 8 are listed their values for the residual resistivities, \( \rho_{res} \), the resistivities at room temperature, \( \rho(300 \text{ K}) \), the ratio of \( \rho_{300}/\rho_{res} \) (residual resistivity ratio, RRR), and the temperature dependence (fit up to 60 K) of the low temperature resistivity minus the residual resistivity. The \( Y_{50s4Ge10} \)

\( ^{h} \text{This is true only for small concentrations.} \)
Figure 27. Electrical resistivity normalized to the value at 300 K versus temperature for Sc$_5$Co$_4$Si$_{10}$, Sc$_5$Rh$_4$Si$_{10}$, Sc$_5$Ir$_4$Si$_{10}$, and Y$_5$Ir$_4$Si$_{10}$
Figure 28. Electrical resistivity normalized to the value at 300 K versus temperature for Lu$_5$Rh$_4$Ge$_{10}$, Lu$_5$Ir$_4$Ge$_{10}$, Y$_5$Ir$_4$Ge$_{10}$, Y$_5$Os$_4$Ge$_{10}$, and Y$_5$Os$_4$Ge$_{10}$
Figure 29. Electrical resistivity normalized to the value at 300 K versus temperature for $Y_5Rh_4Ge_{10}$, $Lu_5Ir_4Si_{10}$, and $Lu_5Rh_4Si_{10}$.
Table 8. Electrical resistivity parameters for the RE$_5$T$_4$X$_{10}$ compounds

<table>
<thead>
<tr>
<th>Compound</th>
<th>$\rho_{\text{res}} (\mu\Omega\text{cm})$</th>
<th>$\rho_{300} (\mu\Omega\text{cm})$</th>
<th>$\rho_{300}/\rho_{\text{res}}$</th>
<th>$T^a$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sc$_5$Co$<em>4$Si$</em>{10}$</td>
<td>9.5</td>
<td>105</td>
<td>11</td>
<td>$T^{2.5}$</td>
</tr>
<tr>
<td>Sc$_5$Rh$<em>4$Si$</em>{10}$</td>
<td>45</td>
<td>408</td>
<td>9.1</td>
<td>$T^{2.6}$</td>
</tr>
<tr>
<td>Sc$_5$Ir$<em>4$Si$</em>{10}$</td>
<td>75</td>
<td>1430</td>
<td>19</td>
<td>$T^{4.1}$</td>
</tr>
<tr>
<td>Y$_5$Ir$<em>4$Si$</em>{10}$</td>
<td>100</td>
<td>360</td>
<td>3.6</td>
<td>$T^{3.2}$</td>
</tr>
<tr>
<td>Lu$_5$Rh$<em>4$Si$</em>{10}$</td>
<td>160</td>
<td>193</td>
<td>1.2</td>
<td>$T^{2.2}$</td>
</tr>
<tr>
<td>Lu$_5$Ir$<em>4$Si$</em>{10}$</td>
<td>195</td>
<td>590</td>
<td>3.0</td>
<td>$T^{2.4}$</td>
</tr>
<tr>
<td>Y$_5$Rh$<em>4$Ge$</em>{10}$</td>
<td>4.3</td>
<td>125</td>
<td>28</td>
<td>$T^{3.5}$</td>
</tr>
<tr>
<td>Y$_5$Ir$<em>4$Ge$</em>{10}$</td>
<td>6.0</td>
<td>391</td>
<td>65</td>
<td>$T^{3.1}$</td>
</tr>
<tr>
<td>Y$_5$Os$<em>4$Ge$</em>{10}$</td>
<td>92</td>
<td>248</td>
<td>2.6</td>
<td>$T^{2.1}$</td>
</tr>
<tr>
<td>Lu$_5$Rh$<em>4$Ge$</em>{10}$</td>
<td>7.2</td>
<td>178</td>
<td>25</td>
<td>$T^{2.8}$</td>
</tr>
<tr>
<td>Lu$_5$Ir$<em>4$Ge$</em>{10}$</td>
<td>230</td>
<td>563</td>
<td>2.6</td>
<td>$T^{2.8}$</td>
</tr>
</tbody>
</table>

This column represents the temperature dependence of the low temperature ($T < 60 \text{ K}$) resistivity minus the residual resistivity of each compound.
resistivity data, as already mentioned, were analyzed using the method of van der Pauw. He showed that the resistivity of a flat sample of thickness \( d \) with an arbitrarily-shaped perimeter could be calculated by solving the equation

\[
\frac{nR_{ab,cd}}{e} - \frac{nR_{bc,da}}{e} + \frac{1}{\rho} = 1
\]

for \( \rho \) (specific resistivity), given the resistances \( R_{ab,cd} \) and \( R_{bc,da} \). Four wires are affixed at points around the circumference of the sample, the points of contact are cyclically designated as a, b, c, and d. Resistance \( R_{ab,cd} \) is defined as the potential difference \( V_d - V_c \) between contacts d and c per unit current through contacts a and b; the resistance \( R_{bc,da} \) is defined similarly. Since this equation is non-linear, it was solved numerically for the resistivity value.

The resistivities of Sc\(_5\)Co\(_4\)Si\(_{10}\), Sc\(_5\)Rh\(_4\)Si\(_{10}\), Sc\(_5\)Ir\(_4\)Si\(_{10}\) shown on Figure 27, Lu\(_5\)Rh\(_4\)Ge\(_{10}\) and Y\(_5\)Ir\(_4\)Ge\(_{10}\) shown on Figure 28 and Y\(_5\)Rh\(_4\)Ge\(_{10}\) on Figure 29, seem to exhibit behavior slightly different from that manifested by normal metals at low temperatures. On close inspection of these curves a small negative curvature is evident, though this is probably due to the change-over in temperature dependence of the resistivity. All of these samples have fairly high RRR values, the lowest being 9.1 for Sc\(_5\)Rh\(_4\)Si\(_{10}\). Note also the large value of \( \rho_{300} \) and the \( T^4 \) dependence of the low \( \rho(T) \) data for Sc\(_5\)Ir\(_4\)Si\(_{10}\) relative to the other Sc\(_5\)Co\(_4\)Si\(_{10}\)-type compounds. The resistivity curve for Lu\(_5\)Ir\(_4\)Ge\(_{10}\) shows a little more negative curvature than the previous compounds discussed, plus a much lower RRR = 2.5. A significantly more pronounced
negative curvature is evident in the data for $YOSGe_{10}$ and $YIrSi_{10}$, being greater for the latter. Both resistivities eventually become relatively linear above a temperature equal to 240 K. The relatively high residual resistivities exhibited by some of these compounds are probably more attributable to the presence of the many cracks found in these samples upon completion of synthesis.

Looking at Figure 29 one immediately notices an anomaly present in the $LuIrSi_{10}$ and $LuRhSi_{10}$ resistivity curves. As the temperature increases, the resistivity of $LuIrSi_{10}$ drops fairly sharply at about 80 K. This anomaly has also been observed in an independent sample. A similar, though less sharp, drop in the resistivity of $LuRhSi_{10}$ occurs at about 140 K. In addition, $LuRhSi_{10}$ seems to have an extraordinarily low RRR value of 1.2 below this jump. Similar, seemingly related anomalies occur in the magnetic susceptibilities of some of these samples.

3. Discussion

The presence of negative curvature in the resistivity data and the deviation of the low temperature $p(T)$ dependence from $T^5$ has been observed in high $T_c$ A-15 and other compounds. A variety of theories has been proposed in an attempt to explain the various anomalous behaviors exhibited by the resistivities of these materials.

As already mentioned, the Bloch-Grueneisen model for a normal metal predicts that the resistivity is proportional to $T^5$ for low and $T$ for high temperatures. This theory is based on the fact that $s-s$
intraband scattering is dominant in the material. A $T^3$ dependence of 
the low temperature resistivity ($T < 50$ K) and a $T$ dependence at high 
temperatures follows from the Wilson $s$-$d$ interband scattering model. With both models the Debye approximation is assumed for the phonon 
spectrum. Possible explanations for the negative curvature in the 
resistivity curves were put forth by Cohen et al. and Allen et al. An attempt to explain another anomaly observed in some high temperature 
resistivities, namely, saturation of $\rho(T)$, was given by Fisk and Webb. Other possible explanations for the observed anomalies do exist; 
however, the few mentioned are well-known and provide a starting place 
for further reading.

With the resistivity data taken on the Sc$_5$Co$_4$Si$_{10}$-type compounds 
studied, it is not possible to arrive at any definite quantitative 
conclusions concerning the temperature dependences and exact mechanisms 
causing the behavior of the resistivity. However, a few qualitative 
observations are obvious from the previous discussion as well as the 
data. First, it is evident from Table 8 that none of the samples 
investigated shows a strictly integral power of the temperature 
dependence of the low temperature resistivity ($T < 60$ K). It is 
possible, however, that the low $\rho(T)$ data for Y$_{50}$Si$_4$Ge$_{10}$ follow a $T^2$ law. 
This has been observed for Nb$_3$Sn, Nb$_3$Al, and Nb$_3$Ge. The fact that the 
temperature dependences are so odd can most likely be attributed to the 
complex phonon structure of these compounds; several mechanisms of 
scattering could be important in determining the overall resistivity 
behaviors. Second, whether or not saturation in the resistivity at very
high temperatures ($T > \Theta_D$) occurs in these compounds cannot be determined. The resistivity data were only taken up to a maximum of 390 K and, as has already been stated, the Debye temperatures for these compounds are quite large in comparison to other ternary superconductors and are well above our maximum measuring temperature.

The anomalous behaviors exhibited by the resistivities of $Y_5\text{Ir}_4\text{Si}_{10}$, $Lu_5\text{Rh}_4\text{Si}_{10}$ and $Lu_5\text{Ir}_4\text{Si}_{10}$ will be discussed in detail following the presentation of the static magnetic susceptibility results.

C. Static Magnetic Susceptibility Measurements

1. Introduction

The magnetic susceptibility of a sample (magnetic response), $\chi$, is defined as

$$\chi = \frac{M}{H}$$  \hspace{1cm} (17)

where $M$ is the magnetization (the dipole moment per unit volume) of the sample and $H$ is the applied macroscopic magnetic field intensity.$^1$

Materials are typically grouped into three magnetic classes, depending upon the sign and magnitude of $\chi$. Materials that are paramagnetic have a positive $\chi$ which means $M$ is parallel to $H$. Examples are the ions of transition metals and rare earths which have incomplete atomic shells. Diamagnetic materials exhibit negative values for $\chi$ implying $M$ is

---

$^1$In the Gaussian system, the units of $M$ are Gauss (G) or Oersted (Oe) and the units of $H$ are Oersted (Oe).
opposite to $\mathbf{H}$. Well known examples of diamagnetic materials are ionic and covalent crystals; these substances have atoms or ions with complete electron shells. The third class is comprised of what are known as ferromagnetic materials. These samples exhibit very large values of $\chi$ and become spontaneously magnetized below a certain temperature. Some examples are Co, Fe, and Ni.

To begin, we discuss the contributions to the magnetic susceptibility of $N$ ions in a solid (in an applied magnetic field) that do not interact magnetically. First, there is a temperature independent diamagnetic contribution to the susceptibility due to the core electrons (or filled shells). This is usually called the Larmor diamagnetic susceptibility. If the ions have a partially filled shell, then there exists a paramagnetic correction to the Larmor diamagnetic susceptibility known as the Van Vleck paramagnetic susceptibility.

In addition, if the unfilled shell does not have $J = 0$ ($J$ being the magnitude of the total angular momentum), the total magnetic susceptibility then includes a paramagnetic term considerably larger than either of the two contributions discussed already (Note: the quantum theory of paramagnetism is used. This quantum treatment takes into account the fact that the magnetic moment of the atom cannot take on just any angle with respect to the magnetic field; it can only assume a finite number of values). This paramagnetic susceptibility is given by

---

This contribution is sometimes referred to as the Langevin susceptibility.
\[ \chi = \frac{g_J^2 \mu_B^2 J(J + 1)N}{3k_B TV} \]  

(for very small magnetic energy compared to \( k_B T \)) where \( g_J \) is the Lande \( g \)-factor given by

\[ g_J = \frac{3 + S(S + 1) - L(L - 1)}{2 \sqrt{2J(J + 1)}} \]  

in which \( S \) is the magnitude of the spin vector, \( L \) is the magnitude of the orbital angular momentum vector, and \( J \) is the magnitude of the total angular momentum vector, \( k_B \) is Boltzmann's constant, \( N \) is the number of atoms in a solid, and \( V \) is the volume.

The susceptibility is usually more useful written in the form

\[ \chi = \frac{\mu_{\text{eff}}^2 N}{3k_B TV} = \frac{p^2 \mu_B^2 N}{3k_B TV} = \frac{C}{T} \]  

where \( \mu_{\text{eff}}^2 = g_J^2 \mu_B^2 J(J + 1) = p^2 \mu_B^2 \), \( C \) is known as the Curie constant and \( p \) is called the effective number of Bohr magnetons.

If we are discussing metals, we must also take into account the contributions the conduction electrons make to the overall susceptibility. They make two contributions. The first, spin (Pauli) paramagnetism, is due to the interaction of the electron spin with the applied magnetic field. The Pauli paramagnetic susceptibility is essentially independent of temperature and is given by

\[ \chi_{\text{Pauli}} = \mu_B^2 g(c_F) \]
where $\mu_B$ is the Bohr magneton and $g(e_F)$ is the density of states at the Fermi level. The second contribution is diamagnetic and comes about because the spatial motion of the electron is affected by the applied field. This contribution is known as the Landau diamagnetic susceptibility and is similar in form to $\chi_{\text{Pauli}}$ (being $-1/3 \chi_{\text{Pauli}}$ for free electrons).

In reality, however, ions in a solid do interact magnetically. Ferromagnetism and antiferromagnetism are a couple of examples of cooperative magnetic phenomena. The molecular field theory (or Weiss molecular field theory) was proposed by Pierre Weiss (cited in Ref. 16) in 1907. This simple phenomenological theory was first put forth by Weiss to explain many of the facts associated with ferromagnetism. This theory arrives at an expression known as the Curie-Weiss law

$$\chi = \frac{C}{T - T_c}$$

(22)

where $C$ is the usual Curie constant. The difference between the Curie law ($\chi$ goes as $1/T$) and the Curie-Weiss law is that in the former $\chi$ diverges at $T = 0$ K, whereas in the latter $\chi$ diverges at some $T = T_c$ known as the ferromagnetic transition temperature (or Curie temperature). Above this temperature the material is paramagnetic, below the material spontaneously magnetizes. In 1932 Néel suggested the possibility that a magnetic material could have neighboring dipoles antiparallel to each other, thus possessing no net macroscopic magnetism; this is known as antiferromagnetism. The ideas from molecular field theory can be applied to antiferromagnetic materials in
a manner similar to what was done for ferromagnetic materials. The expression above the Néel temperature, $T_N$ ($T_N$ is the antiferromagnetic transition temperature) is given by

$$\chi = \frac{C}{T + \Theta} \quad (23)$$

where $C$ is the usual Curie constant and experimentally it is usually found $\Theta > T_N$.

A proviso must be made here. One should realize that the mean field theory gives a very inadequate picture of the critical region. To do a more detailed analysis of the magnetic interaction (such as exchange interactions, etc.) in solids, more sophisticated techniques, such as quantum mechanics, must be applied to the magnetic problem. However, though this is a rather simple, intuitive model, it does predict the very different behaviors for ferro- and antiferromagnetic materials. The magnetic susceptibilities of many materials can be fit fairly well with a Curie-Weiss law. The experimenter can use the goodness of the fit as an indication of whether the sample is ferro- or antiferromagnetic (or paramagnetic). For a new compound, this knowledge is useful; if the fit is not good, then some other type of magnetic ordering could be occurring and more complete theories of magnetism must be used.

2. Results

The variation of the static molar magnetic susceptibility with temperature for the eleven samples studied in this work are presented in
Figures 30 through 32. Where possible, a least-squares fit of the data over the entire temperature range (2.6 K to 380 K) was made to the following expression

$$\chi_m = \chi_0 + \frac{C}{T - \Theta}$$  \hspace{1cm} (24)

where $\chi_0$ is the temperature-independent susceptibility which represents contributions from Van Vleck paramagnetism, core diamagnetism (Larmor), Pauli paramagnetism of the conduction electrons, and Landau diamagnetism, $C = N_A \mu_{\text{eff}}^2/3k_B$ is the Curie-Weiss constant, $k_B$ is the Boltzmann constant, and $\Theta$ is the Curie-Weiss temperature. For those samples whose susceptibilities could be fit, values for $\chi_0$, $p$, $\Theta$, and $n = (p_{\text{measured}}/p_{\text{spin 1/2}})^2$ (n gives the percent of spin 1/2 magnetic impurities) are given in Table 9.

From the graphs one notices that the Sc$_5$Co$_4$Si$_{10}$ has the largest susceptibility of all the superconducting compounds. Utilizing the parameters from the fit of the Co data yields an effective paramagnetic moment per Co atom of 0.26$\mu_B$. The measured value of $p$ for Co$^{+2}$ is 4.8. This fact could be evidence for magnetic tendencies of Co in Sc$_5$Co$_4$Si$_{10}$. The magnetic susceptibilities of the other four samples on Figure 30 and of Lu$_5$Ir$_4$Ge$_{10}$ on Figure 31 seem to maintain a relatively constant value until, at the lowest temperatures, an upturn in the data occurs; however, this is most likely attributable to a few ppm of paramagnetic impurity.

The rest of the samples shown in Figures 31 and 32 show some anomalous behavior in the molar magnetic susceptibilities. Lu$_5$Rh$_4$Si$_{10}$
Figure 30. Static molar magnetic susceptibility as a function of temperature for $\text{Sc}_5\text{Co}_4\text{Si}_{10}$, $\text{Sc}_5\text{Rh}_4\text{Si}_{10}$, $\text{Sc}_5\text{Ir}_4\text{Si}_{10}$, $\text{Y}_5\text{Os}_4\text{Ge}_{10}$, and $\text{Y}_5\text{Ir}_4\text{Ge}_{10}$ measured in a field of 5.0 kOe.
Figure 31. Static molar magnetic susceptibility as a function of temperature for Lu$_5$Ir$_4$Si$_{10}$, Y$_5$Ir$_4$Si$_{10}$, and Lu$_5$Ir$_4$Ge$_{10}$ measured in a field of 5.0 kOe.
Figure 32. Static molar magnetic susceptibility as a function of temperature for Lu₅Rh₄Si₁₀, Lu₅Rh₄Ge₁₀, and Y₅Rh₄Ge₁₀ measured in a field of 5.0 kOe.
Table 9. Static magnetic susceptibility parameters for some \( \text{Re}_2\text{T}_4\text{X}_{10} \) compounds

<table>
<thead>
<tr>
<th>Compound</th>
<th>( \chi_0 )</th>
<th>( \Theta )</th>
<th>( p )</th>
<th>( n^a )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{Sc}_5\text{Co}<em>4\text{Si}</em>{10} )</td>
<td>( 3.6 \times 10^{-4} )</td>
<td>-530</td>
<td>1.872</td>
<td>_b</td>
</tr>
<tr>
<td>( \text{Sc}_5\text{Rh}<em>4\text{Si}</em>{10} )</td>
<td>( 3.4 \times 10^{-4} )</td>
<td>-19</td>
<td>0.180</td>
<td>0.5</td>
</tr>
<tr>
<td>( \text{Sc}_5\text{Ir}<em>4\text{Si}</em>{10} )</td>
<td>( 5.9 \times 10^{-4} )</td>
<td>-4</td>
<td>0.127</td>
<td>0.3</td>
</tr>
<tr>
<td>( \text{Y}_5\text{Os}<em>4\text{Ge}</em>{10} )</td>
<td>( 3.7 \times 10^{-4} )</td>
<td>3</td>
<td>0.290</td>
<td>1.3</td>
</tr>
<tr>
<td>( \text{Y}_5\text{Ir}<em>4\text{Ge}</em>{10} )</td>
<td>( 0.81 \times 10^{-4} )</td>
<td>-0.5</td>
<td>0.049</td>
<td>0.04</td>
</tr>
<tr>
<td>( \text{Lu}_5\text{Ir}<em>4\text{Ge}</em>{10} )</td>
<td>( 7.2 \times 10^{-4} )</td>
<td>-11</td>
<td>0.111</td>
<td>0.2</td>
</tr>
</tbody>
</table>

\(^a_n = \text{percent of spin 1/2 magnetic impurity.}\)

\(^b\text{The Co atom in this sample exhibits a small magnetic moment of 0.26} \mu_B \text{; this is discussed in the text.}\)
and \( \text{Lu}_5\text{Ir}_4\text{Si}_{10} \) both exhibit a jump in the susceptibility as the temperature increases. This jump is quite sharp for \( \text{Lu}_5\text{Ir}_4\text{Si}_{10} \), occurring at about 80 K. This behavior has also been observed in a separate sample.\(^7\) For the \( \text{Lu}_5\text{Rh}_4\text{Si}_{10} \) data, the jump is not quite as sharp as for the previous compound, having a broader minimum; however, it is quite noticeable, occurring at about 140 K. The \( \text{Lu}_5\text{Ir}_4\text{Si}_{10} \) data maintain a relatively constant value of \( \chi = 1.05 \times 10^{-4} \) emu/mol after the jump. The value for \( \chi \) after the jump for the \( \text{Lu}_5\text{Rh}_4\text{Si}_{10} \) sample continues rising a little, ranging from \( 0.06 \times 10^{-4} \) to \( 0.17 \times 10^{-4} \) emu/mol. The anomaly featured in the \( \text{Y}_5\text{Ir}_4\text{Si}_{10} \) data has a fairly broad minimum; the susceptibility then rises slowly, leveling off with a relatively constant value of \( 0.59 \times 10^{-4} \) emu/mol at about 230 K. The \( \text{Lu}_5\text{Rh}_4\text{Ge}_{10} \) susceptibility feature is a very broad trough the minimum value of which occurs at about 160 K. The data then rise quite slowly, never achieving a constant value up to the highest temperatures investigated; it is possible the susceptibility would level off at higher temperatures. The anomalous behavior shown by the susceptibility of the last sample, \( \text{Y}_5\text{Rh}_4\text{Ge}_{10} \), is a little different from the rest. The presence of a valley is evident, though quite small; however, the data then begin to rise quickly and continue to increase with a relatively steep slope.

Five of the \( \text{Sc}_5\text{Co}_4\text{Si}_{10} \)-type compounds investigated show anomalous behavior in the magnetic susceptibility. It is believed the same mechanism is responsible for this behavior in each of these isostructural materials. The following section discusses possible causes of this effect.
3. Discussion

Several minor observations will be made before discussing the anomalous behaviors exhibited by the resistivities and magnetic susceptibilities of some of the Sc$_5$Co$_4$Si$_{10}$-type compounds.

As noted earlier, the Co atom does appear to have small magnetic moment of $0.26\mu_B$ in disagreement with the value of $0.078\mu_B$ reported by Braun and Segre.$^{56}$ A concentration of 860 ppm Gd in the Sc would be necessary to attribute the observed moment to the presence of RE impurities. This is too large considering the purities of rare earths used in synthesizing the compounds. Since there exists only one Co sublattice, it is likely that all Co atoms possess the same moment. This fact could explain the reason for the low $T_C$ of Sc$_5$Co$_4$Si$_{10}$ relative to those of Sc$_5$Rh$_4$Si$_{10}$ and Sc$_5$Ir$_4$Si$_{10}$. As Table 9 shows, the fits to the susceptibility data of these six sample indicate the presence of a small magnetic moment on the compounds. This is most likely attributable to a few ppm of RE impurity in the Sc, Y, or Lu.

Let us now turn our attention to the aforementioned anomalies observed in the resistivity and molar magnetic susceptibility data of Lu$_5$Rh$_4$Si$_{10}$, Lu$_5$Ir$_4$Si$_{10}$, Y$_5$Ir$_4$Si$_{10}$, Y$_5$Rh$_4$Ge$_{10}$, and Lu$_5$Rh$_4$Ge$_{10}$. The anomalous behaviors exhibited by the Lu$_5$Ir$_4$Si$_{10}$ compound have been confirmed in a separate, smaller sample.$^{78}$ In addition, this material has a pronounced sensitivity of $T_C$ to pressure which results in a discontinuous but reversible increase in $T_C$ from 3.8 K to a value in excess of 9.1 K at a critical pressure, $p_c$, of 21 kbar.$^{60}$ Bulk modulus measurements taken up to 26 kbar at four different temperatures ranging
from 293 K to 14 K revealed no volume anomaly due to this transition. The conclusion reached was that the phase transition observed was electronic in nature. The temperature at which the anomaly in the resistivity and susceptibility data occurs for this separate sample is reported at $T_o = 79$ K. Low temperature polycrystalline X-ray measurements (down to 21 K) revealed no structural phase transition at this temperature. Subsequent high pressure resistivity experiments show that $T_o$ decreases with pressure, resulting in the complete suppression of this phase transition at the critical pressure, $p_c = 21$ kbar. Based on the experimental data to date on $\text{Lu}_5\text{Ir}_4\text{Si}_{10}$, the contention is that this electronic phase transition may involve the development of a charge- or spin-density wave (CDW or SDW) that opens an energy gap over a portion of the Fermi surface.

The presence of CDWs and the effect of pressure on their formation has been dealt with quite extensively for anisotropic metals such as the one-dimensional conductors$^{90}$ and two-dimensional compounds such as the transition-metal dichalcogenides.$^{91-92}$ It is now also apparent that charge density waves may form in compounds with a three dimensional crystal lattice. CDW formation has been observed in the spinel compound $\text{CuV}_2\text{S}_4$$^{93-94}$ and, just recently, been suggested as the reason for the phase transition at 17.5 K in the heavy-fermion compound $\text{URu}_2\text{Si}_2$.$^{95}$

The suggestion of this work is that charge- or spin-density wave formation is responsible for not only the anomalies observed in the resistivity and magnetic susceptibility data of $\text{Lu}_5\text{Ir}_4\text{Si}_{10}$, as has been discussed above, but also for the anomalous behaviors in the $\rho(T)$ and
\( \chi_m(T) \) curves for Lu\(_5\)Rh\(_4\)Si\(_{10}\), Y\(_5\)Ir\(_4\)Si\(_{10}\), Y\(_5\)Rh\(_4\)Ge\(_{10}\), and Lu\(_5\)Rh\(_4\)Ge\(_{10}\). Comparing the shape of the anomalies observed in the corresponding measurements for CuV\(_2\)S\(_4\)\(^93\) and URu\(_2\)Si\(_2\)\(^95\) to those featured in some of our data, an obvious match is immediately apparent for the Lu\(_5\)Rh\(_4\)Si\(_{10}\) and Lu\(_5\)Ir\(_4\)Si\(_{10}\) compounds. In all four cases, the anomaly in \( \rho(T) \) is characterized by a small peak and correlated with the anomaly in \( \chi(T) \), at the same temperature, characterized by a distinct change in slope at the transition followed by a minimum as the temperature decreases. The experimental basis for this work’s contention is the most clear-cut for these two compounds.

Upon close inspection of both the resistivity and magnetic susceptibility data for Y\(_5\)Ir\(_4\)Si\(_{10}\), a correlation is apparent between the anomalies observed in each measurement. For this sample, the susceptibility data show a more gradual change in slope at the phase transition temperature than evidenced by the four compounds already discussed; however, this slope change is followed by a minimum (though less deep) similar to other materials showing this anomaly. In addition, the temperature at which the resistivity anomaly occurs correlates well with the \( T_0 \) of \( \chi(T) \). The \( \rho(T) \) anomaly is far from a peak; however, the resistivity data indicate a very definite change in curvature at \( T_0 \) going from a strong negative curvature to an essentially linear temperature dependence.

The suggestion that CDW formation is also responsible for the anomalous \( \chi(T) \) behavior in Y\(_5\)Rh\(_4\)Ge\(_{10}\) and Lu\(_5\)Rh\(_4\)Ge\(_{10}\) is not quite as apparent experimentally as no obvious resistivity anomaly is present in
the data; however, the susceptibility anomalies appear to exhibit some of the same features (a change in slope and a minimum) as the more clear-cut cases. The effect might just be extended over a larger temperature range explaining the absence of any sharp anomalous feature in the resistivity.

The formation of a CDW causing the apparent electronic phase transitions in these five mentioned compounds is just a hypothesis at this point in time. To arrive at a more definite conclusion, a great deal of work is still necessary. Low temperature X-ray measurements must be done on Lu$_5$Rh$_4$Si$_{10}$, Y$_5$Ir$_4$Si$_{10}$, Y$_5$Rh$_4$Ge$_{10}$, and Lu$_5$Rh$_4$Ge$_{10}$ to confirm the absence of a volume anomaly due to the phase transition and hence, substantiate the claim that the transition is electronic in nature. Specific heat measurements at higher temperatures could provide additional evidence for the formation of a CDW as it did in the case of URu$_2$Si$_2$. However, the most conclusive evidence for this formation would come from X-ray diffraction work on single crystals of these compounds; this is presently in progress for Lu$_5$Ir$_4$Si$_{10}$.

D. Upper Critical Magnetic Field Measurements

1. Introduction

Superconductors are usually placed in one of two classifications: 1) type I or 2) type II. To discuss the difference between these two types of superconductors, consider a long cylindrically shaped sample with the applied magnetic field, H, parallel to the cylinder’s axis (this eliminates the need for a demagnetizing factor).
In type I superconductors there is one critical magnetic field, \( H_c(T) \), below which the sample remains superconducting i.e. there are only surface currents and no magnetic flux penetrates the sample; it thus behaves as a perfect diamagnetic material. However, when the applied field is greater than \( H_c \), the entire sample becomes normal; the magnetic flux completely penetrates the sample and the magnetization drops approximately to zero. Another way of characterizing type I superconductors is by the Ginzburg-Landau parameter \( \kappa \). The GL parameter is a ratio of the two characteristic lengths in superconductivity: the coherence length, \( \xi \) (a measure of the spatial extent of the Cooper pair wave function), and the penetration depth, \( \lambda \). The GL parameter is given by

\[
\kappa = \frac{\lambda}{\xi}.
\]  

If \( \kappa \ll 1 \), we have a type I superconductor. Most elements belong to this type. For pure elemental superconductors \( \lambda \approx 500 \, \text{Å} \) and \( \xi \approx 10,000 \, \text{Å} \).

Type II superconductors are much more complex. In this case there are two critical magnetic fields. If \( H_{\text{applied}} \) is below some lower critical field, \( H_{c1} \), there is no magnetic flux penetration and the sample behaves as a type I superconductor. Above an upper critical field, \( H_{c2} \), as above, the bulk of the sample becomes normal. The difference between the two types of superconductors occurs when \( H_{c1} < H_{\text{applied}} < H_{c2} \); here the sample is in what is called the mixed or vortex state. Zero resistance but partial flux penetration characterize this state. The magnetic flux penetrates in the form of very thin filaments (or vortices); inside these filaments the material is normal
but outside the material is still superconducting. For type II superconductors \( \kappa \gg 1 \). Most compounds are type II with \( \xi \) on the order of 100 Å and \( \lambda \) on the order of 1000 Å.\(^k\)

2. Results

The upper critical magnetic field data and the generated theoretical curves for the six samples studied are presented in Figure 33. The data were analyzed using the theory put forth by Werthamer, Helfand, and Hohenberg (better known as the WHH theory),\(^{96-97} \) in the dirty limit (i.e., short mean free paths). The WHH theory incorporates a) the interaction of the applied magnetic field with the orbital motion of the electrons and b) the effect of the applied magnetic field on the electron spin magnetic moment; i.e., it takes into account both spin paramagnetism and spin-orbit scattering. This theory also assumes the electrons interact via the weak-coupling BCS model potential and have a spherical Fermi surface in addition to assuming the transition to the normal state is of second order.

The equation we fit the data to is expressed in terms of digamma functions and dimensionless variables and is given by

\[
\ln \frac{1}{t} = \left( - \frac{\lambda_{so}}{2 \gamma} \right) \psi \left( - \frac{h + \frac{1}{2} \lambda_{so} + i \gamma}{2t} \right) + \left( \frac{1}{2} - \frac{i \lambda_{so}}{4 \gamma} \right) \psi \left( - \frac{h + \frac{1}{2} \lambda_{so} - i \gamma}{2t} \right) \psi \left( \frac{1}{2} \right)
\]

\(^{26}\)

\(^k\)Abrikosov showed that the exact breakpoint between type I and type II superconductors occurred at \( \kappa = 2^{1/2} \).
Figure 33. Upper critical field versus temperature for Sc$_5$Co$_4$Si$_{10}$, Sc$_5$Rh$_4$Si$_{10}$, Sc$_5$Ir$_4$Si$_{10}$, Lu$_5$Rh$_4$Si$_{10}$, Lu$_5$Ir$_4$Si$_{10}$, and Y$_5$Os$_4$Ge$_{10}$. The curves represent the best fit of the data to the WHH theory.
\[ \gamma^2 = \left( \alpha n \right)^2 - \left( \frac{1}{2} \lambda_{SO} \right)^2 \]

\( t = T/T_C \) (reduced temperature)

\( h = 2eH(v_F^2/6\pi^2) \) (reduced field)

\( \alpha = 3/2mv_F^2\tau_1 \quad \text{and} \quad \lambda_{SO} = 1/3\pi T_C\tau_2 \)

digamma function, \( \psi \), is given by,

\[ \psi(z) = -\gamma - \sum_{n=1}^{\infty} \left[ \frac{1}{(z + n)} - \frac{1}{n} \right] \]

\( \gamma = \text{Euler-Mascheroni constant}, \quad k_B = \hbar = c = 1 \).

Note that \( \alpha \) (the Maki parameter)\(^{98-99}\) is a measure of the spin paramagnetic effect and \( \lambda_{SO} \) a measure of the spin-orbit effect. In order to fit the upper critical field data to the above equation, various values of \( \alpha \) and \( \lambda_{SO} \) were chosen until the best fit to the data was achieved. The theoretical curve generated for each sample thus yields values for 1) the slope of the upper critical field curve at \( T_C \), \((-dH_{c2}/dT)_{T_C}\) and 2) the value of the upper critical field curve at \( T = 0 \) K, \( H_{c2}(0) \). Henceforth, the values of these parameters will be referred to as experimental \( H_{c2}(0) \) and experimental \((-dH_{c2}/dT)_{T_C}\).

The values of the various critical field parameters for the six samples investigated are listed in Tables 10 and 11. Upon inspection of Figure 33 and the Table 11, the \( Y_5Os_4Ge_{10} \) sample clearly stands out. As can be seen, the values \( H_{c2}(0) = 60.4 \text{ kOe} \) and \((-dH_{c2}/dT)_{T_C} = 10.2 \text{ kOe/K} \) are very high compared to the corresponding values of these quantities for the silicides. Since the SQUID magnetometer utilized for these measurements only has a 2T magnet, data below 6 K could not be taken for
Table 10. Upper critical magnetic field parameters for some Re$_5$T$_4$X$_{10}$ compounds

<table>
<thead>
<tr>
<th>Compound</th>
<th>$\alpha$</th>
<th>$\lambda_{so}$</th>
<th>$H_{c2}(0)$</th>
<th>$\left(-\frac{dH_{c2}}{dT}\right)_{T_c}^a$</th>
<th>$\left(-\frac{dH_{c2}}{dT}\right)_{T_c}^b$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{Sc}_5\text{Co}<em>4\text{Si}</em>{10}$</td>
<td>0.11</td>
<td>10</td>
<td>7.1</td>
<td>2.1</td>
<td>0.77</td>
</tr>
<tr>
<td>$\text{Sc}_5\text{Rh}<em>4\text{Si}</em>{10}$</td>
<td>0.11</td>
<td>10</td>
<td>12.2</td>
<td>2.1</td>
<td>1.9</td>
</tr>
<tr>
<td>$\text{Sc}_5\text{Ir}<em>4\text{Si}</em>{10}$</td>
<td>0.08</td>
<td>9.9</td>
<td>9.0</td>
<td>1.5</td>
<td>1.8</td>
</tr>
<tr>
<td>$\text{Lu}_5\text{Rh}<em>4\text{Si}</em>{10}$</td>
<td>0.34</td>
<td>1.0</td>
<td>14.8</td>
<td>6.4</td>
<td>8.9</td>
</tr>
<tr>
<td>$\text{Lu}_5\text{Ir}<em>4\text{Si}</em>{10}$</td>
<td>0.21</td>
<td>10</td>
<td>10.4</td>
<td>3.9</td>
<td>10.5</td>
</tr>
<tr>
<td>$\text{Y}_5\text{Os}<em>4\text{Ge}</em>{10}$</td>
<td>0.54</td>
<td>1.0</td>
<td>60.4</td>
<td>10.2</td>
<td>2.5</td>
</tr>
</tbody>
</table>

$^a$ These values were obtained from a fit of the data to the WHH theory.

$^b$ These values were calculated using Equation 30 in which the value of $\gamma$ comes from the heat capacity and $\rho_{\text{res}}$ from the resistivity measurements.
Table 11. Upper critical magnetic field parameters for some \( \text{Re}_5\text{T}_4\text{X}_{10} \) compounds

<table>
<thead>
<tr>
<th>Compound</th>
<th>( \rho_{\text{res}} )</th>
<th>( \gamma_n )</th>
<th>( H_{c2}^* (0) )(^a)</th>
<th>( H_p (0) )(^b)</th>
<th>( \xi_{\text{GL}} )</th>
<th>( \lambda_{\text{GL}} )</th>
<th>( \kappa_{\text{GL}} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{Sc}_5\text{Co}<em>4\text{Si}</em>{10} )</td>
<td>10</td>
<td>1807.3</td>
<td>7.1</td>
<td>91</td>
<td>450</td>
<td>1400</td>
<td>3.1</td>
</tr>
<tr>
<td>( \text{Sc}_5\text{Rh}<em>4\text{Si}</em>{10} )</td>
<td>45</td>
<td>922.3</td>
<td>12.2</td>
<td>155</td>
<td>180</td>
<td>1810</td>
<td>10.1</td>
</tr>
<tr>
<td>( \text{Sc}_5\text{Ir}<em>4\text{Si}</em>{10} )</td>
<td>75</td>
<td>529.7</td>
<td>8.8</td>
<td>157</td>
<td>180</td>
<td>2310</td>
<td>12.8</td>
</tr>
<tr>
<td>( \text{Lu}_5\text{Rh}<em>4\text{Si}</em>{10} )</td>
<td>160</td>
<td>1244.6</td>
<td>15.0</td>
<td>62</td>
<td>220</td>
<td>9510</td>
<td>43.2</td>
</tr>
<tr>
<td>( \text{Lu}_5\text{Ir}<em>4\text{Si}</em>{10} )</td>
<td>195</td>
<td>1197.9</td>
<td>10.2</td>
<td>69</td>
<td>170</td>
<td>8550</td>
<td>50.3</td>
</tr>
<tr>
<td>( \text{Y}_5\text{Os}<em>4\text{Ge}</em>{10} )</td>
<td>92</td>
<td>593.7</td>
<td>62.5</td>
<td>163</td>
<td>150</td>
<td>2500</td>
<td>16.7</td>
</tr>
</tbody>
</table>

\(^a\) Prediction of \( H_{c2} (0) \) assuming only the orbital diamagnetic effect.

\(^b\) Prediction of \( H_{c2} (0) \) assuming only the spin paramagnetic effect; i.e. the Pauli limiting field.
Unfortunately, the behavior of the upper critical magnetic field for the other germanides in this group could not be studied as the $T_c$'s of these samples were either well below or fairly close to 2.2 K, the low temperature limit of the susceptometer. Perhaps the other germanides, relative to the silicides, would exhibit similar high $H_{c2}(0)$ values. The silicides studied all exhibit fairly moderate values for $H_{c2}(0)$ being on the order of 10 kOe. The values for $(-dH_{c2}/dT)_{T_c}$ are also generally moderate; note, however, $Lu_5Rh_4Si_{10}$ does exhibit the largest value of the silicides.

3. Discussion

To begin, several observations will be made concerning only the upper critical magnetic field data for the six samples studied. A subsequent discussion will then deal with any conclusions possible utilizing the results from low temperature heat capacity, DC electrical resistivity, and upper critical magnetic field measurements.

From Tables 10 and 11, one notes the very small values of the Maki parameter, $\alpha$. As mentioned previously, $\alpha$ is a measure of the Pauli spin paramagnetism. The parameter $\alpha$ can also related to the critical field slope at $T_c$ in the following manner,\(^97\)

$$\alpha = 5.28 \times 10^{-5} \left( -\frac{dH_{c2}}{dT} \right)_{T_c} \quad (27)$$

Thus a small $\alpha$ implies a small $(-dH_{c2}/dT)_{T_c}$. Assuming only the presence of the Pauli paramagnetic effect, Clogston\(^100\) and Chandrasekhar\(^101\) independently pointed out that the Pauli effect placed
a limit on the upper critical fields $H_{c2}$ of type II superconductors. This upper limit is referred to as the Pauli-limiting field, $H_p$, and is given by

$$H_{c2}(0) \leq H_p(0) = 1.84 \times 10^4 T_C$$

(28)

where $H_{c2}(0)$ and $H_p(0)$ denote the values at $T = 0$ K and the units are in Oe. Taking only the orbital diamagnetic effect into account leads to a prediction for $H_{c2}(0)$ given by

$$H_{c2}^*(0) = 0.69 T_C \left( \frac{-dH_{c2}}{dT} \right)_{T_C}$$

(29)

The Pauli limiting fields and the values of $H_{c2}^*(0)$ for the six compounds studied are listed in Table 11. It is clear that the experimental $H_{c2}(0)$ values fall far below the predicted $H_p(0)$ values; however, they agree quite well with the predicted $H_{c2}^*(0)$.

Although only one value for the measure of the spin-orbit effect, $\lambda_{so}$, is listed, any other value would be equally correct. It turns out that the fit to the upper critical magnetic field data is quite insensitive to the choice of $\lambda_{so}$ when $\alpha$ is small; using $\lambda_{so} = 10,000$ (very large) and $\lambda_{so} = 0.1$ (very small) yields values of $H_{c2}(0)$ and $(-dH_{c2}/dT)_{T_C}$ very close to those listed in the Table 10. It is found that $\lambda_{so}$ very large ($\lambda_{so} \to \infty$) leads to no Pauli paramagnetic limiting; the spin-orbit effect compensates for Pauli limiting. Since $\alpha$ is so small in these samples studied, we are unable to determine $\lambda_{so}$. However, noting the good agreement between the experimental $H_{c2}(0)$ and $H_{c2}^*(0)$ leads to the following conclusions. First, there is little or
no Pauli limiting in the compounds consistent with the small $\alpha$ values and the ability for $\lambda_{SO}$ to be quite large. Secondly, the spin-orbit effect in these materials appears to be negligible, consistent with the insensitivity of the fits to the value of $\lambda_{SO}$.

An independent determination of $(-dH_{c2}/dT)_{Tc}$ can be calculated using the following BCS relation in the "dirty limit" (very short mean free path)\textsuperscript{74}

$$\left(\frac{-dH_{c2}}{dT}\right)_{T_c} = 4.48 \times 10^{-4} \gamma \rho$$ (30)

where $\gamma$ is the electronic contribution to the normal state heat capacity with units of erg/cm$^3$-K$^2$, $\rho$ is the residual resistivity in 2 cm, and the units of $(-dH_{c2}/dT)_{Tc}$ are Oe/K. As already indicated, the values of $\gamma$ from the heat capacity data are given in mJ/mol-K. The $\gamma$ values listed in Table 11 are the measured $\gamma$'s multiplied by $(10^4 \text{ erg/J})(2 \text{ formula units/Volume of unit cell})N_A^{-1}$ where $N_A$ is Avogadro's number.

The agreement between the experimental and calculated values of $(-dH_{c2}/dT)_{Tc}$ is quite good for Sc$_5$Rh$_4$Si$_{10}$ and Sc$_5$Ir$_4$Si$_{10}$, and reasonably good for Sc$_5$Co$_4$Si$_{10}$ and Lu$_5$Rh$_4$Si$_{10}$. Poorer agreement is found for Lu$_5$Ir$_4$Si$_{10}$ and Y$_5$Os$_4$Ge$_{10}$. The discrepancy between these two values could be attributed in part to the error introduced in calculating the residual resistivity. Although the samples used were fairly symmetrical, a difference of as little as a 0.1 mm in the measurement of the dimensions can change $\rho_{res}$ significantly. A more probable reason, however, is the presence of the many large and small cracks exhibited
throughout the bulk of each sample. These crystal defects alone could drastically increase $\rho_{\text{res}}$. Scanning the tables, the generally high residual resistivities are apparent. If better quality resistivity samples of Sc$_5$Ir$_4$Si$_{10}$, Lu$_5$Rh$_4$Si$_{10}$, and Lu$_5$Ir$_4$Si$_{10}$ could be synthesized, a better agreement between the experimental and calculated $(-dH_{c2}/dT)_{T_C}$ could probably be attained; this indicates that the high residual resistivities of these samples are not intrinsic. On the other hand, the large value of $\rho_{\text{res}}$ is probably an intrinsic property of Sc$_5$Co$_4$Si$_{10}$, Sc$_5$Rh$_4$Si$_{10}$ and Y$_5$Os$_4$Ge$_{10}$ since if $\rho_{\text{res}}$ values for these compounds were decreased the discrepancy between the two values of $(-dH_{c2}/dT)_{T_C}$ would increase.

The values at 2.6 K of the Ginzburg-Landau (GL) coherence length, $\xi_{\text{GL}}$, the GL penetration depth, $\lambda_{\text{GL}}$, and GL parameter, $\kappa_{\text{GL}}$, in the "dirty limit" are listed in Table 11. To calculate each parameter, the corresponding BCS relations$^{74}$ were utilized (dimensions are in cm)

$$\xi_{\text{GL}} = 8.57 \times 10^{-7} \left(\gamma_{pT_C}\right)^{1/2} (1 - t)^2$$  \hspace{1cm} (31)

$$\lambda_{\text{GL}} = 6.42 \times 10^{-3} \left(\frac{\rho}{T_C}\right)^{1/2} (1 - t)^2$$  \hspace{1cm} (32)

$$\kappa_{\text{GL}} = 7.49 \times 10^3 \gamma^2 \rho$$  \hspace{1cm} (33)

where $t = T/T_C$. As is evident from these values, these ternary compounds are indeed type II superconductors, as had already been hypothesized.
V. CONCLUSION AND SUMMARY

The investigations of the superconducting and normal state properties of the ternary rare earth transition metal silicides and germanides with the Sc$_2$Co$_4$Si$_{10}$-type structure reported in this work have raised many questions and opened up several new areas of research. Low temperature heat capacity measurements yielded several important observations. Fitting the normal state heat capacity data for the high $T_c$ compounds Sc$_5$Rh$_4$Si$_{10}$, Sc$_5$Ir$_4$Si$_{10}$, and Y$_5$Os$_4$Ge$_{10}$ to a modified Debye model yielded physically unrealistic results for the electronic and lattice contributions to the specific heat. These poor fits indicate that the phonon spectrum of these high $T_c$ compounds is too complex to be adequately described by the Debye model which utilizes only one characteristic temperature. It is suggested that a better description of the phonon spectrum for these high $T_c$ materials would be given by a model proposed by Junod et al.68-70 for the high $T_c$ A-15 compounds. Physically, using a minimum of three characteristic temperatures, the parametrized model for the phonon density of states proposed is just a Debye model with an additional peak at lower frequencies representing the "soft modes" present in most high $T_c$ compounds. The high $T_c$ compounds in this ternary system also exhibit large electron-phonon interaction parameters indicating they are strong-coupled superconductors. The presence of the strong electron-phonon coupling in these compounds is one additional reason for the deviation of the normal state lattice contribution from the Debye model.
Several other observations about the heat capacity data may be made. Fitting the normal state data for the rest of the compounds with the modified Debye model yields reasonable results; however, the relatively large contribution of the anharmonic term is probably another indication of the complex phonon structure of these materials. The Debye temperatures of the silicides in this system are generally higher than those found in other ternary superconducting systems. This is most likely attributable to the fact that Si has a Debye temperature of 630 K, is a major constituent in these materials, and forms planar networks in this structure. In general, the germanides have lower Debye temperatures than the silicides; the major constituent, Ge, has a value of $\Theta_D = 370$ K. The results of the fits of the heat capacity data of these compounds below $T_C$ indicate that the BCS theory does not afford an adequate description of the superconducting state of these silicides and germanides. The fact that these compounds do not adhere to the predictions of this theory is most likely another experimental manifestation of the complex phonon structure inherent in these compounds. Future work leading to a better understanding of the normal and superconducting state of these compounds would include 1) an attempt to fit the normal state data of the high $T_C$ compounds with the new model proposed by Junod et al., 2) quenching the $T_C$'s by the application of a magnetic field to extend the normal state data to lower temperatures, 3) inelastic neutron scattering or tunneling to yield either the phonon density of states, $F(\omega)$ or the form of the electron-phonon spectral function, $\alpha^2F(\omega)$, and 4) a more complete treatment of the superconducting state than the BCS theory affords.
Electrical resistivity measurements indicate anomalous behavior in some of the data. The resistivities of $\text{Sc}_5\text{Co}_4\text{Si}_{10}$, $\text{Sc}_5\text{Rh}_4\text{Si}_{10}$, $\text{Sc}_5\text{Ir}_4\text{Si}_{10}$, $\text{Y}_5\text{Rh}_4\text{Ge}_{10}$, $\text{Y}_5\text{Ir}_4\text{Ge}_{10}$, and $\text{Lu}_5\text{Rh}_4\text{Ge}_{10}$ exhibit behavior slightly different from that manifested by normal metals at low temperatures. A small negative curvature is evident in these data; however, this is probably due to the change-over in temperature dependence of the resistivity from a linear high temperature region to a higher power law at low temperature. The resistivity curves for $\text{Y}_5\text{Ir}_4\text{Si}_{10}$, $\text{Lu}_5\text{Ir}_4\text{Ge}_{10}$, and $\text{Y}_5\text{Os}_4\text{Ge}_{10}$ show pronounced negative curvature, being the greater for the two Y-based compounds. The corresponding curves for $\text{Lu}_5\text{Rh}_4\text{Si}_{10}$ and $\text{Lu}_5\text{Ir}_4\text{Si}_{10}$ indicate relatively sharp drops at temperatures $T = 140 \text{ K}$ and $T = 80 \text{ K}$ respectively as one increases the temperature. None of the compounds investigated shows a strictly integral power of the temperature dependence of the low temperature resistivity ($T < 60 \text{ K}$) ranging from a $T^{2.1}$ to a $T^{4.1}$ dependence. This fact can most likely be attributed to the complex phonon structure of these compounds. Several mechanisms of scattering could be important in determining the overall resistivity behaviors. It is obvious that additional investigations are necessary in order to arrive at more quantitative conclusions concerning these compounds. More closely spaced resistivity data need to be taken to accurately determine the temperature dependence of $\rho(T)$, thereby enabling one to have some idea of the contribution of the various scattering mechanisms possible. High temperature data (above 380 K) would also be quite useful in determining whether or not saturation of $\rho(T)$ occurs well above the Debye temperatures of these materials.
Static molar magnetic susceptibility measurements yield several observations. The data for Sc\textsubscript{5}Co\textsubscript{4}Si\textsubscript{10}, Sc\textsubscript{5}Rh\textsubscript{4}Si\textsubscript{10}, Sc\textsubscript{5}Ir\textsubscript{4}Si\textsubscript{10}, Y\textsubscript{5}Ir\textsubscript{4}Ge\textsubscript{10}, Y\textsubscript{5}Os\textsubscript{4}Ge\textsubscript{10}, and Lu\textsubscript{5}Ir\textsubscript{4}Ge\textsubscript{10} can be fit very well with a Curie-Weiss law. The fit for Sc\textsubscript{5}Co\textsubscript{4}Si\textsubscript{10}, however indicates that the Co atom carries a small effective magnetic moment of $0.26 \mu_B$. The susceptibility data for Lu\textsubscript{5}Rh\textsubscript{4}Si\textsubscript{10}, Lu\textsubscript{5}Ir\textsubscript{4}Si\textsubscript{10}, Y\textsubscript{5}Ir\textsubscript{4}Si\textsubscript{10}, Lu\textsubscript{5}Rh\textsubscript{4}Ge\textsubscript{10}, and Y\textsubscript{5}Rh\textsubscript{4}Ge\textsubscript{10}, on the other hand, all show anomalous behaviors. The anomalies featured in Lu\textsubscript{5}Rh\textsubscript{4}Si\textsubscript{10} and Lu\textsubscript{5}Ir\textsubscript{4}Si\textsubscript{10} are jumps in $X(T)$ at the same temperature at which the drops in $\rho(T)$ occur. For Y\textsubscript{5}Ir\textsubscript{4}Si\textsubscript{10} the susceptibility shows a broad minimum; this then rises slowly eventually leveling off. Both Lu\textsubscript{5}Rh\textsubscript{4}Ge\textsubscript{10} and Y\textsubscript{5}Rh\textsubscript{4}Ge\textsubscript{10} data also have a minimum; however, the minimum in the former sample is quite broad, rising slowly, whereas the one in the Y\textsubscript{5}Rh\textsubscript{4}Ge\textsubscript{10} sample is fairly small with the data rising quite sharply thereafter. It is believed that the same mechanism is responsible for these anomalous behaviors exhibited by the magnetic susceptibilities and resistivities of some of the Sc\textsubscript{5}Co\textsubscript{4}Si\textsubscript{10}-type compounds. Similar anomalies in the resistivity and magnetic susceptibility data have also been observed in a separate sample of Lu\textsubscript{5}Ir\textsubscript{4}Si\textsubscript{10}.\textsuperscript{78} Low temperature (down to 21 K) polycrystalline X-ray measurements on this independent sample reveal no structural phase transition at the temperature where the anomalies occur. The conclusion reached was that the phase transition observed was electronic in nature. It is now also apparent that charge density waves (CDWs) may form in compounds with a three dimensional lattice.\textsuperscript{93-95} Thus, it is hypothesized\textsuperscript{78} that the formation of a charge- or spin-density wave is
responsible for the anomalous behaviors in the \( \rho(T) \) and \( \chi(T) \) data for this \( \text{Lu}_5\text{Ir}_4\text{Si}_{10} \) compound. The suggestion of this work is that CDW or SDW formation is the cause for not only the anomalous behaviors exhibited by the resistivity and susceptibility of the \( \text{Lu}_5\text{Ir}_4\text{Si}_{10} \) sample in this study but also for the anomalies featured in the \( \rho(T) \) curves for \( \text{Lu}_5\text{Rh}_4\text{Si}_{10} \) and \( \text{Y}_5\text{Ir}_4\text{Si}_{10} \) and the \( \chi(T) \) curves for \( \text{Lu}_5\text{Rh}_4\text{Si}_{10} \), \( \text{Y}_5\text{Ir}_4\text{Si}_{10} \), \( \text{Lu}_5\text{Rh}_4\text{Ge}_{10} \), and \( \text{Y}_5\text{Rh}_4\text{Ge}_{10} \). Additional work is necessary, however, to confirm the above hypothesis. Low temperature polycrystalline X-ray measurements need to be done on \( \text{Lu}_5\text{Rh}_4\text{Si}_{10} \), \( \text{Y}_5\text{Ir}_4\text{Si}_{10} \), \( \text{Lu}_5\text{Rh}_4\text{Ge}_{10} \), and \( \text{Y}_5\text{Rh}_4\text{Ge}_{10} \) to confirm that no structural phase transition occurs at the temperature at which the anomalies in \( \chi(T) \) and \( \rho(T) \) are seen. Secondly, single-crystal X-ray work is necessary to confirm the presence of CDW or SDW formation. This is presently in progress for the independent sample of \( \text{Lu}_5\text{Ir}_4\text{Si}_{10} \).

Upper critical magnetic field measurements on \( \text{Sc}_5\text{Co}_4\text{Si}_{10} \), \( \text{Sc}_5\text{Rh}_4\text{Si}_{10} \), \( \text{Sc}_5\text{Ir}_4\text{Si}_{10} \), \( \text{Lu}_5\text{Rh}_4\text{Si}_{10} \), \( \text{Lu}_5\text{Ir}_4\text{Si}_{10} \), and \( \text{Y}_5\text{Os}_4\text{Ge}_{10} \) is the last experiment discussed in this work. Using the WHH theory to fit the data yielded moderate values of \( (-dH_{c2}/dT)_T \text{c} \sim 7 \text{kOe/K} \) and \( H_{c2}(0) \sim 10 \text{kOe} \) for the silicides but rather high values of \( (-dH_{c2}/dT)_T \text{c} \sim 10 \text{kOe/K} \) and \( H_{c2}(0) \sim 60 \text{kOe} \) for \( \text{Y}_5\text{Os}_4\text{Ge}_{10} \). It was found that the values for \( \alpha \) (a measure of the spin paramagnetic) were very small, whereas the value of \( \lambda_{so} \) (a measure of the spin-orbit effect) could vary considerably without affecting the fit. The values of \( H_p \), the Pauli limiting field, are much larger than the values of \( H_{c2}(0) \) obtained from the WHH fit; however, the value of \( H_{c2}^*(0) \), the predicted \( H_{c2}^*(0) \)
ignoring the spin paramagnetic and spin-orbit effect, is very close to this value. The conclusions reached are 1) there is little or no Pauli limiting in these materials consistent with the small $\alpha$ values and and the ability of $\lambda_{SO}$ to be quite large and 2) the spin-orbit effect in these compounds appears to be negligible, consistent with the insensitivity of the fits to the value of $\lambda_{SO}$.

Comparing $(-dH^2/dT)_{Tc}$ obtained from the WHH fit of the data to the calculated $(-dH^2/dT)_{Tc}$, which utilizes the normal-state $\gamma$ value from heat capacity and the experimentally determined residual resistivity, yielded varying degrees of discrepancy for the six compounds investigated. Good agreement was found for Sc$_5$Rh$_4$Si$_{10}$ and Sc$_5$Ir$_4$Si$_{10}$. The agreement was reasonable for Lu$_5$Rh$_4$Si$_{10}$ and Sc$_5$Co$_4$Si$_{10}$ but poor for Lu$_5$Ir$_4$Si$_{10}$ and Y$_5$Os$_4$Ge$_{10}$. The discrepancy between these two values could be attributed in part to the error introduced in calculating the residual resistivities; however, a more probable reason is the presence of the many crystal defects found in these samples which could drastically increase $\rho_{res}$. It was concluded that the large $\rho_{res}$ of Sc$_5$Ir$_4$Si$_{10}$, Lu$_5$Rh$_4$Si$_{10}$, and Lu$_5$Ir$_4$Si$_{10}$ is not intrinsic; if better quality resistivity samples could be synthesized a better agreement between the two values of $(-dH^2/dT)_{Tc}$ could be attained. On the other hand, if the $\rho_{res}$ of Sc$_5$Co$_4$Si$_{10}$, Sc$_5$Rh$_4$Si$_{10}$ and Y$_5$Os$_4$Ge$_{10}$ were decreased, the discrepancy between the two $(-dH^2/dT)_{Tc}$ would increase; thus, the large $\rho_{res}$ of these compounds are probably intrinsic. The calculation of $\xi_{GL}$, $\lambda_{GL}$, and $\kappa_{GL}$ confirm the hypothesis that these samples are type II superconductors.
It is clear from the investigations reported in this work much can yet be learned about these ternary silicides and germanides. However, these experiments have to some degree succeeded in better characterizing the superconducting compounds in the Sc$_5$Co$_4$Si$_{10}$-type system as well as indicated further areas of research that will add to the present knowledge of the superconducting and normal properties of this complex family of materials. It is hoped that this work has contributed to a better understanding of the mechanisms involved in ternary superconductors in general as well as opened up other avenues of investigations into this fascinating phenomenon in these materials.
VI. REFERENCES

1. H. Kamerlingh Onnes, Leiden Comm. 120b, (1911).
5. W. Meissner and R. Ochsenfeld, Naturwissenschaften 21, 787 (1933).


90. For example, see the following conference proceedings: Molecular Metals, edited by W. E. Hatfield (Plenum, New York, 1979); The Physics and Chemistry of Low Dimensional Solids, edited by L. Alcâcer (D. Reidel, Boston, 1980).


VII. ACKNOWLEDGMENTS

Many people have aided me in my endeavor since coming to Iowa State University. I would first like to thank all the faculty, staff, and secretaries for all the help extended to me during my time in the Physics Department. Much gratitude is felt especially for my major professor, Professor Robert Shelton, for being around to guide and help me through this project. Without the aid of our lab technician, Peter Klavins, this project would undoubtedly have taken longer. My profound thanks are extended to him.

In addition to the help given me at Iowa State, support from other people has been very important in enabling me to finish this work. It is difficult to say what effect my parents have had on my career thus far. For one thing I am grateful, namely, that throughout my younger years they let me develop to my full potential, never attempting to stifle me in any way. However, the one person who deserves the most thanks is my husband, Steve. Without his infinite patience and understanding the completion of this work would have been much more difficult.
## VIII. APPENDIX: SOURCES AND PURITIES OF STARTING MATERIALS

<table>
<thead>
<tr>
<th><strong>Element</strong></th>
<th><strong>Source</strong></th>
<th><strong>Purity</strong></th>
</tr>
</thead>
<tbody>
<tr>
<td>Si</td>
<td>Research</td>
<td>7N pieces</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Organic/Inorganic Chemical Corp.</td>
</tr>
<tr>
<td>Ge</td>
<td>Ventron Alfa Products Lot#041377</td>
<td>6N+ pieces</td>
</tr>
<tr>
<td>Co</td>
<td>Ventron Alfa Products Lot#051573</td>
<td>m2N5 pieces</td>
</tr>
<tr>
<td>Rh</td>
<td>Purchases from USDOE stockpile P.O. A3-1197</td>
<td>4N powder</td>
</tr>
<tr>
<td>Ir</td>
<td>Research Organic/Inorganic Chemical Corp. #IR-002 DOE stores #01213642</td>
<td>3N powder</td>
</tr>
<tr>
<td>Os</td>
<td>Ventron Alfa Division Lot#010279 Lot#111478</td>
<td>3N powder</td>
</tr>
<tr>
<td>Sc</td>
<td>Ames Laboratory batch 112481, rod major impurities (atomic): O 118 ppm F 109 ppm H 89 ppm C 64 ppm W 36 ppm Fe 20 ppm N 6.4 ppm Cu 6 ppm La 5 ppm Ni 5 ppm Pr 4 ppm other impurities are all less than 4 ppm</td>
<td></td>
</tr>
</tbody>
</table>
Y
Ames Laboratory
batch 12381B, rod
major impurities (atomic):
  O 834 ppm
  H 704 ppm
  C 141 ppm
  W 22 ppm
  Pb 20 ppm
  F <14 ppm
  Fe 10 ppm
  Cu 5 ppm
  Tb 4.5 ppm
  Pr 4 ppm
other impurities are all
less than 4 ppm

Lu
Ames Laboratory
batch 51585, rod
major impurities (atomic):
  H 346 ppm
  C 189 ppm
  O 130 ppm
  Fe 78 ppm
  N 37 ppm
  F <27 ppm
  W 5.6 ppm
other impurities are all
less than 5 ppm