Low temperature properties of ternary magnetic rare earth transition metal germanides with the Sc5Co4Ge10-type structure

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Low temperature properties of ternary magnetic rare earth transition metal germanides with the Sc$_5$Co$_4$Ge$_{10}$-type structure

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Iowa State University, 1988
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Low temperature properties of ternary magnetic rare earth transition metal germanides with the Sc$_5$Co$_4$Ge$_{10}$-type structure

by

Chanson Parengkuan

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

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1

1. INTRODUCTION

1.1. Related Studies

The studies of magnetic properties have long been a challenging subject for magnet technology, the understanding of critical phenomena and the mechanism of magnetic ordering in solids.

One interesting fact is the great variety of magnetic ordering observed in rare earth compounds, providing an area to understand structure, critical behavior, specific heat, crystal field, magnetoresistance, magnetostriction, and related phenomena. The studies of magnetic properties of rare earth elements and their compounds began in the 1950s. A review of the lanthanide elements has been given by S. K. Sinha, while lanthanide compounds have been reviewed by H. R. Kirchmayr and C. A. Poldy, K. A. McEven. The more recent work focused on $\text{RT}_4\text{B}_4^{14-15}$ and $\text{R}_2\text{Fe}_3\text{Si}_5^{12}$ ($\text{R} = \text{rare earth, T} = \text{Rh}$).

The $\text{R}_5\text{T}_4\text{X}_{10}$ series was first reported by Braun et al. in 1980. Compounds with $\text{R} = \text{Y, Sc}$ and nonmagnetic lanthanide have been reported to be superconducting. On the other hand, compounds with rare earths having an incomplete 4f shell show magnetic ordering. A detailed study of the superconducting compounds has been done by L. S. Hausermann-Berg. The study of high pressure properties of silicides compounds has been studied by H. D. Yang et al. and Shelton et al. In the present study, compounds with magnetic rare earth elements are investigated to find new magnetic phenomena and to get a better understanding on the magnetic interaction in solids.
1.2. Heavy Lanthanides

The magnetic behavior of these compounds is mainly due to the lanthanides constituent. For our materials we focus on the heavy lanthanides Dy, Ho, Er, and Tm. The electronic configuration of lanthanides, as isolated atoms, can be written as \([\text{Xe}]4f^{n+1}6s^2\), where \([\text{Xe}]\) is the electronic configuration of closed shell atom Xe, and \(n\) is nine, ten, eleven and twelve for Dy, Ho, Er, and Tm, respectively.

In solids, the distances between the atoms are comparable with the radius of the outer shells 5d and 6s, so that the outer electrons do not only interact with their core but also with the nearby atoms. Their energy levels decrease and disperse into conduction bands. The three electrons in the 5d\(^1\)6s\(^2\) shell fuse with surrounding electrons to be conducting electrons, leaving \([\text{Xe}]4f^n\) shell as a core. For Ce, Eu, and Yb, because the tendency to form a closed or half-filled shell, \(n\) can often be zero, seven, and fourteen, instead of one, six, and thirteen, respectively. Therefore, the valence of most lanthanides is three. However, that for Ce is between three and four, and Eu, Yb are two or some fraction between two and three.

On the other hand, the distances between atoms are much larger than the radius of the 4f shell. The radius of the 4f shell is smaller for heavier lanthanides since the screening of electrons of the same shell is small. Because of the smallness of the mean radius of the f shell of heavy lanthanides compared with the distances of the surrounding atoms, the influence of surrounding atoms (crystal or ligand field) is small. The total angular momentum \(J\) is still a good quantum number. According
to Hund's rule,\textsuperscript{26-31} considering Coulomb interaction and the Pauli exclusion principle, the lowest energy configuration is that the orbital angular momentum of \( n \) electrons \( l_1, l_2, \ldots \) couple to be the largest total orbital angular momentum \( L \), and the spins couple to be the largest total spin \( S \), then these \( L \) and \( S \) couple to be a total angular momentum \( J \), which is equal to \( L - S \) and \( L + S \) for the first half and the second half of lanthanides, respectively. This ground state angular momentum configuration has \( 2J + 1 \) sub-states. They have different moments along the symmetry direction, \( J_z \) ranging from \(-J\) to \( J\). Without any other interaction, they are equally probable, so that the net moment is zero.

The electronic distribution of substate is shown in Fig. 1.2.1.\textsuperscript{32} These pictures are useful to predict qualitatively the energy shift of the substate in the presence of crystal field potentials. The energy is shifted down for states that have electronic distribution directed to the lower potential, away from more electro-negative surrounding ions or close to metallic ions.\textsuperscript{32-34}

The most common method to calculate crystal field states\textsuperscript{35-40} is as follows. In the presence of an electric field produced by the surrounding ions, the \( 2J + 1 \) degenerate substates split into several crystal field states, which are the eigenstates of the perturbed Hamiltonian. To calculate the perturbed Hamiltonian, the electric potential due to the surrounding ions is expanded in terms of spherical harmonics. Then, the \( x, y, z \) in the spherical harmonics are replaced by the corresponding angular momentum operators \( J_x = J_+ + J_- \), \( J_y = (J_+ - J_-)/i \), \( J_z \), and the corresponding spherical harmonics become the so-called Steven equivalent operators. The latter are easier to
Fig. 1.2.1. Probability distribution $P_{j,M}(\Theta)$ of the second half rare earth series for various $M$ in polar coordinate representation.
evaluate since the angular part of the n 4f electrons states are well known, and the unknown radial parts may be left as parameters. Because $x, y, z$ and $J_x, J_y, J_z$ are transformed as vector operators, their corresponding matrix elements are proportional, according to the Wigner-Eckart theorem which states that matrix elements of an operator can be written as a multiplication of reduced term and Clebsch-Gordan coefficients. Therefore, the matrix elements of the original spherical harmonics and their equivalent operators are proportional, and the proportionality constants depend only on the degree of the spherical harmonics and type of atoms. The most important proportionality constants, quadrupole coefficients, $C_\ell$ are listed in Table 1.2.1. The diagonalization the new Hamiltonian yields the crystal field states and energy.

An other effect worth mentioning is Kramer degeneracy. Due to the Coulomb interaction character of crystal fields, which is invariant under time reversal, the states of an odd electron systems are always double degenerate. Therefore, the multiplicity of crystal field states of an odd number electron systems which have total spin equal to half of an odd integer is always an even number. Contrary to even number 4f electron systems (total $J = integer$), the multiplicity of crystal field levels can be a singlet or triplet. A level of multiplicity $n$ can approximately be described by a state with pseudo angular momentum $S$, which is equal to $(n - 1)/2$, and a singlet state does not have a magnetic moment.

At temperatures much lower than the energy of the crystal field splitting, only the lowest energy state is populated, so the physical
properties are determined by the ground and first excited states. However, the energy splitting of heavy lanthanides due to the crystal field are usually small, less or about room temperature, so at temperatures higher than the crystal field splitting, all states have nonzero occupancy probability, and $J_z$ can be any quantized value between $-J$ to $J$. Therefore, the physical properties are the same as if there were no crystal field splitting.

Unlike the d shell, the f shell is very localized, so the exchange integral between the f shell of an ion and that of the neighbors is small. Therefore, it can not be the main factor for f-f correlation, which is in fact quite strong in the occurrence of magnetic ordering. Another exchange should be considered. For example, the exchange integral between f-s bands that causes correlation between the f electrons and conduction electrons. These correlated conduction electrons extend to neighbor ions and correlate also with their f electrons. Therefore, there will be a net f-f correlation through conduction electrons. This interaction is called RKKY interaction. The strength of this interaction should be proportional to the de Gennes factor: $(g - 1)^2 J(J + 1).$ The exchange interaction causes cooperative states of 4f states in a periodic lattice, where the $2J + 1$ substates disperse to become bands. An other exchange, superexchange, is the exchange mediated by the electron orbital of the neighbor atoms may also be considered.

If one ignores the crystal field as well as the exchange interaction, and considers only the effect of an external magnetic field, the degenerate $2J + 1$ sub-states split because of the Hamiltonian
The Zeeman term
\[ H_{\text{Zeeman}} = \beta (L + 2S) \cdot \mathbf{H} = g_J \mathbf{J} \cdot \mathbf{H}, \] (1.2.1)
where \( \beta \) is the Bohr magneton, and \( g \) is the Lande factor.\(^{26-31} \)
\[ g = \frac{3}{2} + \frac{(S(S+1) - L(L+1))}{2J(J+1)} \] (1.2.2)
This expression factorizes the projection of the magnetic moment \( (L + 2S) \) on total angular momentum \( \mathbf{J} \) about which the former precesses.

This additional term does not change the diagonalization of the original Hamiltonian, but it changes the eigen-energies. The difference in energy causes difference in population probability by the Boltzmann factor. Therefore, the net moment is nonzero.

\[ M = N g_J \frac{B(gJH/kT)}{B} \] and \( B \) is Brillouin function (1.2.3)
\[ B(x) = \frac{(2J+1)}{(2J)} \coth\left(\frac{(2J+1)x}{2J}\right) - \frac{1}{2J} \coth\left(\frac{x}{2J}\right) \] (1.2.4)
For small \( x = gJH/kT \), the magnetic moment approaches
\[ M = N \frac{(gJ)^2 J(J+1)H}{3kT} \] (1.2.5)
which is called Curie law.

Both crystal field and external magnetic field must be considered in the case experimental measurement of the magnetization. The crystal field states will recombine to a new set of states. For a small external magnetic field, we can say that the levels mix with the other nearby states. For a Kramer doublet system, this will split the doublets, and one can see \( J = 1/2 \) behavior of the magnetization, but \( g \) not necessarily the same as that of high temperature. For example, the doublet of \( J \) and \(-J\) can be considered as \( J = 1/2 \) system with \( g \) being \(|J|\) times the original. For a singlet system, the singlet levels recombine with nearest crystal field only singlet states to form new singlet
states which possesses temperature independent induced magnetic moment called Van Vleck paramagnetism. The isothermal magnetization curve at low temperature starts with high slope at low field, then quickly saturate to a small moment at high field. This nonlinearity becomes less prominent as the temperature increases. At constant field, one will see a saturation of the magnetization at low temperatures, so the inverse magnetization becomes flat at near $T = 0$ K.41-52

If we consider both crystal field and exchange interaction, a variety nonisotropic magnetic ordering can occur. Due to crystal fields, the f shell energy levels split into crystal field states. Each has a preferable moment direction, relative to the crystal axis. Since at low temperature, the lower energy state is more preferable, the magnetization will also have this preferable direction, called the easy axis.33-34 The magnetization along this direction is the largest. The exchange interaction causes the correlation between these crystal field states and those of the other ions, giving rise to magnetic order. The direction of the ordered magnetic moment is usually in the easy direction. In this case one can not consider single ion, but must involve the whole assembly of ions. The mean field approximation is usually used to simplify this problem, where the interactions with surrounding ions are replaced with an average static potential.54-56

Since ions sit in a periodic lattice, and the crystal field levels disperse into bands, whose lowest energy $K$ vector determines the periodicity of the magnetic ordering. Therefore, the ordering is usually very complicated. In fact, it is more complicated, since the entropy ($S$) of the ordering must also be considered.33 The minimum of
free energy $F = U - ST$ indicates the role of ST term, that a structure of more positive energy could be in favor at high temperature, provided it possesses large enough entropy. This effect and the temperature dependent crystal field exchange behavior can cause a variety of magnetic structure transformations.\textsuperscript{57-64}

All the heavy lanthanides crystallize in the hcp structure with the $c$ axis shorter than ideal hcp. They order magnetically at low temperature, and their magnetic structures are different at different temperature regions. At high temperatures, they all show Curie-Weiss paramagnetism. For Dy, which has a negative $\alpha_J$, below $T_{\text{Neel}}$, their magnetic moment in the basal plane direction orders ferromagnetically in two dimensions (the basal plane), but the moment direction rotates around the $c$ axis from plane to plane with a turn angle $\Theta$, forming spiral structure. This angle decreases as the temperature decreases, until $T_{\text{Curie}}$ is reached, then the angle changes to zero rapidly, becoming ferromagnetically order in three dimension. Similar to Dy, Ho forms a spiral structure below $T_N$, but unlike Dy, below $T_{C1}$ moments in $z$ direction order ferromagnetically, forming a cone structure. At another $T_C$, the spiral component collapses to basal ferromagnetism, forming a three dimensional ferromagnetic structure with the moment pointing $30^\circ$ off the $c$ axis. For Tm which has positive $\alpha_J$, below $T_N$, the magnetic moment in the $c$ direction orders ferromagnetically in two dimensions (basal plane), but the magnitude varies sinusoidally from plane to plane. As the temperature decreases, the higher odd harmonics intensify slowly, until $T_C$ is reached, the modulating sinusoidal becomes square. The magnetic structure of Er is a mixture of those of Dy and Tm. Below
$T_N$, its magnetic moments order in spiral structure, but below $T_{C1}$, the c axis moments order as $T_m$ to form antiphase-cone structure. Finally, below $T_{C2}$ the spiral component becomes ferromagnetic, so that they order ferromagnetically in three dimension with the moment pointing at a certain angle in space.

For later reference, some of the useful parameters are listed.

Table 1.2.1. Angular parameters of heavy lanthanides$^{26,28}$

<table>
<thead>
<tr>
<th>Ion</th>
<th>Conf</th>
<th>L</th>
<th>S</th>
<th>J</th>
<th>g</th>
<th>$\alpha_J$</th>
<th>$P_{\text{eff}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dy$^{3+}$</td>
<td>4$f^9$</td>
<td>5</td>
<td>5/2</td>
<td>15/2 (13/2)</td>
<td>4/3</td>
<td>-2/9.35</td>
<td>10.6</td>
</tr>
<tr>
<td>Ho$^{3+}$</td>
<td>4$f^{10}$</td>
<td>6</td>
<td>2</td>
<td>8 (7)</td>
<td>5/4</td>
<td>-1/30.15</td>
<td>10.4</td>
</tr>
<tr>
<td>Er$^{3+}$</td>
<td>4$f^{11}$</td>
<td>6</td>
<td>3/2</td>
<td>15/2 (13/2)</td>
<td>6/5</td>
<td>4/45.35</td>
<td>9.5</td>
</tr>
<tr>
<td>Tm$^{3+}$</td>
<td>4$f^{12}$</td>
<td>5</td>
<td>1</td>
<td>6 (5)</td>
<td>7/6</td>
<td>1/99</td>
<td>7.3</td>
</tr>
</tbody>
</table>

1.3. Structure of $R_5T_4X_{10}$

The ternary compounds $R_5T_4X_{10}$ ($R$ = rare earth, including Sc and Y, $T$ = Co, Rh, Ir, or Os, and $X$ = Si or Ge) crystallize in tetragonal $Sc_5Co_4Si_{10}$ type crystal structure$^{14-18}$ which have the space group $P4/mmb$ (#127), and lattice parameters $a = b = 12.013(2)$, $c = 3.936(1)$. There are 38 atoms per unit cell. The atomic positions are listed in Table 1.3.1., and the picture of the structure is shown in Fig. 1.3.1.
Table 1.3.1. Positional and equivalent isotropic thermal parameters

<table>
<thead>
<tr>
<th>Atom</th>
<th>Position</th>
<th>Symmetry</th>
<th>x</th>
<th>y</th>
<th>z</th>
<th>Ueq(A)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sc(1)</td>
<td>2(a)</td>
<td>4/m</td>
<td>0.0000</td>
<td>0.0000</td>
<td>0.0</td>
<td>86.(4)</td>
</tr>
<tr>
<td>Sc(2)</td>
<td>4(h)</td>
<td>mm</td>
<td>0.1756(1)</td>
<td>0.6756(1)</td>
<td>0.5</td>
<td>10.6(4)</td>
</tr>
<tr>
<td>Sc(3)</td>
<td>4(h)</td>
<td>mm</td>
<td>0.3882(1)</td>
<td>0.8882(1)</td>
<td>0.5</td>
<td>11.8(4)</td>
</tr>
<tr>
<td>Co</td>
<td>8(i)</td>
<td>m</td>
<td>0.2540(1)</td>
<td>0.5240(1)</td>
<td>0.0</td>
<td>86.(4)</td>
</tr>
<tr>
<td>Si(1)</td>
<td>4(g)</td>
<td>mm</td>
<td>0.0679(1)</td>
<td>0.5679(1)</td>
<td>0.0</td>
<td>89.(5)</td>
</tr>
<tr>
<td>Si(2)</td>
<td>8(1)</td>
<td>m</td>
<td>0.1575(1)</td>
<td>0.1985(1)</td>
<td>0.0</td>
<td>126.(5)</td>
</tr>
<tr>
<td>Si(3)</td>
<td>8(j)</td>
<td>m</td>
<td>0.1638(1)</td>
<td>0.0031(1)</td>
<td>0.5</td>
<td>138.(5)</td>
</tr>
</tbody>
</table>
Fig. 1.3.1. Sc$_5$Co$_4$Si$_{10}$-type crystal structure. View from approximately the c-axis (left); The projection on a,b-plane (right). Solid and open circles represent $z = 0$ and 1/2, respectively.
Table 1.3.2. Selected bond distances (Å)

<table>
<thead>
<tr>
<th>Bond</th>
<th>Distance 1 (Å)</th>
<th>Distance 2 (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sc(1)-Si(2)</td>
<td>4 X 3.043(2)</td>
<td>Si(1)-Sc(2)</td>
</tr>
<tr>
<td>Si(3)</td>
<td>8 X 2.783(2)</td>
<td>Sc(3)</td>
</tr>
<tr>
<td>Co</td>
<td>4 X 2.969(3)</td>
<td>Si(1)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Co</td>
</tr>
<tr>
<td>Sc(2)-Si(2)</td>
<td>4 X 2.823(2)</td>
<td>Si(2)-Sc(1)</td>
</tr>
<tr>
<td>Si(1)</td>
<td>2 X 2.688(2)</td>
<td>Si(2)</td>
</tr>
<tr>
<td>Si(3)</td>
<td>2 X 2.831(2)</td>
<td>Sc(2)</td>
</tr>
<tr>
<td>Co</td>
<td>4 X 2.842(2)</td>
<td>Sc(3)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Si(2)</td>
</tr>
<tr>
<td>Sc(3)-Si(2)</td>
<td>4 X 3.060(2)</td>
<td>Si(3)</td>
</tr>
<tr>
<td>Si(1)</td>
<td>4 X 2.968(2)</td>
<td></td>
</tr>
<tr>
<td>Si(3)</td>
<td>2 X 3.028(3)</td>
<td>Co</td>
</tr>
<tr>
<td>Co</td>
<td>4 X 3.074(2)</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Co-Sc(1)</td>
<td>1 X 2.969(3)</td>
<td>Si(3)-Sc(1)</td>
</tr>
<tr>
<td>Sc(2)</td>
<td>2 X 2.842(2)</td>
<td>Sc(2)</td>
</tr>
<tr>
<td>Sc(3)</td>
<td>2 X 3.074(2)</td>
<td>Sc(3)</td>
</tr>
<tr>
<td>Si(2)</td>
<td>1 X 2.253(2)</td>
<td>Si(2)</td>
</tr>
<tr>
<td></td>
<td>1 X 2.350(2)</td>
<td></td>
</tr>
<tr>
<td>Si(1)</td>
<td>1 X 2.297(2)</td>
<td>Si(3)</td>
</tr>
<tr>
<td>Si(3)</td>
<td>2 X 2.216(2)</td>
<td>Co</td>
</tr>
</tbody>
</table>
This structure type may be described in two ways:

1) Planar nets of pentagons and hexagons consist of Co and Si atoms as the basal planes are stacked, connected through Si atoms sitting between planes as zigzag Co-Si-Co chains, in the c direction, forming a three-dimensional net. This three-dimensional net is characterized by short Co-Si or Si-Si bonds. In the open site of this net, rare earth atoms sit. There are three different sites of rare earth atoms. They all have a horizontal mirror symmetry. The first sites are in the basal planes. They have 4/m symmetry, four-fold rotation along c, and a horizontal mirror plane. Their nearest neighbor atoms are four Si and four Co in the plane, and four Si in planes halve c above and below. The second sites are sandwiched in between basal planes as the center of pentagons prism. They have mm symmetry, a vertical and a horizontal mirror planes. The third sites are also sandwiched between planes, but they sit as the center of hexagons prism. They have the same symmetry as the second, with vertical mirror planes perpendicular to the former.

2) This description comes from the common pattern in rare-earth transition metal silicides structure. It describes the structure as parallel stacking of two kinds of basic building blocks along c axis. The first kind is a trigonal prism consisting of six Sc atoms on its vertexes, with Si atom at the center. The second kind is a tetragonal antiprism consisting of four Sc atoms forming a square vertical plane, and four Si atoms forming nearly square planar configuration, with a Si atom at the center of the Sc prism. They are shown in Fig. 1.3.2.
Fig. 1.3.2. The two basic building blocks in the Sc₅Co₄Si₁₀-type structure
2. EXPERIMENTAL METHODS

2.1. Sample Preparation and Characterization

All samples investigated in this work were prepared by arc-melting stoichiometric amount of high purity (at least 99.9 %) elements in a Zr gettered Argon atmosphere. The source and purity of the starting elements are listed in the Appendix.

The ingots were turned over and remelted several times, holding the arc on the sample for at least thirty seconds for each melt, to ensure homogeneity. Mass losses were typically less than 0.2 %. The samples were then sealed in quartz tubes under 200 torr argon atmosphere, and annealed in 850°C for one week, followed by a water quench.

A Rigaku X-Ray diffractometer with Cu Kα radiation and a diffracted beam graphite monochromator at a step scan rate 0.01 deg/sec over the 2θ angular range of 10 to 80 degrees were used to obtain powder diffraction data. Peaks angles of samples and silicon were fitted using the least-squares routine FINAX, and the resulting peak intensities and lattice parameters were compared respectively with X-ray peak height and data reported by Braun, Segre, Venturini et al.14,18

The ingot obtained by low power and slowly removed arc looks smooth on its surface, and the X-ray diffraction peaks were very sharp. On the other hand, the ingot obtained by high power and quickly removed arc looks dendritic structure on the top. However, the X-ray diffraction peaks look the same except that they were a little bit broader. The observation under optical microscope on the fracture ingots and flakes
shows the highly directional character of these compounds. In the center, crystals grew from the bottom. On the peripheral, crystals grew fast upward along the surface, and then on the top they grew radially in, creating porous and dendritic structure on the top. No observable secondary or impurity phase was found in either one.

The attempts to grow single crystals which are necessary for a thorough, three dimensional understanding of the magnetic structure in this system has been tried. Seven mm thick molybdenum was cut from the top to form cone cavity, and the tip of the cone makes the 1 mm diameter hole on the bottom. It was put into the arc furnace with an ingot in its cone cavity. Using a small current, the ingot was arc-melted again in argon atmosphere. The melt, through the 1 mm opening, touches the copper base of arc furnace at a point, so that one can expect that the melt starts to solidify from that point and to grow a few crystals when the arc was slowly removed. This method was done only in Ho₅Rh₄Ge₁₀ compound, and the result was far from ideal.

Optical microscope results were used to select fracture flakes of one directional grain for magnetization measurement. One 1 X 0.5 X 0.5 mm³ single crystal of Ho₅Rh₄Ge₁₀ compound was found. Buerger precession x-ray photograph confirmed that the direction of the grain is the unique axis c. The resulting pictures are shown in Fig. 2.1.1. From the similarity of grain appearance, the relation between the grain direction and c axis is assumed for the other compounds.
Fig. 2.1.1. Buerger precession photographs of single crystal Ho$_5$Rh$_4$Ge$_{10}$. The horizontal and vertical axes represent c and a axes. Left and right figures are the first and zero layers, respectively. $\lambda = 0.71 \, \text{Å}, \, L = 60 \, \text{mm}$
2.2. Magnetization Measurements

The dc magnetic susceptibility for these samples was measured in the Quantum Design's Magnetic Property Measurement System (MPMS). This fully automated device consists of:

1) Superisolated He dewar.

2) Cryostat facilitated with temperature sensors, gas circulation system and heaters to control temperature, superconducting magnet, SQUID and its pick up coil, and sample chamber in which the sample probe is inserted. The sample probe is attached to the sample transporter located at the top of the cryostat to move the sample across pickup coil.

3) Electronic module for SQUID detector, magnetic field, and also a pump to control temperature. The entire system is controlled by a personal computer.

Some of the important parts are shown in Figs. 2.2.1 and 2.2.2.

The sample is suspended on the lower end of a sample probe by a dental floss string. As the sample transporter moves the probe up and down, the sample moves across the quadrupole pickup coil, creating an emf on the coil, which is then sensed by the SQUID.

By gluing the sample in a certain orientation, we are able to measure the anisotropic magnetization. In this work, two kinds of orientation (the magnetic fields were parallel and perpendicular to the direction of the grain's direction) were studied. Ge 7031 was used as glue. It was also applied to the string, to fix the sample's
Fig. 2.2.1. The lower end of MPMS's cryostat
Fig. 2.2.2. Gas handling system (upper), and SQUID sensor circuit (lower)
For each orientation, the measurements were done in two ways: The first is by varying magnetic field at a given temperature to get loops of magnetization versus magnetic field curves, and repeat at different temperatures. The second is to fix the magnetic field and vary the temperature to get the magnetization versus temperature curves, and repeat at different magnetic fields. From the very distinct feature of the magnetization curve, we indeed have separated these two orientations. Measurements were done in the temperature range between 2.2 K to 300 K, and the magnetic field up to 20 K Gauss.

2.3. Resistivity Measurements

The dc resistivity measurements of these samples were done in the same device used for the magnetization measurements, but with a different sample probe. Therefore, magnetoresistivity measurements can also be done by turning on the superconducting magnet. The temperature range for these measurements was between 2.4 and 300 K. Samples were cut, using a diamond saw, into typically 0.1 X 0.1 X 0.8 cm$^3$ blocks. Four leads of two thousandth of an inch diameter platinum wires were spot-welded on the samples, two at the ends as current leads, and two at near the ends as voltage leads. The samples were aligned perpendicular to the probe, thus also the magnetic field if any. However, we could not align the grain orientation, since relatively large samples were required for these measurements, and it is difficult to select uniform grain direction in a piece of big
polycrystalline sample. The sample was enclosed in a copper container to ensure temperature uniformity.

A Keithley 228 was used as constant current source, and a Keithley 181 nanovoltmeter was used to measure voltage difference between the voltage leads. To avoid problems from electrical heating, a small constant 10 mA direct current is used. Measurements were done in the forward and reverse current direction to avoid contact potential error. From the current (I), voltage differences ($\Delta V_+$ and $\Delta V_-$), cross section area ($A$), and the distance between the two voltage leads ($L$), the absolute dc resistivities were calculated.

$$\rho = \frac{A (\Delta V_+ - \Delta V_-)}{2 LI}$$

2.4. Specific Heat Measurements

Heat capacity measurements were done in a heat pulse type semi-adiabatic calorimeter, in the temperature range between 0.6 to 30 K, on typically one gram samples. The cooling system of the cryostat consists of two steps. The He$^4$ cooling system which is able to cool down to 1.2 K, and He$^3$ system which can go as low as 0.5 K. On the latter the calorimeter is attached. Fig. 2.4.1. shows the overview of the whole system.13

In the He$^4$ cooling system, liquid He$^4$ flows slowly, through a capillary stainless steel tube, from the He$^4$ bath to the coneva, a closed copper container partially filled with sintered copper, in which He$^4$ is pumped continuously to maintain temperature at 1.2 K. In it there is also a He$^3$ capillary line as a heat exchanger to condense He$^3$. 
Fig. 2.3.1. Gas handling system and heat capacity cryostat
He$^3$ gas flows into the system through the first condenser at 4.2 K then into the coneva in which it is liquefied. Liquid He$^3$ flows down through a capillary line into a He$^3$ pot, in which it is collected and pumped to reach the temperature about 0.5 K. In the bottom of the He$^3$ pot there is a heat switch, a copper bar to conduct or isolate heat from He$^3$ pot to sample holder (addenda). The calorimeter is composed of a thin nylon tube supported sample holder with a Ge resistance thermometer and 1000 Ω Pt-W fine wire heater, and copper radiation shield. Another heater is also available on the mounting of radiation shield to control the surrounding temperature of the sample and addenda so that the heat leak can be kept minimum.

A Ge thermometer is connected to conductance bridge using four wire method. The output of the conductance bridge is connected to Y input of X-Y chart recorder. Time is represented on the X axis. In the measurement, the conductance of the sample thermometer was read, then a predetermined time-length constant current was applied to the sample heater. The temperature change ($\Delta T$) was calculated using small calculator from graphically determined conductance changes on the X-Y chart. The input energy ($E$) was calculated from the current ($I$), the voltage difference between the heater ($AV$), and the time duration ($At$).

$$E = I \cdot AV \cdot At$$

(2.4.1)

Then the total heat capacity of the addenda and the sample were calculated:

$$C = \frac{E}{\Delta T}$$

(2.4.2)

Empty addenda heat capacity obtained from a separate run was fitted to a polynomial, which was used to subtract the addenda's heat capacity from the total to get the sample's heat capacity.
3. METHOD OF ANALYSIS

3.1. Analysis of Resistivity Data

Following Matthiessen's rule, resistivity of a metal can be written as the sum of impurity and defects, magnetic, and two phonon terms.

\[ \rho = \rho_0 + \rho_m + \rho_{sd} + \rho_{ph}. \]  

(3.1.1)

\(\rho_0\) is resistance caused by scattering of conduction electrons by defects and impurities. This term is independent of temperature. Experimentally it is determined from the extrapolated resistance value at \(T = 0\), because any other scattering mechanism ceases at that temperature.

\(\rho_m\) is the resistance caused by scattering of conduction electrons by localized magnetic ions. Here, we only talk about magnetic ions that sit in a lattice rather than diluted uncorrelated magnetic ions. Above the magnetic ordering temperature, only weak short range correlation exist, so that electrons are scattered randomly, causing a temperature independent resistivity \((\rho_{mio})\). However, below the magnetic ordering temperature, the long range correlations also exist, so that electrons are scattered periodically which may alter the band structure. It has been known that in lanthanide elements or compounds, the complicated magnetic ordering may introduce a superlattice of periodicity up to seven of the lattice, creating new Brillouin zone. The energy gap at the zone boundary, if the gap locates near the fermi energy, obviously will cause the depletion of mobile
electrons, so the resistivity increases sharply at the band structure transition. This is called superzoning. The magnetic ordering in lanthanides usually only creates new periodicity in z direction, and they are two dimensional ferromagnetism in the plane perpendicular to the z direction. So the zoning of the band structure that causes the increasing resistivity will only be observed in the resistivity in the z direction. The resistivity in the xy plane shows a sudden slope change as in usual ferromagnetic ordering. The resistivity in an unchanged band structure region is decreasing with temperature. In part, because the larger the magnetic ordering parameter, the less random are electrons scattered. Since the gap is only one directional, it always remains metallic, so this term decreases to zero at T = 0. Therefore, \( \rho_\infty \) can be measured as the difference between \( \rho(0) \) and the extrapolation of the high temperature resistivity at T = 0.\(^{74,75}\) Unfortunately for these compounds, the magnetic ordering is not complete above our lower limit of cryogenic systems. Therefore, these values were not estimated.

Even though we do not have the values of \( \rho_\infty \), it is worth mentioning that since this scattering by magnetic ions is caused by a nonvanishing s-f exchange, which also causes the RKKY mediated magnetic ordering \( \rho_\infty \) and \( \Theta \) are related.\(^{79}\) In fact \( \rho_\infty / \Theta \) is expected to be a constant for the same series of compounds.

This magnetic resistivity is approximately proportional to the correlation function, and thus the integral of magnetic specific heat, for antiferromagnetism.\(^{80}\)

\[
\rho_m = A \left( 1 - \xi \right). \quad (3.1.2)
\]
Here $A$ is a proportionality constant, and $\xi$ is the correlation function.

$$\xi = \chi T/C, \quad C = \text{Curie constant.} \quad (3.1.3)$$

$\rho_{sd}$ is the resistance caused by the scattering of $s$-band conduction electrons by phonons into the $d$ band. The theoretical calculation by Wilson$^{81-82}$ gives:

$$\rho = \frac{A}{7.212} \int_{T}^{\Theta/T} \frac{x^3}{(e^x-1)(1-e^{-x})} \, dx \quad (3.1.4)$$

Here $\Theta$ is Debye temperature, and $\Theta_{sd}$ has been set to 0, since $s$ and $d$ bands are assumed to overlap. At low temperature, $\rho$ is proportional to $T^3$, and at high temperature, it becomes proportional to $T$.

$\rho_{ph}$ is the resistance caused by scattering of conduction electrons by phonons. That is intraband $s$-electron scattering. The theoretical calculation by Gruneisen gives:

$$\rho = \frac{A}{124.43} \int_{T}^{\Theta/T} \frac{x^5}{(e^x-1)(1-e^{-x})} \, dx \quad (3.1.5)$$

At low temperature, this term is approximately proportional to $T^5$, and at higher temperature it becomes proportional to $T$.

Therefore, at high temperature, $\rho_{sd}$ and $\rho_{ph}$ are difficult to differentiate. In the plot of log scale, from the slope one can find the low temperature exponent. In addition, one can also see if there is a reduced form such as:

$$\rho = A f(T/\Theta), \quad \text{which can be written as:} \quad (3.1.6a)$$

$$\log \rho = \log A + \log f'(\log T - \log \Theta). \quad (3.1.6b)$$

Here $f'$ is composite function $f(exp(x))$. The variations of constants $\log A$ and $\log \Theta$ from compound to compound appear as vertical and horizontal rigid shift on the curves. The resistivities above the
Fig. 3.1.1. The phonon resistivities of $R_5T_4Ge_{10}$ as functions of temperature in log-log scale.
ordering temperature of such a plot are given in Fig. 3.1.1. To find unambiguous slopes, the subtraction values which are supposed to be the magnetic disorder resistivity, are chosen so that the curves are as straight as possible at the low temperature region. It was found that the slopes give an unscattered exponent around 3.2. Therefore, the $\rho_{sd}$ was believed to be the dominant part. The application of Wilson’s resistivity here is theoretically sound, since in these compounds the conduction bands are mainly composed of s and d states of rare earth and transition metal ions.

For practical calculations, Wilson’s ($\rho_{sd}$) and Gruneisen’s ($\rho_{ph}$) functions were evaluated numerically at a set of points, then they were fitted to a fraction form as:

$$\rho_{sd} = \frac{T}{2 + \frac{(1.664 + (7.6 T)^{2.4})}{12 T^2 (1 + (7.6 T)^{2.4})}}$$  (3.1.7)

$$\rho_{ph} = \frac{T}{4 + \frac{2}{9 T^2} + \frac{2.003 + (10.12 T)^{2.644}}{249.225 T^4 (1 + (10.12 T)^{2.644})}}$$  (3.1.8)

The end parameters were obtained by comparing their expansions and the known analytical asymptotic behavior, and the other coefficients were adjusted numerically using a least squares method. The maximum error of these approximation is less than 0.3%.

However, the linear behavior of phonon resistivity at high temperature is seldom or maybe never found in ternary compounds or maybe any high resistance compounds. One of the explanations is because there is a limit for the conduction electron mean free path, namely, the
interatomic distances. To include this limiting factor, people usually write:\(^{83-85}\)

\[
\frac{1}{\rho_{\text{obs}}} = \frac{1}{\rho_{\text{ideal}}} + \frac{1}{\rho_{\text{max}}},
\]

(3.1.9)

Therefore, the plot of conductivity (inverse resistivity) versus \(1/T\) might be useful to study the high temperature behavior, because the dominant ideal conductivity varies as \(1/T\), which is the high temperature conductance of Gruneisen or Wilson result. They were shown in Fig. 3.1.2.

In the present study, finally, resistivities above the magnetic ordering temperature were fitted to

\[
\rho = \frac{1}{\frac{1}{\rho_{\text{sd}}(T/\Theta)} + C}
\]

(3.1.10)

Where \(A\) is directly proportional to the sd scattering cross-section, and it is inversely proportional to the electron density at the fermi energy; \(\rho_0\) is the sum of imperfection and magnetic scattering resistance; \(C\) is the minimum conductance or inverse maximum resistance. \(A, \Theta, \rho_0\), and \(C\) are adjusted so that the sum of the percentage deviation square is minimum.

The results of the fitting curves are shown with the data points in Chapter 4, and the resulting parameters are given in Table 3.1.1.
Fig. 3.1.2. The inverse of phonon resistivities of $R_{5}T_{4}Ge_{10}$ as functions of inverse temperature.
Table 3.1.1. Resistivity parameters (fits to eq. 3.1.10.).

<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Dy₃Rh₄Ge₁₀</td>
<td>259.35</td>
<td>193.54</td>
<td>14.544</td>
<td>250.74</td>
</tr>
<tr>
<td>Ho₃Rh₄Ge₁₀</td>
<td>267.13</td>
<td>179.01</td>
<td>11.981</td>
<td>381.86</td>
</tr>
<tr>
<td>Er₃Rh₄Ge₁₀</td>
<td>301.81</td>
<td>185.06</td>
<td>29.129</td>
<td>331.35</td>
</tr>
<tr>
<td>Tm₃Rh₄Ge₁₀</td>
<td>214.15</td>
<td>187.74</td>
<td>14.748</td>
<td>221.86</td>
</tr>
<tr>
<td>Dy₅Ir₄Ge₁₀</td>
<td>215.86</td>
<td>181.98</td>
<td>17.293</td>
<td>296.77</td>
</tr>
<tr>
<td>Ho₅Ir₄Ge₁₀</td>
<td>312.22</td>
<td>176.94</td>
<td>69.131</td>
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</tr>
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<td>Er₅Ir₄Ge₁₀</td>
<td>370.52</td>
<td>187.13</td>
<td>8.4207</td>
<td>335.81</td>
</tr>
<tr>
<td>Tm₅Ir₄Ge₁₀</td>
<td>452.50</td>
<td>200.63</td>
<td>10.190</td>
<td>289.02</td>
</tr>
</tbody>
</table>

3.2. Analysis of Specific Heat Data

Specific heat of these compounds is comprised of electronic, phonon, magnetic, crystal field, and nuclear parts.\(^{86-88}\)

\[ C_p = C_e + C_{ph} + C_m + C_{cf} + C_n. \]  

(3.2.1)

\( C_e \) is specific heat of conduction electron, which increases linearly at low temperature, and starts to saturate only at very high temperature, for example the half Fermi temperature.\(^{89}\) Thus in the range of this studies, it is expressed as\(^{90}\)

\[ C_e = \frac{n^2 k^2 g(E_f)}{3} T = \gamma T. \]  

(3.2.2)

Here \( k \) is Boltzmann's constant \((1.380662 \times 10^{-23} \text{ J/K})\), \( g(E) \) and \( E_f \) are
the electronic density of states and Fermi energy, respectively.

\( C_{\text{ph}} \) is specific heat of the lattice phonons. At high temperature, it saturates to the Dulong-Petit value.

\[
C_{\text{ph}} = 3 \, nR \quad \text{at } T \to \infty. \tag{3.2.3}
\]

Here \( n \) is the number of atom per molecule, \( R \) is the gas constant (8.31 J/ mol K), \( R = Nk \), and \( N \) is Avogadro's number (6.023 \times 10^{23} /mol), number of molecules per mole. At finite temperature, there are many methods to approximate this term.\(^{91-98}\) Einstein's approximation takes \( C_{\text{ph}} \) as the specific heat of 3 \( nN \) single-frequency independent oscillators, corresponding to \( nN \) atoms vibrating in 3 degree of freedom motion. Using Bose-Einstein statistics, energy and specific heat are calculated.

\[
E = \frac{3nR \, h \nu}{(\exp(h\nu/kT)-1)} \tag{3.2.4}
\]

\[
C_{\text{ph}} = \frac{dE}{dT} = \frac{3nR \, x^2 \exp(x)}{(\exp(x)-1)^2} \tag{3.2.5}
\]

\[
= 3nR \, x^2 \exp(-x) \quad \text{for } T \ll \Theta_D. \tag{3.2.6}
\]

Here \( x = h\nu/kT = \eta\Theta_D/T \).

Debye's approximation considers \( C_{\text{ph}} \) as the specific heat of a continuous medium. The energy and specific heat of the acoustic wave (phonon) are calculated. The phonon mode density is proportional to the volume of wave vector (\( q \)) space.

\[
g(q) = 3V/\pi^3 \, d^3q, \quad \text{or using} \tag{3.2.7}
\]

\[
\psi^2 = q^2c^2/4\pi^2, \tag{3.2.8}
\]

\[
g(\psi) = 4\pi\psi/c^2 \, \psi^2 \, d\psi. \tag{3.2.9}
\]

Here \( V \) is bulk volume; \( c \) and \( \psi \) are the speed and frequency of sound.
This continuous media model should be invalid for the vibration of wavelength less than the interatomic distance, so the cut off Debye's Frequency $\nu_D$ is introduced, beyond which the phonon mode density vanishes. Therefore, the resulting $E$ is just the integration of Einstein's $E$ over that frequency range with the above phonon mode density distribution function as a weighting factor. Finally one gets:

$$C_{ph} = 9nR \left(\frac{T}{\Theta_D}\right)^3 \int_0^{\Theta_D/T} \frac{x^6 \exp(x) \, dx}{(\exp(x) - 1)^2} \quad (3.2.10)$$

$$\alpha nR \frac{12}{5} \left(\frac{T}{\Theta_D}\right)^3 \quad T \ll \Theta_D \quad (3.2.11)$$

Here, $x = h\nu_D/kT$. At low temperature, the boundary of integration 0 to $\Theta_D/T$ approaches 0 to $\infty$, and the integral approaches $12n^4/45$.91

Because the Debye phonon mode density is only correct at low frequency, the combination of the Debye and Einstein models is often used.98 Several Einstein modes are introduced in addition Debye mode. This involves more parameters, so that the fitting is usually good.

However, the resulting parameters are physically less meaningful when we do not know how many dips or peaks are actually in the phonon spectrum. Then the Einstein's peaks are just substitutes of ranges of smooth phonon spectrum with the median frequencies equal to those Einstein's frequencies. This method has been elaborated by increasing the number of Einstein modes, spanning over a wide frequency range with the weighing factor of each mode adjusted to get a bar chart of the phonon spectrum.97

For practical calculation the following functions were used.

$$C_E = \frac{1}{(2 \times \sinh(0.5/x))^2} \quad \text{or} \quad (3.2.12)$$
\[
\frac{\exp(-1/x)}{x^2} \quad \text{for } x < 0.09 \quad (3.2.13)
\]

\[
C_p = \frac{1}{1 + 0.0128324783/x^3} - \frac{0.05 (x - 0.1681)}{x^3 + 0.1391 x + (0.047019/x)^3 + (0.094967/x)^6}
\]

or

\[
C_p = 77.92727 x^3 \quad \text{for } x < 0.04, \text{ and} \quad (3.2.15)
\]

\[
C_p = 1. - 0.05/x^2 \quad \text{for } x > 10. \quad (3.2.16)
\]

These approximations are correct to the 4th digit.

The next term \(C_m\) is the specific heat due to the magnetic moment. At the transition temperature region, it usually looks like a peak.\(^{99-104}\) So far, only 1 or 2-dimensional moments problems have been solved exactly.\(^{105-111}\) The results from 1 dimensional moments indicated that the specific heat is not a sharp peak, but a bump at the magnetic ordering temperature. In 2 dimension moments, the ordering does give a sharp peak. On the other hand the 3-dimensional problem has only been solved approximately,\(^{112}\) and that only for simple structures. In these compounds, the lanthanides coordination is much more complicated. Theory is impossible to calculate, but it may help to compare one physical measurement to another. Here Fisher's relation\(^{113-119}\) will be used to relate the magnetic specific heat and susceptibility. Let us assume the Hamiltonian.

\[
H_0 = H_0' + \sum_i \sum_j \left( J_{zij} S_i S_j + J_{xyij} (S_i S_j + S_j S_i) \right). \quad (3.2.17)
\]

\(H_0'\) is the moment independent Hamiltonian. \(N\) is sum over magnetic ion, and \(Q\) is sum over the neighboring magnetic ions. \(J_{kij}\) are the \(k\)
direction exchange interaction between \( i \) and \( j \) ions. Here according to the experimental results, we assume a unique axis \( z \), and the two direction perpendicular to it are equivalent. The difference between \( J_z \) and \( J_{xy} \) is a measure of the anisotropy. \( S_{z1} \) are the \( z \) direction angular momentum operators for ion \( i \).

Thus, the magnetic energy can be written as

\[
U_m = L_N L_Q J_{zij} \langle S_{z1} S_{zj} \rangle + L_N L_Q J_{xyij} (\langle S_{x1} S_{xj} \rangle + \langle S_{y1} S_{yj} \rangle).
\] (3.2.18)

To go on further, we have to assume that only the nearest neighbors are dominant which is true for antiferromagnetic interaction, then one can simplify to get:

\[
U_m = J_z L_N L_Q \langle S_{z1} S_{zj} \rangle + J_{xy} L_N L_Q (\langle S_{x1} S_{xj} \rangle + \langle S_{y1} S_{yj} \rangle).
\] (3.2.19)

Remembering that \( L_N L_Q \langle S_{z1} S_{zj} \rangle \) is proportional to \( \chi_z T \), one can write

\[
U_m = A (\chi_z + 2B \chi_{xy}) T,
\] (3.2.20)

so the magnetic specific heat is proportional to its derivative.

\[
C_m = A \frac{d}{dT} (\chi_z + 2B \chi_{xy}) T.
\] (3.2.21)

For this reason, from magnetization, we plot \( \chi T \) versus \( T \), and find its derivative. Without any additional information, the best assumption is to set \( B = 1 \), the exchange interaction being isotropic. For some compounds, the derivative with respect to \( T \) is also given. The exact match cannot be expected because of the nearest neighbor approximation, which according to Fisher can cause a slow variation of \( A \) with temperature. On the other hand, our susceptibility measurements were done in a finite applied magnetic field which was found to affect the magnetization significantly below the critical temperature.
Nevertheless, Fisher's relation is very useful for identifying the origin of some specific heat anomalies.

Near the transition temperature, the critical exponents $^{120-122}$ $\alpha$ may be evaluated.

\[ C_m = A/(T-T_c)^\alpha \quad \text{or} \quad (3.2.22a) \]

\[ = A \ln|T - T_c| \quad \text{as} \quad \alpha \to 0 \quad (3.2.22b) \]

Far below the ordering temperature, one could also find the exponent to compare with the theoretical value 1, 3/2, or 3, etc., depending on the magnetic structure and theory's approximation. However, here the ordering temperatures were so low that the range of validity is too narrow to determine the exponents.

The next term $C_{cf}$ is the specific heat due to $f$ shell electronic states (crystal field states) excited to higher states. It usually shows up as bumps or Schottky-type specific heat behavior. The energy

\[ E_{sch} = \frac{N \sum e_i^j \exp(-e_i/kT)}{\sum g_i \exp(-e_i/kT)} \quad \text{and} \quad (3.2.23) \]

the specific heat is

\[ C_{sch} = E_{sch}'/dT. \quad (3.2.24) \]

If the energy gap between the second excited state is much higher than the first excited state, the single lowest specific heat bump is segregated, then we approximate the system as a two level system. In this case, one can write

\[ C_{sch} = R (\delta/T)^2 \frac{g_1/g_0 \exp(\delta/T)}{(g_1/g_0 + \exp(\delta/T))^2} \quad (3.2.25) \]

\[ = R (g_1/g_0) (\delta/T)^2 \exp(-\delta/T) \quad \text{for} \quad T \ll \delta \quad (3.2.26) \]
39

\[ R \frac{g_0 g_1}{(g_0 + g_1)^2} (\delta/T)^2 \quad \text{for } T >> \delta \]  

(3.2.27)

Where \( \delta \) is the energy gap; \( g_1 \) and \( g_0 \) are the multiplicity of first excited state and ground state. The characteristics of this function are given in Table 3.2.1.

Table 3.2.1. Characteristic parameters for a 2-level system

<table>
<thead>
<tr>
<th>( g_1/g_0 )</th>
<th>( C_{\text{Sch}}(\text{max})/R )</th>
<th>( T_m/\delta )</th>
<th>Entropy/R</th>
</tr>
</thead>
<tbody>
<tr>
<td>1/2</td>
<td>0.241</td>
<td>0.448</td>
<td>ln 3/2</td>
</tr>
<tr>
<td>1</td>
<td>0.438</td>
<td>0.417</td>
<td>ln 2</td>
</tr>
<tr>
<td>3/2</td>
<td>0.609</td>
<td>0.394</td>
<td>ln 5/2</td>
</tr>
<tr>
<td>2</td>
<td>0.759</td>
<td>0.377</td>
<td>ln 3</td>
</tr>
<tr>
<td>5</td>
<td>1.444</td>
<td>0.320</td>
<td>ln 6</td>
</tr>
</tbody>
</table>

From this theory, the property of the two lowest states may be determined.

The last term \( C_n \) is the specific heat due to the excitation of the nuclear state. It also shows up as Schottky peaks, but since the energy gaps of these states are usually small, the location of peaks is usually below 1 K.

Experimentally, we obtain the superposition of these terms, and the separation is a very difficult task. Fortunately, the first two terms, thus also their sum, are approximately the same for all compounds in the series, so that sum can be acquired from the specific heat of the completely filled 4f shell Lu compound. For that purpose, in this work
the specific heat of Lu$_3$Rh$_4$Ge$_{10}$ and Lu$_5$Ir$_4$Ge$_{10}$ are fitted to

$$C_p = \gamma T + A_0 C_D(T/\Theta_D) + \sum A_i C_E(T/\Theta_E). \quad (3.2.28)$$

Here $C_D$ and $C_E$ are the Debye and Einstein specific-heat terms. $\Theta_D$ and $\Theta_E$ are adjusted. $A_0$ and $A_i$ are also adjustable constants whose sum were constrained to 3nR. The result without an Einstein term did not give a good fit, with a $\Theta_D$ about 180 K which is close to $\Theta_D$ obtained from the resistivity.

Several Einstein terms have been tried, but it was found that one Einstein term is sufficient to get a very good fit. The results are presented in Figs. 3.2.1. and 3.2.2. For Lu$_3$Rh$_4$Ge$_{10}$, the fitting between 3.5 to 30 K gives $\gamma = 16.56$, $A_0 = 0.8632 \times 3$ nR, $\Theta_D = 264.52$ K, $A_1 = 0.13685 \times 3$ nR, $\Theta_E = 88.82$ K. For Lu$_5$Ir$_4$Ge$_{10}$, the fitting between 6 to 30 K gives $\gamma = 10.4$, $A_0 = 0.87081 \times 3$ nR, $\Theta_D = 250.12$ K, $A_1 = 0.1292 \times 3$ nR, and $\Theta_E = 90.17$ K. Increasing the number of $C_E$ components gave better fits, and they gave a value of $\gamma$ closer to the Berg's result. This function is then subtracted from the magnetic compounds, so one gets the remainder as the sum of magnetic, crystal field, and nuclear term.

The entropy of these remainder terms was then calculated using trapezium integration, and it was compared with the theoretical value. Theoretically, the entropy involved in magnetic ordering is equal to $R$ times $\ln$ of the ground states multiplicity number before ordering.

$$\Delta \text{entropy} = R \ln(2S + 1).$$

Here, $S$ is pseudo-spin.
The specific heats of Lu₅Rh₄Ge₁₀. The inset shows the rough phonon spectrum used in the fitting function. Einstein's delta function has been replaced by equi-area arbitrary width Gaussian to make it visible.
Exp data

\[ C_p = \gamma T + 3 nR \left( (1-a) \frac{C_p(T/\theta_D)}{\theta_D} + a \frac{C_p(T/\theta_E)}{\theta_E} \right) \]

\[ \gamma = 10.4 \quad \theta_D = 250.12 \]

\[ a = 0.129 \quad \theta_E = 90.17 \]

Fig. 3.2.2. The specific heats of Lu$_5$Ir$_4$Ge$_{10}$. The inset shows the rough phonon spectrum used in the fitting function. Einstein's delta function has been replaced by equi-area arbitrary width Gaussian to make it visible.
3.3. Analysis of Magnetization Data

Magnetization along the z direction can be written as:113-119

$$M_z = N g \beta Z^{-1} \text{Tr} \{ S_{z0} \exp((-H_0 - g \mu_B S_{z1})/kT) \}. \quad (3.3.1)$$

Here $N$ is Avogadro's number $(6.023 \times 10^{23}/\text{mol})$; $g$ is the Lande's factor; $\beta$ is the electron Bohr-magneton $(9.27 \times 10^{-21} \text{gauss cm}^3)$; $S_{z1}$ is $z$ component angular momentum operator for ion $i$; $H_0$ is the Hamiltonian; and $Z$ is the partition function.

$$Z = \text{Tr} \exp(-H_0/kT). \quad (3.3.2)$$

The magnetic moment of an ion $\vec{g}(L + 2S)$, precesses around the total angular momentum $J$, so the net moment is in the same direction as $J$ with magnitude $g \mu J(J+1)$. The maximum moment is attained when all $J$ are oriented in one direction.

$$M_{\text{max}} = N \beta g \mu J(J+1)$$

$$= 5583.2 \mu_{\text{eff}} \quad \text{[gauss cm}^3/\text{mol}] \quad (3.3.3)$$

Here $\mu_{\text{eff}} = g \mu J(J+1)$, effective Bohr magneton.

Eq. 3.3.1. is difficult to evaluate, so one must consider approximations.

When the exchange interaction is not strong and it can be ignored, then the ions become isolated, and eq. 3.3.1. becomes a Brillouin behavior magnetization.

$$M(H,T) = M_{\text{max}}B_{J}(M_{\text{max}}H/RT) \quad (3.3.4)$$

$B_{J}$ is Brillouin function given in Section 2.1., and the gas constant $R = 0.831 \text{Tesla cm}^3/\text{K}$

One can include the exchange interaction in eq. 3.3.4. using a mean
field approximation by replacing the exchange interaction with its average \( \lambda M \). Then \( M(H,T) \) is the solution of the implicit equation.

\[
M = M_{\text{max}} B_j\left(\frac{M_{\text{max}}(H+\lambda M)}{RT}\right) \quad (3.3.5)
\]

For low field magnetization:

\[
M = H \chi, \quad (3.3.6)
\]

where \( \chi \) is the magnetic susceptibility, the differential of \( M_z \) with respect to \( H \).

Eq. 3.3.5 becomes

\[
M = M_{\text{max}}^2 \frac{(H+\lambda M)}{RT}, \quad \text{which gives}
M = \frac{M_{\text{max}}^2}{RT} H, \quad \text{Curie-Weiss law.} \quad (3.3.7)
\]

The plot of \( H/M \) versus \( T \) will be a straight line. From the slope, one can find the Curie constant \( M_{\text{max}}^2/R \), and from the \( T \) intercept one can find the Curie temperature. These plots are shown in Figs. 3.3.1 and 3.3.2.

On the other hand eq. 3.3.1 becomes

\[
\chi_z = \frac{N g^2}{k T} \sum \langle S_{z0} S_{zi} \rangle - \langle S_{z0} \rangle^2 \quad \text{and} \quad (3.3.8)
\]

\[
\langle S_{z0} S_{zi} \rangle = Z^{-1} \text{Tr} \{ S_{z0} S_{zi} \exp(-H_0/kT) \}. \quad (3.3.9)
\]

Since the spontaneous magnetization \( \langle S_{z0} \rangle = 0 \) above \( T_C \), and their sum is always 0 in antiferromagnetism. One writes

\[
\chi = \frac{N g^2}{k T} \sum \langle S_{z0} S_{zi} \rangle. \quad (3.3.10)
\]

Isolating \( i=0 \), we write:

\[
\chi = \frac{N g^2}{k T} \langle S_{z0}^2 \rangle + \Sigma' \langle S_{z0} S_{zi} \rangle. \quad (3.3.11)
\]

As long as the magnetic field is weak, the above equation is exact. At high temperature there is no correlation between ion \#0 and \#i, so the second term in the bracket vanishes, and since the ion is also
Fig. 3.3.1 The inverse susceptibilities of Rh compounds as functions of temperature.
Fig. 3.3.2 The inverse susceptibilities of Ir compounds as functions of temperature.
 isotropic,
\[ <S_{20}^2> = <S^2>/3 = J(J + 1)/3. \] (3.3.12)

Therefore, it is often written as:
\[ \chi = N g^2 \beta^2 J(J+1)/3kT \left( 1 + \Sigma' <S_{20}S_{21}^>/ <S_{20}^2> \right) \] (3.3.13)

In the ferromagnetic exchange, the terms in the summation are positive, so the sum blows up at \( T_C \). On the other hand, in the antiferromagnetic case, the terms alternate in sign, and as the temperature goes down, the sum has a singular slope at \( T_N \) and finally goes to zero at \( T=0 \).

Experimentally one gets
\[ \chi = M/H \]
\[ = N g^2 \beta^2 J(J+1)/3kT \left( 1 + \Sigma' <S_{20}S_{21}^>/ <S_{20}^2> \right) + \chi_0. \] (3.3.14)

Where \( \chi_0 \) is the susceptibility due to the sum of core diamagnetism (Larmor's), Pauli paramagnetism, and Landau diamagnetism. In the plot of \( T M/H \) versus \( T \), from the high temperature slope, \( \chi_0 \) is calculated.

Subtraction of this part gives:
\[ (M/H - \chi_0)T = N g^2 \beta^2 J(J+1)/3k \left[ 1 + \Sigma' <S_{20}S_{20}^>/ <S_{20}^2> \right]. \] (3.3.15)

The high temperature value will give the Curie constant
\[ C = N g^2 \beta^2 J(J+1)/3k \] (3.3.16)

But usually people are interested in:
\[ P_{\text{eff}} = g \downarrow J(J+1) = \downarrow 3k/Ng^2 \downarrow C \]
\[ = 2.828 \downarrow C, \quad C \text{ in cm}^3 \text{K/mol} \] (3.3.17)

By comparing eq. 3.3.7. with eq. 3.3.15., one can approximate the term in the bracket of eq. 3.3.15., called correlation function \( \xi \) by
\[ 1/(1+\Theta/CT), \] the mean field approximation. \( C \) is Curie constant, and \( \Theta \) is Curie temperature, which is positive or negative for antiparallel correlation (alternating series) or parallel correlation (positive
definite series). Its magnitude is proportional to the exchange energy.

The inverse of the correlation function is drawn against 1/T, since it becomes linear.

\[ 1/(\chi T) = 1/C + \Theta/C \cdot 1/T. \]  \hspace{1cm} (3.3.18)

The validity of the Curie-Weiss law at lower temperature but just above \( T_C \) is justified by the linearity of the data. The extrapolated value at \( 1/T = 0 \) corresponds to the inverse of the Curie constant, and the slope corresponds to the Curie temperature \( \Theta \) divided by the Curie constant.

As the temperature decreases, the magnetization may be anisotropic, because of depopulation of the crystal field exciting states. In this case, let us start from zero exchange, so we can consider the isolated ion states. \(^{30-31}\)

\[ M_k(H,T) = N \bar{g}_k Z^{-1} \text{Tr} S_k \rho \]

\[ M_k(H,T) = \frac{N \bar{g}_k \sum \langle i | S_k | j \rangle \langle j | \exp((V_{cf} + gHS_k)/kT) | i \rangle}{\sum \langle i | \exp((V_{cf} + gHS_k)/kT) | i \rangle} \]  \hspace{1cm} (3.3.19)

Here \( \rho \) is density matrix, \( |i\rangle \) the crystal field state, \( S_k \) is \( k \) direction angular momentum operator, the denominator is the partition function \( Z = \text{Tr} \rho \), and sum over \( 2J+1 \) crystal field states. In principle, eq. 3.3.19 can be evaluated, at least by a brute force method. However, crystal field-only eigenstates may be the easiest one to use as a basis. This equation corresponds to eq. 3.3.4, when the crystal field potential is zero.

Thing becomes more complicated when the competition of crystal field and exchange field are equally strong, since exchange causes cooperation states, mixing and dispersing the \( f \) states into bands. However, a mean field approximation is often used, by solving the implicit equation.
\[ M_k = M_k(H+\lambda M_k, T). \]  
(3.3.5b)

A detailed discussion of this system can be found in Bleaney's, Elliot's, Trammell's, and Cooper's literature.

Because of crystal fields, J favors a certain direction. Therefore, it is useful to introduce a factor \( f = \frac{S_{z0}^2}{J(J+1)} = \cos^2 \Theta \). Here, \( \Theta \) is the angle between J and magnetic field. Therefore, eq. 3.3.13 is written as

\[ \chi = N g^2 \beta^2 J(J+1) f/kT \left[ 1 + \sum S_{z0}^2 S_{z1}^2 / S_{z0}^2 \right] \]  
(3.3.13b)

Because of this, it is still useful to study the magnetization for the z and x directions separately through \( \chi_z T \) and \( \chi_x T \) as functions of \( T \), since we leave the unknown in the \( f \), \( f S_{z0} S_{z1} \) and \( f S_{x0} S_{x1} \). The \( \chi \) T's value above the high temperature value, the Curie constant, tell us the formation of easy direction (\( f > 1/3 \)) or the parallel (ferromagnetism) nature of the moments correlation in that direction, and the value below the Curie constant tells the formation of hard axis (\( f < 1/3 \)), strong crystal field singlet ground state or antiparallel correlation. To find the Curie parameters, we consider \( 1/\chi T \) as functions of \( 1/T \) (see Chapter 4).

Demagnetization factors were not considered, because the corrections were found to be smaller than the measurement error. To make a correction, we just need to convert external or applied field to internal magnetic field.

\[ H_{in} = H_{ex} + N m. \]  
(3.3.21)

Here \( H_{in} \) and \( H_{ex} \) are the internal and external or magnetic field; \( N \) is demagnetization factor; and \( m \) is the magnetization per volume whose unit
is the same as the magnetic field. The value of \( N \) is 0, \( 4\pi/3 \), \( 2\pi \), and \( 4\pi \) for a rod parallel to the field, a sphere, a rod perpendicular to the field, and the maximum \( 4\pi \) for a plate perpendicular to the field. For the samples we have, \( N \) should be between 0 and \( 4\pi/3 \) for symmetry axis measurements, and between \( 4\pi/3 \) and \( 2\pi \) for perpendicular axis measurements, since the crystals are longer on symmetry axis.
4. DATA ANALYSIS AND INTERPRETATION

4.1. Dy₅Rh₄₄Ge₁₀

The absolute dc resistivities were measured at a temperature range between 2.4 and 355 K, and the fitting was done in the temperature range between 14 and 355 K. They are shown in Fig. 4.1.1. The resulting parameters are given in Table 3.1.1. The slope of the curve changes rapidly between 5 and 7 K, as a sign of long range magnetic ordering below that temperature. Below this transition temperature, the resistivity curve does not look smooth. At about 4.5 K, it drops rapidly. This is possibly caused by another transition of the complex magnetic structure.

The specific heat was measured at temperature between 0.6 and 29 K, and is shown in Fig. 4.1.2. Four sets of data points are presented. The first is the heat capacity per mole (specific heat) of this compound. The second is the specific heat of Lu₅Rh₄₄Ge₁₀ calculated at the same temperature as the data points, using the fitting function shown in Section 3.2. The third is the difference of the first two, and the last is the entropy of the third. It can be seen that the dominant component of the third is the magnetic specific heat. The large magnetic ordering peak appears at temperature Tₙᵣ = 6.24 K, but there is another transition at T = 4.52 K, where the slope is discontinuous. Below this temperature, other than the two deviation points, the curve is smooth. The slope on a log-log plot of this region gives the exponent value about 1.3. The entropy shows the saturation value about
Fig. 4.1.1. The resistivities of Dy$_5$Rh$_4$Ge$_{10}$ as functions of temperature. The inset shows the low temperature close up.
Fig. 4.1.2. The specific heats of Dy$_5$Rh$_4$Ge$_{10}$ and Lu$_5$Rh$_4$Ge$_{10}$, their difference $\Delta$C$_p$, and the entropy of $\Delta$C$_p$ as functions of temperature.
Therefore, if one believes that the ordering happens on all five magnetic ions, this means that the electronic crystal field ground states have multiplicity of 4, or two Kramer's doublets for every ion (odd 4f electron).

The magnetization results for this compound were measured on a polycrystalline sample in the temperature range between 2 and 375 K at 2 K Gauss magnetic field. The $1/X$ vs. $T$ data are shown in Fig. 3.3.1. The value of $X_0$ was found to be very small compared with the local moment. The magnetic susceptibility times temperature ($T M/H = T X = N g \beta E <S_z S_z>$) and its temperature derivative in the temperature range between 2 and 30 K are given in Fig. 4.1.3. The diving of the $X$ curve (not the peak) corresponds to the peak of $dX T/dT$ curve. Similar to the specific heat, the $dX T/dT$ curve also shows an anomaly at 4.5 K, showing the applicability of the Fisher relation. However, the peak is a little lower than the 6.24 K peak of specific heat. This may be caused by the suppression of antiferromagnetism by the 2 K Gauss magnetic field.

Following this fluctuation theory, the slow decrease of the $X T$ curve above $T_H$ corresponds to the slowly increasing strength of the antiferromagnetic exchange interaction energy between nearest neighbor magnetic ions. As the temperature approaches $T_N$, the longer range correlations take over, and at $T_N$, the infinite range correlation appear suddenly, causing a discontinuity in slope of the $X T$ curve. The inverse of $X T$ versus $1/T$ is shown in Fig. 4.1.4. The plot is quite straight above 10 K ($1/T = .1$). It indicates the validity of the Curie-Weiss law above this temperature. The inverse of the $Y$-axis intercept gives a Curie constant $C = 66.6$ which corresponds to $P_{eff} = 10.33$. 
Fig. 4.1.3. The magnetic susceptibilities, magnetic susceptibilities multiplied by temperature (unnormalized correlation function) and their temperature derivative of Dy$_5$Rh$_4$Ge$_{10}$ as functions of temperature.
Inverse temperature \([1/K]\)

Fig. 4.1.4. The inverse of magnetic susceptibilities times temperature (inverse of un-normalized correlation function) of Dy₅Rh₄Ge₁₀ as functions of inverse temperature
Fig. 4.1.5. The resistivities, specific heats, and magnetic susceptibilities of Dy$_5$Rh$_4$Ge$_{10}$ as functions of temperature, near the transition points.
Using this number and the slope of the straight line, Θ Curie is found to be 6.9 K which is quite close to \( T_N \). The \( 1/X \) versus \( T \) plot was not used to find these numbers because it is difficult to see what part of the line should be fit to Curie-Weiss law, since different regions give different values. It is very interesting that the extension of the line in Fig. 4.1.4. coincides with the data again below 2.5 K \( (1/T = 0.4) \).

For comparison, resistivity, specific heat, and magnetization curves are simultaneously shown in Fig. 4.1.5.

4.2. \( Ho_5Rh_4Ge_{10} \)

The absolute dc resistivity was measured in the temperature range between 2.4 and 255 K, and fitting was done in the temperature range between 14 and 255 K, as shown in Fig. 4.2.1. The resulting parameters are given in Table 3.1.1. The curve shows a slope discontinuity at about 7 K, indicating that long range magnetic ordering occurs below this point. There is also a rapid drops at about 4.5 K as a sign of another magnetic structure change.

The magnetoresistance measurements were done in the temperature range between 2.2 and 15 K, at magnetic fields ranging from 0 to 10 K Gauss with 1 K Gauss steps. They are shown in Fig. 4.2.2. For clarity only some of the data are shown. Unfortunately, the direction of the current with respect to the crystal axis can not be determined due to the polycrystalline sample, and the cut with respect to crystal growth of the ingot was not determined. In addition, the sample position with respect to magnetic field has also been overlooked. For \( H = 0 \), the
Fig. 4.2.1. The resistivities of $Ho_5Rh_4Ge_{10}$ as functions of temperature. The inset shows the low temperature close up.
Fig. 4.2.2. Magnetoresistance of Ho$_5$Rh$_4$Ge$_{10}$ versus temperature
Fig. 4.2.3. The specific heats of Ho$_5$Rh$_4$Ge$_{10}$ and Lu$_5$Rh$_4$Ge$_{10}$, their difference $\Delta C_p$, and the entropy of $\Delta C_p$ as functions of temperature.
resistivity shows slope discontinuities at T about 7, 4.9, and 2.5 K. As we apply a magnetic field, the resistivity between T = 7 and 5 K is suppressed (phase III), so that it creates an upturn at about 4.5 K. As we increase the magnetic field, this point moves to lower temperature. This behavior can be explained by the existence of superzoning caused by a complex magnetic structure (phase II) on the direction of the current. At lower temperature, as we apply a magnetic field, the resistivity below 2.5 K is also suppressed, making the slope discontinuity at 2.5 K more prominent. As we increase the magnetic field, this transition point moves to higher temperature, then stops at 3.3 K. Therefore, below this transition temperature, the magnetic structure at low field posses a ferromagnetic component (phase I). As we increase the magnetic field above 8 K Gauss, the superzone at higher temperature disappears, so only the slope discontinuity at 3.3 K survives, and this point moves back to lower temperature. This suggests that as we increase the magnetic field, the free energy decreases with the rate in the following order: phase II, phase I, phase III, the latter being the fastest.

Using

\[ \Delta G = \Delta U - S \Delta T - M \Delta H, \]

and since \( \Delta U \) and \( \Delta T \) are zero for isothermal magnetization, then we can write:

\[ \Delta G = -M \Delta H. \]

Therefore, the susceptibility also increases in that order, phase II, phase I, and phase III. We will discuss this point further in connection with the magnetization data.

The specific heat was measured in the temperature range between T =
1.73 and 29.62 K as shown in Fig. 4.2.3. The result of subtracting the specific heat of Lu$_5$Rh$_4$Ge$_{10}$ from these specific heat data is flat and high. Two small peaks are observed at around 7 and 4.9 K. These two temperatures happen to be the boundaries of phase III. A large flat specific heat above the transition temperature makes the identification of contributing mechanism difficult. Failure to measure the specific heat of this sample below the indicated value was caused by insufficient cooling power of our cryogenic system to handle a big heat load from transition at about 1 K. It probably corresponds to the phase II to Phase I transition.

The crystal field of this even 4f electron system in very low symmetry sites can be a singlet, and the entropy curve continues to increase because of the large flat specific heat. Therefore, the analysis becomes impossible.

Constant 2 K Gauss magnetization measurements on varying temperatures between 2 and 225 K have been done on a polycrystalline sample. The resulting inverse susceptibilities are shown in Fig. 3.3.1.

The magnetization measurements were also done on a single crystal sample. The isothermal magnetization data are shown in Fig. 4.2.6. The magnetization curves show very prominent anisotropic behavior. Using Buerger's precession X-ray diffraction photograph, the magnetic easy direction was found to be the c crystal axis.

Single crystal magnetization measurements in the temperature range between 2 and 350 K were done with constant 5 K Gauss magnetic field in both directions. The resulting $X T$ versus $T$ and its temperature derivative curves in the temperature range between 2 and 30 K are shown
Fig. 4.2.4. The magnetic susceptibilities, magnetic susceptibilities multiplied by temperature (unnormalized correlation function) and their temperature derivative of Ho$_5$Rh$_4$Ge$_{10}$ as functions of temperature.
Fig. 4.2.5. The inverse of magnetic susceptibilities times temperature (inverse of unnormalized correlation function) of Ho₅Rh₄Ge₁₀ as functions of inverse temperature
Fig. 4.2.6. Isothermal magnetizations versus applied magnetic field for Ho$_5$Rh$_4$Ge$_{10}$
in Fig. 4.2.4. The $\chi T$ curve for the easy direction deflects down at about 6 K, and has a sharp drop at 3 K, corresponding to the transitions from paramagnetism to phase II and phase II to phase I, respectively. The negative deviation of this curve from the Curie constant shows that the inter-ion correlation is negative, and the magnitude increases at both transitions.

The $d\chi T/dT$ curve is small at temperatures higher than 7 K, but below this temperature, it increases rapidly as temperature decreases, until the temperature reaches 3.25 K, where a sharp peak is observed. Since Fisher's relation works well above the ordering temperature, we conclude that the large flat specific heat above the ordering temperature does not originate from magnetic interaction. Crystal fields may be responsible. From these data, we can not see the transition temperature at about 4.5 K observed in the magnetoresistance. On the other hand, $\chi T$ in the hard direction smoothly decreases as the temperature decreases. No anomaly is observed in this direction.

The plot of inverse $\chi T$ vs. $1/T$ is given in Fig. 4.2.5. The plot of the magnetization parallel to c crystal axis consists of two sections of lines, joined at $T = 3$ K. For temperatures between 5.5 and 300 K ($1/T = 0.18$ and $0.03$), a Curie-Weiss law is followed, and it gives $\Theta = 10.233$ and $\Theta = 3.774$ K, which is close to the boundary of phase I and phase II. For magnetization perpendicular to c crystal axis, a straight line can be fitted all the way from room temperature to 2 K, which means that the Curie-Weiss law is perfectly followed. It gives $\Theta = 11.55$ K. Note that this high $\Theta$ does not come entirely from a negative exchange but also from the hardening of the axis (see also section 4.2).
The isothermal magnetization on single crystal samples were measured at different temperatures, but for clarity, only $T = 2, 3, 3.7 \text{ K}$ on the easy direction, and $T = 2, 2.7, 3.6 \text{ K}$ for the hard direction are shown in Fig. 4.2.6. At $T = 2 \text{ K}$, the easy direction magnetization has a large slope at low field, and then slowly levels off. At about one tesla (10 K Gauss), it undergoes a transition. The slope increases suddenly and levels off again. Therefore, at each region, a saturation-like behavior is observed. This is often observed in even number electron lanthanides, in which the singlet states are mixed to lower the energy in the presence of external magnetic field or exchange field by creating induced moments. The saturation value of this moment is determined by the off diagonal matrix elements of $J_g$. The behavior observed here matches very well to that described by Cooper et al. and Trammell. As the temperature increases, the curve becomes more linear, and the transition field decreases, until it finally becomes almost straight at about $T = 6 \text{ K}$.

By observing magnetoresistance curves and the magnetization curve as function of temperature for different fields, we get the following results. The large slope section at low field corresponds to phase I. The level region in the lower field section corresponds to phase II. There is no observable transition between these two phases on this isothermal magnetization data, unlike the magnetoresistivity data which show a clear boundary between phase I and phase II. Therefore, there must be a rapid change of the isothermal magnetization curves profile at $T$ about $3 \text{ K}$. The high slope region above the transition field corresponds to phase III. Therefore, it is consistent with the earlier
Fig. 4.2.7. Estimated free energy versus temperature (upper), and estimated H,T phase diagram (lower) for Ho₅Rh₄Ge₁₀.
Fig. 4.2.8. The resistivities, specific heats, and magnetic susceptibilities of Ho₅Rh₄Ge₁₀ as functions of temperature, near the transition points.
discussion on free energy. These lead us to the free energy curves and phase diagram as shown in Fig. 4.2.7. It is not clear whether phase III is the same as the paramagnetic phase at high field.

The isothermal magnetization on the hard direction shows very similar behavior, except that the transition happens at a much higher field, about 3 Tesla at \( T = 2 \) K.

For comparison, resistivity, specific heat, and magnetization are plotted in the Fig. 4.2.8.

4.3. \textit{Er}_5\textit{Rh}_4\textit{Ge}_{10}

The absolute dc resistivities were measured in the temperature range between 2.4 and 370 K, and the fitting was done in the temperature range between 15 and 325 K. Results are shown in Fig. 4.3.1 with the resulting parameters are given in Table 3.3.1. The low temperature resistivity curve shows superzone effects at \( T \approx 6 \) K and below, which suggests the formation of a complex magnetic structure.

The specific heats were measured in temperature range between .73 to 27.57 K, and are shown in Fig. 4.3.2. One observes two magnetic transition at \( T = 0.988 \) and 5.606 K. Above the transition temperatures, the specific heat value is large and flat, which is believed to be due to sparse crystal field levels. Therefore, the entropy at the higher temperature region is difficult to analyze. However, the entropy difference between temperature up to the lower transition peak is close to 5.76 J/mol K (\( R \ln 2 \)). This entropy change corresponds to a Kramer’s doublet, so we infer that only one site of magnetic ions is involved in
Fig. 4.3.1. The resistivities of $\text{Er}_5\text{Rh}_4\text{Ge}_{10}$ as functions of temperature. The inset shows the low temperature close up.
Fig. 4.3.2. The specific heats of $\text{Er}_5\text{Rh}_4\text{Ge}_{10}$ and $\text{Lu}_5\text{Rh}_4\text{Ge}_{10}$, their difference $\Delta C_p$, and the entropy of $\Delta C_p$ as functions of temperature.
the 0.988 K transition.

The magnetization measurements were done on two samples, a polycrystalline and single oriented grain sample. The inverse susceptibility of the polycrystalline sample is represented in Fig. 3.3.1. Since this polycrystalline sample has large mass, it is good for studying high temperature behavior where the magnetization is relatively weak. It is also good for the high temperature region where the moment is isotropic. The analysis for low temperature was done on the single oriented grain sample. We did not use single crystal X-ray diffraction to see whether it is a single crystal. Its magnetization data at different fields and directions for temperature between 2 and 45 K are shown in Fig. 4.3.3. At low field, the magnetization on the easy axis shows a plateau at temperature where the large peak on specific heat is observed and a bending down at the low temperature end. The latter could correspond to the anomaly at lower temperature 0.988 K on specific heat. As the magnetic field increases, the plateau anomaly at the temperature about 5 K grows to an antiferromagnetic like peak, and it moves down to lower temperature. This peak decreases back to a smaller amplitude as the magnetic field increases beyond 8 K Gauss. No prominent anomaly was observed on hard direction. Therefore, in this temperature range, only the c crystal axis moments order, and the moments in the a and b crystal axes do not order.

For clarity, the plot of $\chi T$ versus $T$ is shown in two figures, Fig. 4.3.4. to show the anisotropy behavior of paramagnetic region, Fig. 4.3.5. to show the behavior near ordering temperature. From Fig. 4.3.4, one can see that the $\chi T$ in the easy axis direction positively deviates
Fig. 4.3.3. Isofield magnetizations as functions of temperature for Er$_5$Rh$_4$Ge$_{10}$
from the Curie constant, and the hard axis direction negatively deviates. This can be caused by the following two possible mechanisms. First, the magnetic correlation on c axis is positive, and the correlation on a and b directions are negative above the ordering temperature, but the correlation on the easy direction changes sign as it is cooled below the ordering temperature, so that a turning point is observed in easy direction. However, it was found that the sum of squares of these two curves is flat in the paramagnetic region, and no maximum was observed. The curve starts to decrease at near transition temperature. This suggests another possibility; namely, that f factor becomes anisotropic below 90 K.

Kramer's doublet system of Er ions in the strong axial symmetry site may have its largest f factor ground state along that axis. As temperature decreases, this ground state becomes dominant, and the $g^2fJ(J+1)$ factor in eq. 3.3.13b for the easy direction may increase faster than the slowly decreasing effect of negative correlation, so that the over all $\chi T$ increases. However, near the ordering temperature, the correlation function decreases very rapidly, so $\chi T$ also decreases. On the other hand, the decreasing f factor along the hard direction may reinforce the appearance of the negative correlation. The second theory is believed to apply to this material.

The plot of $\chi T$ and its derivative for low temperatures are shown in Fig. 4.3.5. The transition at about 5 K is obviously shown as a peak in the $d\chi T/dT$ curve. It predicts a small magnetic specific heat above the transition temperature. Therefore, it is believed that the large flat specific heat data are attributed to a Schottky crystal field anomaly.
Fig. 4.3.4. The magnetic susceptibilities multiplied by temperature (unnormalized correlation function) and their temperature derivative of Er$_5$Rh$_4$Ge$_{10}$ as functions of temperature.
Fig. 4.3.5. The magnetic susceptibilities multiplied by temperature (unnormalized correlation function) and their temperature derivative of $\text{Er}_5\text{Rh}_4\text{Ge}_{10}$ as functions of temperature, near the transition points.
Fig. 4.3.6. The inverse of magnetic susceptibilities times temperature (inverse of unnormalized correlation function) of $\text{Er}_5\text{Rh}_4\text{Ge}_{10}$ as functions of inverse temperature.
Fig. 4.3.7. The resistivities, specific heats, and magnetic susceptibilities of Er₅Rh₄Ge₁₀ as functions of temperature, near the transition points.
The plot of inverse $\chi T$ vs $1/T$ is shown in Fig. 4.3.6. Below the transition temperature, the data in the easy direction are very sensitive to applied magnetic field. The increasing moment on that direction manifests itself as a minimum at about $1/T = 0.06$. On the other hand, the data for hard axis direction at 6 and 8 K Gauss field are quite straight, despite the 2 K Gauss curve that looks irregular. The high temperature limit value of these two directions meet at a point, which results in a Curie constant $= 55.2$, corresponds to $I_{\text{eff}} = 9.4$. The slope of the straight line on the hard direction gives $\Theta = 7.066$ K. Following the earlier discussion, $\Theta$ shown here is not a measure of the correlation strength, since it is an effect of both, decreasing moment along this direction and negative correlation. This also explains the phenomena on some other compounds, where the $\Theta$ along hard direction is larger than that along easy direction.

For comparison, resistivity, specific heat, and magnetization are shown in Fig. 4.3.7. It shows that small superzone structure on resistivity, specific heat peak, and magnetization plateau happen at the same temperature.

4.4. Tm$_5$Rh$_4$Ge$_{10}$

The absolute dc resistivities were measure in the temperature range between 2.4 and 350 K, and the fitting was done between 15 and 325 K. Results are shown in Fig. 4.4.1. with the fitting parameters given in Table 3.1.1. The data show two slope discontinuities at about 7 and 4.5 K. The former indicates the existence of long range magnetic ordering,
Fig. 4.4.1. The resistivities of $\text{Tm}_5\text{Rh}_4\text{Ge}_{10}$ as functions of temperature. The inset shows the low temperature close up.
Fig. 4.4.2. The specific heats of $\text{Tm}_5\text{Rh}_4\text{Ge}_{10}$ and $\text{Lu}_5\text{Rh}_4\text{Ge}_{10}$, their difference $\Delta C_p$, and the entropy of $\Delta C_p$ as functions of temperature.
the latter may indicate a transformation of magnetic structure.

The specific heat data for temperature between 0.59 to 29.29 K are given in Fig. 4.4.2. Those two transitions observed in resistivity appear as a peak at 6.78 K and a broad peak at about 4.5 K. The latter can not be fitted to a Schottky specific heat term, even though they are similar in shape. It probably originates from the one dimensional magnetic ordering. The total entropy involved in those two transition is about 40 Joule/mol K which corresponds to 4.81 R. This entropy is difficult to interpret, because of the singlet crystal field states.

The magnetization measurements of this compound were done on two samples, polycrystalline and single oriented grain samples. The polycrystal's inverse susceptibility versus temperature data are shown in Fig. 3.3.1. The anisotropic properties of the magnetization at low temperature were studied on single oriented grain sample. The low temperature magnetization for different field and directions are given in Fig. 4.4.3. The magnetization on the hard direction is only about half of that the easy direction, and it does not show any anomaly. This suggests that the moments point to 30° off the z axis. However, on the easy direction, at 2 K Gauss, the magnetization shows an antiferromagnetic ordering at about 6.7 K, and the lower end is a little bit bent down, as a sign of either saturation or another magnetic transition at lower temperature. As the magnetic field increases, the antiferromagnetic peak grows bigger and moves to lower temperature. In addition, the magnetic transition at lower temperature moves up, so it becomes observable at 6 K Gauss. It seems that these two anomalies meet, then only the moving down transition is observable. It is clearly
Fig. 4.4.3. Isofield magnetizations as functions of temperature for Tm$_5$Rh$_4$Ge$_{10}$
Fig. 4.4.4. The magnetic susceptibilities multiplied by temperature (unnormalized correlation function) as functions of temperature.
Fig. 4.4.5. The magnetic susceptibilities multiplied by temperature (unnormalized correlation function) and their temperature derivative of Tm$_5$Rh$_4$Ge$_{10}$ as functions of temperature, near the transition points.
Fig. 4.4.6. The inverse of magnetic susceptibilities times temperature (inverse of unnormalized correlation function) of $\text{Tm}_5\text{Rh}_4\text{Ge}_{10}$ as functions of inverse temperature.
seen that only the easy direction moments order in this temperature range.

To look at it more closely, plots of $\chi T$ and its temperature derivative are given in Fig. 4.4.4. The data above 20 K are field independent. As in the Er$_5$Rh$_4$Ge$_{10}$ compound, the $\chi T$ curves for the easy and hard directions go above and below the Curie constant, respectively, showing the formation of easy direction on the c axis and hard direction on the a and b axes. The close up near the transition temperature is given in Fig. 4.4.5. The derivative curve for 2 K Gauss field shows clearly the magnetic transitions, a peak at about 6.8 K and another small peak at about 5 K, correspond to a peak and a shoulder in specific heat curve.

The inverse $\chi T$ versus $1/T$ plot is given in Fig. 4.4.6. The curves are very irregular. However, their value at high temperature limit give a consistent Curie constant $= 38.59$, corresponds to $P_{\text{eff}} = 7.857$. Since no large straight line section can be found, a Curie-Weiss law is not followed. From the isothermal magnetization data, it can be seen that the upward bending of the curves in Fig. 4.4.6. at low temperature, corresponds to the saturation behavior. Therefore, ideally, one can apply a small magnetic field, so that the curves at low temperature would be straight lines.

For comparison, the resistivity, specific heat, and magnetization (2 K Gauss) are shown in Fig. 4.4.7. At the temperature 6.7 K, all those three curves shows clearly the transition. At the temperature 4.5 K, resistivity and specific heat show a kink and a shoulder, respectively, but susceptibility only shows a smooth upturn.
Fig. 4.4.7. The resistivities, specific heats, and magnetic susceptibilities of Tm₅Rh₄Ge₁₀ as functions of temperature, near the transition points.
4.5. Dy$_5$Ir$_4$Ge$_{10}$

The absolute dc resistivities were measured in the temperature range between 2.4 and 350 K, and the fitting was done between 14 and 350 K. Results are shown in Fig. 4.5.1., with the parameters listed in Table 3.1.1. The slope changes vary rapidly at a temperature of about 8 K as a sign of long range magnetic ordering. The estimated $\rho_m$ and $\rho_0$ are about 10 and 5 u-Ohm cm, respectively.

The specific heat data for temperatures between 0.59 and 29.29 K are given in Fig. 4.5.2. The $\Delta C_p$ looks very complicated. Decreasing in temperature, a sudden increase is seen at a temperature of about 10.5 K, then a plateau is found between this temperature and 8 K. A large peak is found at 6.95 K. Below this peak are also two anomalies, another plateau at about 4.8 and one small sharp peak at 3.75 K. Below this temperature, the curve looks smooth. The log-log plot of this region gives an exponent of about 2.7. The entropy is also attributed to magnetic origins. The value of total entropy saturates at a value of about 57.74 J/mol K, corresponding to 5 R \ln 4. Therefore, as for Dy$_5$Rh$_4$Ge$_{10}$, the ground state is composed of two Kramer's doublets.

The magnetization of this compound was measured only on a polycrystalline sample. The plot of inverse susceptibility is shown in Fig. 3.3.2. The plot of $\chi T$ and its temperature derivative are shown in Fig. 4.5.3. for the paramagnetic region, and in Fig. 4.5.4. for temperatures near the ordering temperature. The decreasing $\chi T$ curve is observed even at temperature as high as 120 K. It is interesting to
Fig. 4.5.1. The resistivities of Dy$_5$Ir$_4$Ge$_{10}$ as functions of temperature. The inset shows the low temperature close up.
Fig. 4.5.2. The specific heats of Dy$_5$Ir$_4$Ge$_{10}$ and Lu$_5$Ir$_4$Ge$_{10}$, their difference $\Delta C_p$, and the entropy of $\Delta C_p$ as functions of temperature.
Fig. 4.5.3. The magnetic susceptibilities multiplied by temperature (unnormalized correlation function) and their temperature derivative of Dy$_5$Ir$_4$Ge$_{10}$ as functions of temperature
Fig. 4.5.4. The magnetic susceptibilities multiplied by temperature (unnormalized correlation function) and their temperature derivative of Dy$_5$Ir$_4$Ge$_{10}$ as functions of temperature.
Fig. 4.5.5. The inverse of magnetic susceptibilities times temperature (inverse of unnormalized correlation function) of $\text{Dy}_5\text{Ir}_4\text{Ge}_{10}$ as functions of inverse temperature.
Fig. 4.5.6. The resistivities, specific heats, and magnetic susceptibilities of Dy$_5$Ir$_4$Ge$_{10}$ as functions of temperature, near the transition points.
note that the $\frac{dX}{dT}$ is indeed similar to the specific heat data. It seems that the transition temperature at 6.95 K is not affected significantly by applied magnetic field. The bump at about 9 K is also observed. However, as for the other compounds, the value at the low temperature end is always higher than the specific heat data. This effect could be caused by two things: the nonzero magnetic field in the magnetization measurement, and large component of long range correlation at temperatures much lower than the ordering temperature, which contribute a lot on magnetization but little on energy.

The inverse of $\chi T$ vs $1/T$ plot is given in Fig. 4.5.5. It shows two sections of straight lines, joining at the transition temperature point. The high temperature section reflects the validity of the Curie-Weiss law from room temperature down to the transition temperature. It gives Curie constant = 82.14, corresponding to $P_{\text{eff}} = 11.46$, and $\Theta = 10.37$ which is close to the highest anomaly temperature in this system. The low temperature section is also quite nearly a straight line, but it is very sensitive to the applied magnetic field.

For comparison, resistivity, specific heat, and susceptibility curves are shown in Fig. 4.5.6. This figure clearly shows the transition at 6.95 K. The small sharp peak at temperature 3.75 K is accompanied by a kink in susceptibility, but no observable anomaly in the resistivity curve.

4.6. Ho$_5$Ir$_4$Ge$_{10}$

The absolute dc resistivities were measured at temperatures between
Fig. 4.6.1. The resistivities of Ho$_5$Ir$_4$Ge$_{10}$ as functions of temperature. The inset shows the low temperature close up.
Fig. 4.6.2. The specific heats of Ho$_5$Ir$_4$Ge$_{10}$ and Lu$_5$Ir$_4$Ge$_{10}$, their difference $\Delta C_p$, and the entropy of $\Delta C_p$ as functions of temperature.
Fig. 4.6.3. The resistivities, specific heats, and magnetic susceptibilities of Ho$_5$Ir$_4$Ge$_{10}$ as functions of temperature, near the transition points.
2.4 and 350 K, and the fitting was done between 7.5 and 300 K. Results are shown in Fig. 4.6.1. with the parameters given in Table 3.1.1. The residual resistivity looks very large, and the magnetic ordering is barely observed at the lower end of the curve. The fitting at low temperature is not good, because the magnetic resistivity seems to contribute at temperatures much higher than the observed ordering temperature.

The specific heat data between .77 and 26.48 K are shown in Fig. 4.6.2., which show a large sharp peak at $T = 1.93$ K. Another small peak is also seen at about 5.5 K, followed by a broad Schottky crystal field peak at about 7.5 K. Such combination was predicted by Cooper for singlet ground states with strong exchange interaction. The 5.0 K anomaly is hardly seen in resistivity data.

The magnetization measurements were only done on a polycrystal sample. The resulting inverse susceptibility is shown in Fig. 3.3.2., which gives a Curie constant $= 68$, corresponding to $P_{\text{eff}} = 10.42$.

For comparison, resistivity, specific heat, and susceptibility curves for temperatures between 2.4 and 30 K are shown in Fig. 4.6.3.

4.7. $\text{Er}_5\text{Ir}_4\text{Ge}_{10}$

The absolute dc resistivities were measured in the temperature range between 2.4 and 350 K, and the fitting was done between 15 and 325 K. Results are shown in Fig. 4.7.1., with the parameters listed in Table 3.1.1. These data show a slope discontinuity at about 5.8 K, as a sign of long range magnetic ordering. However, the decreasing of resistivity
Fig. 4.7.1. The resistivities of $\text{Er}_5\text{Ir}_4\text{Ge}_{10}$ as functions of temperature. The inset shows the low temperature close up.
The specific heats of $\text{Er}_5\text{Ir}_4\text{Ge}_{10}$ and $\text{Lu}_5\text{Ir}_4\text{Ge}_{10}$, their difference $\Delta C_p$, and the entropy of $\Delta C_p$ as functions of temperature.
due to this magnetic ordering is not very large, since it is later known that only one sublattice orders at that temperature.

The specific heat data for temperatures between 0.57 and 27.76 K are shown in Fig. 4.7.2. It seems that the specific heat difference is composed of a Schottky peak as well as a magnetic contribution to the specific heat. It shows a broad Schottky maximum at a temperature of about 14 K, and two sharp magnetic ordering peaks at 5.84 and 1.65 K. Since Er is Kramers doublet system, we only need to consider the even multiplicity. The entropy at just above the 1.65 K magnetic ordering is small (approximately 2 R ln 2). This suggests that the ordering at 1.65 K is due to ordering of moments of doublet crystal field states at 2 magnetic ion sublattices or quartet in one sublattice. If the maximum at 14 K is due to a Schottky crystal field effect, the peak value about 35 J/mol K indicates that about 46 K above the ground state doublet are two close spaced doublets ($g_1/g_0 = 2$).

The magnetization of this sample was measured on a needle-shape crystal. This crystal(s) was composed of one directional grain, but we do not know whether it is a single crystal, since single crystal X-ray photographs were not taken. The measurements were only done on the unique growth axis. The inverse susceptibility plot at $H = 2000$ Gauss is shown in Fig. 3.3.2. It gives $\chi_{eff} = 9.82$. The magnetization at different applied magnetic fields for temperatures between 2.0 to 30.0 K are shown in Fig. 4.7.3. For a 2 K Gauss field, one observes antiferromagnetic ordering below 4.5 K. As one increases the magnetic field, this ordering temperature moves to lower temperatures. The ordering temperature is suppressed strongly by magnetic field.
Fig. 4.7.3. Isofield magnetizations as functions of temperature for Er$_5$Ir$_4$Ge$_{10}$
Fig. 4.7.4. Isothermal magnetizations as functions of applied magnetic field for Er₅Ir₄Ge₁₀
Fig. 4.7.5. The magnetic susceptibilities multiplied by temperature (unnormalized correlation function) and their temperature derivative of Er$_5$Ir$_4$Ge$_{10}$ as functions of temperature.
Fig. 4.7.6. The magnetic susceptibilities multiplied by temperature (unnormalized correlation function) and their temperature derivative of Er₅Ir₄Ge₁₀ as functions of temperature.
Fig. 4.7.7. The inverse of magnetic susceptibilities times temperature (inverse of unnormalized correlation function) of Er₅Ir₄Ge₁₀ as functions of inverse temperature.
The isothermal magnetization data for T = 2, 3, and 7 K are shown in Fig. 4.7.4. The $\chi T$ and its temperature derivative plots are shown in Figs. 4.7.5. and 4.7.6. The $\chi T$ curve in this easy direction positively deviates from a Curie constant, which means that the $f$ factor becomes larger in this direction, assuming negative exchange. The magnetic ordering can clearly be seen on the temperature derivative curves. The magnetic ordering temperature is observed at about 4 K, at H = 2000 Gauss. It moves to about 3 K at H = 4000 Gauss, and it is about 2 K at 6000 Gauss. This $d\chi T/dT$ curve predicts that the specific heat above the ordering temperature is small, so that the large specific heat above the ordering temperature is mainly due to a Schottky crystal field specific heat contribution.

The inverse $\chi T$ vs 1/T plot is shown in Fig. 4.7.7. The value at high temperatures gives a Curie constant $\approx 60.89$, corresponding to $P_{\text{eff}} = 9.87$. For low fields, a Curie-Weiss component in magnetization below the magnetic ordering temperature is observed. From the slope, the ratio of the Curie temperature and the Curie constant is determined.

$$\Theta/C = 0.084$$

As the applied field increases, the ordering temperature decreases, and the curve above this ordering temperature approaches a straight line. Therefore, we attempted to subtract the paramagnetic (Curie-Weiss) component. Using

$$M' = M - C H/(T+0.084 C), \quad \text{with}$$

$$C = n f 0.37511 P_{\text{eff}}^2.$$  

Where $n$ is the number of ions in paramagnetic states, and varies between 1 to 5, $f$ is the fraction of $g^2J^2$ on z axis, and 0.37511 cm$^3$ K/mol is
Fig. 4.7.8. The isofield magnetizations minus the paramagnetic component as functions of temperature for $\text{Er}_5\text{Ir}_4\text{Ge}_{10}$.
Fig. 4.7.9. The isothermal magnetizations minus paramagnetic component as functions of applied magnetic field for Er$_5$Ir$_4$Ge$_{10}$
Fig. 4.7.10. The isofield magnetizations as functions of temperature for 2-dimensional Ising

Fig. 4.7.11. The isothermal magnetizations as functions of applied magnetic field for 2-dimensional Ising
Since we magnetized along the easy direction, $f$ should be greater than 1/3, the random moment value. However, it should not be close to one since the moments were assumed to be paramagnetic. After many trials, we obtained the following self-consistent results. Taking $n = 4$, $f = 0.5$, resulting values are $C = 73.1$ and $\Theta = 6.1$ K. The result is shown in Fig. 4.7.8., which is very similar to the theoretical results of a two dimension Ising model shown in Fig. 4.7.10. The isothermal magnetization of $M'$ is shown in Fig. 4.7.9., and the theoretical graph is shown in Fig. 4.7.11. The comparison between Figs. 4.7.8. and 4.7.10. gives the critical field ($H_c$) about 7000 Gauss, and its zero temperature moment is about 37000 Gauss cm$^3$/mol, which is theoretically equal to 0.70441 of the saturation moment. The saturation moment turned out to be 53000 gauss cm$^3$/mol, corresponding to a saturation moment of one gram-atom of Er ions.

One possibility, since Er has positive $\omega_4$, and assuming that low crystal field potential is on the c axis, is that as temperature decreases, its moments and charge distribution tilt to the easy axis. The result above suggests that only one(two) out of five(ten) Er are antiferromagnetically ordered as a two dimension Ising system at 5.84 K, and the other four(eight) are still paramagnetic. Referring to the structure of this compound, and remembering that two formula units are in a unit cell, the unique sublattice should be the 2(a) sites, and the other 2 4(h) sites are still disordered. Er ions at 4(h) sites have $f = .5$, and ions at 2(a) sites have $f$ approaching 1 as they order. Since the moment of the latter is dominant on z direction, and only the nearest neighbor interaction is dominant, then the Ising model is a very
Fig. 4.7.12. The resistivities, specific heats, and magnetic susceptibilities of Er$_5$Ir$_4$Ge$_{10}$ as functions of temperature, near the transition points.
good approximation. The ordering at 1.65 K could be caused by ions at
the 4(h) sites, remembering that the entropy change is $2R \ln 2$, and the
other ions at the other 4(h) sites are still disordered above 0.6 K.

For comparison, resistivity, specific heat, and magnetization curves
are shown in Fig. 4.7.12. The transition at 5.84 K is clearly shown.
The magnetization shows the transition temperature slightly lower,
because the transition temperature has been suppressed by the 2 K Gauss
magnetic field during the measurement.

4.8. Tm$_5$Ir$_4$Ge$_{10}$

The absolute dc resistivities were measured in the temperature range
between 2.4 and 350 K, and the fitting was done between 15 and 350 K.
Results are shown in Fig. 4.8.1., with the parameters listed in Table
3.1.1. These data show a slope discontinuity at a temperature of about
6.5 K as a sign of long magnetic ordering. The estimated $\rho_m$ and $\rho_0$ are
5.0 and 2.5 $\mu$-Ohm cm.

The specific heat data for temperature between 0.6 and 29 K are
given in Fig. 4.8.2. A sharp peak is observed at $T = 6.45$ K. Above
this temperature the specific heat is flat, and below this temperature,
a shoulder is observed at about 3 K. The entropy is difficult to
analyze, since it looks like that the magnetic peak superimposes with a
Schottky crystal field peak.

The magnetization measurements were done on a fiber crystal sample,
and they were only in the easy direction. The inverse susceptibility
plot is shown in Fig. 3.3.2. It gives a Curie constant = 38.16, which
The resistivities of $\text{Tm}_5\text{Ir}_4\text{Ge}_{10}$ as functions of temperature. The inset shows the low temperature close up.
Fig. 4.8.2. The specific heats of Tm$_5$Ir$_4$Ge$_{10}$ and Lu$_5$Ir$_4$Ge$_{10}$, their difference $\Delta C_p$, and the entropy of $\Delta C_p$ as functions of temperature.
corresponds to $P_{\text{eff}} = 7.8$. The magnetization data at different fields for temperatures between 2.0 and 30 K are shown in Fig. 4.8.3. A bump is observed at a temperature of about 7 K. It looks prominent at low fields, and it is buried by the paramagnetic component in high field.

The analysis was done by studying the $\chi T$ curve shown in Fig. 4.8.4. The magnetization bump appears as a peak, and this peak decreases as the magnetic field increases, which indicates that the extra moment is not enhanced by a magnetic field. The division of this fixed moment by the magnetic field strength yields a value of $\chi$ which decreases as the field increases. This moment seems to exist even at zero field. This suggests that there is a spontaneous magnetization that has a ferromagnetic component along the easy direction. However, this component saturates with a very small moment. Above this transition temperature, $\chi T$ versus $T$ curve looks very level, so we assume that $fg^2j^2$ is isotropic.

To find the paramagnetic subtraction, we studied the inverse $\chi T$ vs $1/T$ plot shown in Fig. 4.8.4. From the high temperature limit, a Curie constant was estimated of about 35.7, corresponding to $P_{\text{eff}} = 7.558$. The lines below the ordering temperature are straight, and the lines for different fields are parallel. This encourages us to calculate the slope for finding $\Theta$ of the paramagnetic component.

$$\text{slope} = \Theta/C' = 0.119$$

The same method as that of Er compound was used to determine the paramagnetic component. It is interesting that if one tries to plot $M'$. 

$$M' = M - C'*H/(T+0.119*C'),$$

and 

$$C' = n * C/5, \quad n = 1,2,3,4,5.$$
Fig. 4.8.3. Isofield magnetizations as functions of temperature for Tm$_5$Ir$_4$Ge$_{10}$
Fig. 4.8.4. The magnetic susceptibilities multiplied by temperature (unnormalized correlation function) of $\text{Tm}_5\text{Ir}_4\text{Ge}_{10}$ as functions of temperature for different $H_{//}$
Fig. 4.8.5. The inverse of magnetic susceptibilities times temperature (inverse of unnormalized correlation function) of Tm$_5$Ir$_4$Ge$_{10}$ as functions of inverse temperature for different $H_{//}$. 

$XT = \frac{M}{HT}$

- $H_{//} = 8$ K Gauss
- $H_{//} = 6$ K Gauss
- $H_{//} = 4$ K Gauss
- $H_{//} = 2$ K Gauss
For $n = 5$, one gets a plot as shown in Fig. 4.8.6. The maximum moment does not depend on magnetic field strength, and it is very small, about .21 times the saturation moment of one gram-atom Tm ions per mole. However, it is not due to an impurity, since specific heat shows a high sharp magnetic peak. It also shows that the dynamic magnetization is large at temperature between 5 and 30 K, with a maximum at about 7 K. The extrapolation to zero field shows that the spontaneous magnetization starts to form at a temperature of about 7 K, and it increases rapidly, reaching its maximum at 5 K. At still lower temperatures, it decreases slowly as it is cooled down across that point. The small saturation value suggests the possibility that only a small component of the moment of the ions order. The following mechanism can possibly happen. In the low symmetry coordination, the crystal field splits the 4f states of Tm (even electron), so that the ground state and first excited state are probably singlets, which posses no moment in the absent of exchange and external fields. However, if the exchange field is strong, so that $A = J(0) \frac{\alpha^2}{\Delta}$ is bigger than a critical value, about 1.0406, a moment can be induced, and magnetic ordering can occur. Here $\alpha$ is the off diagonal element of the z direction angular momentum between the ground and first excited crystal field only states, $\langle 0 | J_z | 1 \rangle$; $\Delta$ is the energy gap between the ground and excited state; $J(0)$ is the ferromagnetic exchange. The experimental results that the spontaneous magnetization curve at just below $T_C$ has higher slope than that obtained from a Brillouin function. Its saturation value is very small, on the order of fraction of $\alpha$. The inverse susceptibility is flat at temperatures near zero. The specific heat peak is about $0.8 \text{nR} = 33.24$
Fig. 4.8.6. The isofield magnetizations minus paramagnetic component of Tm$_5$Ir$_4$Ge$_{10}$, for different $H_{//}$.
Fig. 4.8.7. The resistivities, specific heats, and magnetic susceptibilities of Tm$_5$Ir$_4$Ge$_{10}$ as functions of temperature, near the transition points.
J/mol K and matches very well to the theoretical results predicts by Cooper. Unfortunately, the numerical values can not be evaluated since they only posed numerical results from a given strength of the exchange field.

For comparison, resistivity, specific heat, and magnetization curves are shown in Fig. 4.8.7.
5. SUMMARY AND CONCLUSIONS

The dc resistivity, dc magnetization, and specific heat of $R_5T_4Ge_{10}$ ($R = \text{Dy, Ho, Er, Tm, and } T = \text{Rh, Ir}$) were measured. For resistivity data, a $\rho_0$ plus a Wilson resistivity term with the $\rho_{\text{max}}$ model was found to fit well to all compounds in this series. The resulting $\Theta_D$ is slightly below 200 K. For specific heat data, a Debye parabolic term plus an Einstein peak phonon density of states model were found to fit very well to the nonmagnetic compounds measured by L. S. Hausermann-Berg. The results show about 87% Debye component with $\Theta_D$ about 250 K, and 13% Einstein component with $\Theta_E$ about 90 K. The less accurate single Debye phonon density of states model has also been used to compare with the resistivity results, since Wilson's resistivity used one Debye model for the phonon density of states. The resulting $\Theta_D$ were about the same as those determined from resistivity. There is no attempt to determine these numbers accurately, since they are based on a very simple model. An accurate model requires a wider temperature range of accurate data.

The preferred crystallographic grain direction was identified to be the c crystal axis, on which the strong anisotropic properties of the magnetization is based. At high temperature, the Curie-Weiss paramagnetic properties give $P_{\text{eff}}$ close to the free ions values, indicating that Russell-Saunders coupling and Hund's rules are valid. At low temperatures, strong magnetic anisotropy were observed. We did not see magnetic order in the hard direction in all compounds. However the magnetic moments in the easy direction (c crystal axis) always order. Most of them show more than one magnetic transition, which were
studied and confirmed from different physical properties. Data from different physical measurement were considered simultaneously to determine the possible mechanisms in each compound. Fluctuation theory was used extensively. The theory on crystal and exchange field cooperative states proposed by Trammell and Cooper qualitatively explains the magnetization data, but three different sites of magnetic ions makes the detail study of crystal field states impossible at this time. Referring to the z axis easy direction of the Er and Tm compounds, which have positive $\alpha_j$, we may infer that the effective crystal field potential has a minimum along the c axis direction. By the same reasoning, since Dy has negative $\alpha_j$, the moment is expected to be hard on the c direction. The moment tends to lay in the a-b plane. This might explain the decreasing of the $\chi T$ curve of Dy$_3$Ir$_4$Ge$_{10}$ even at moderately high temperature.

The relation between the ordering temperature and either $S(S + 1)$ or de Gennes factor $(g - 1)^2 J(J + 1)$ is not obvious, since as indicated above, crystal fields as well as exchange field have to be considered. Except for dysprosium compounds, the moment ordering at a given transition temperature is believed to happen only on some sublattice of magnetic ions. Each site could have its own ordering temperature. Referring to the crystal structure, one can see that the magnetic ions are surrounded by the germanium or transition metal ion, and there is only one open direction, c axis. The small $\chi_0$ indicates that there are not many electrons at the Fermi surface. Therefore, it is uncertain whether the RKKY interaction could still provide the dominant coupling between the magnetic ions at different sites. Super-exchange seems to
be a reasonable candidate as a dominant interaction mechanism.

A more detailed and conclusive study could be done on large single crystal samples, using neutron diffraction/scattering experiments to determine the magnetic structure and crystal field levels. It would be interesting to know how the magnetic structures change with external magnetic field in different directions. The directional dependence of the resistivity, and how it changes with magnetic structure as external field is applied could also be determined with single crystals.
6. APPENDIX: SOURCE AND PURITIES OF STARTING MATERIALS

<table>
<thead>
<tr>
<th>Element</th>
<th>Source</th>
<th>Purity</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ge</td>
<td>Ventron Alfa Product Lot#041377</td>
<td>6N+ pieces</td>
</tr>
<tr>
<td>Rh</td>
<td>Purchases from USDOE stockpile P.O. A3-1197</td>
<td>4N powder</td>
</tr>
</tbody>
</table>
| Ir      | Research Organic/Inorganic Chem. Corp. #IR-002
          DOE stores #01213642                       | 3N powder    |
| Dy      | Ames Lab.                                   | batch 1578, rod
          major impurities (atomic):
          O 367 ppm
          C 124 ppm
          H 322 ppm
          N 35 ppm
          F 632 ppm
          Ta 30 ppm
          Fe 632 ppm
          Cl 5 ppm
          Mn 4 ppm
          Al 5 ppm
          Ho 6 ppm
          other impurities are all less than 4 ppm |
| Ho      | Ames Lab.                                   | batch 9977, rod
          major impurities (atomic):
          O 309 ppm
          C 301 ppm
          H 653 ppm
          N 47 ppm
          F 651 ppm
          Ni 5 ppm
          Fe 47 ppm
          Ta 30 ppm
          Hf 6 ppm
          Cr 5 ppm
          Cu 3.4 ppm
          other impurities are all less than 3 ppm |
| Er      | Ames Lab.                                   | batch 31584, rod
          major impurities (atomic):
          O 367 ppm
          C 139 ppm
H 994 ppm
N 24 ppm
F <25 ppm
Ta 42 ppm
Fe 19 ppm
Cu 3.6 ppm
other impurities are all less than 3 ppm

batch 32878, rod
major impurities (atomic):
O 10.6 ppm
H 328 ppm
N 24 ppm
C 378 ppm
Fe 25 ppm
F 124 ppm
Cu 11 ppm
Cl 10 ppm
Ce 8 ppm
Si 3 ppm
other impurities are all less than 5 ppm
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I also appreciate the help of all the faculty, staff, and secretaries.

To my parents.
8. REFERENCES


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