Synthesis, crystal growth, magnetic and transport properties of Ln-M-X (Ln=lanthanide, M=transition metal, X=In, Ga) compounds

Willa Maria Williams
Louisiana State University and Agricultural and Mechanical College

Follow this and additional works at: https://digitalcommons.lsu.edu/gradschool_dissertations

Part of the Chemistry Commons

Recommended Citation
Williams, Willa Maria, "Synthesis, crystal growth, magnetic and transport properties of Ln-M-X (Ln=lanthanide, M=transition metal, X=In, Ga) compounds" (2006). LSU Doctoral Dissertations. 3851.
https://digitalcommons.lsu.edu/gradschool_dissertations/3851

This Dissertation is brought to you for free and open access by the Graduate School at LSU Digital Commons. It has been accepted for inclusion in LSU Doctoral Dissertations by an authorized graduate school editor of LSU Digital Commons. For more information, please contact gradetd@lsu.edu.
SYNTHESIS, CRYSTAL GROWTH, MAGNETIC AND TRANSPORT PROPERTIES OF $Ln$-$M$-$X$ ($Ln$ = LANTHANIDE, $M$ = TRANSITION METAL, $X$ = IN, GA) COMPOUNDS

A Dissertation
Submitted to the Graduate Faculty of the
Louisiana State University and
Agricultural and Mechanical College
in partial fulfillment of the
requirements for the degree of
Doctor of Philosophy
in
The Department of Chemistry

by
Willa M. Williams
B.S., Mississippi Valley State University, 1998
August, 2006
ACKNOWLEDGEMENTS

Completing this document would not have been possible without the assistance and support of several individuals. To Dr. Julia Chan for understanding my eclectic thought process and my annoying habit of not leaving two spaces after each period, also for giving me the chance to finish this work. I respect you for always being there to give me encouragement or more often a swift “kick.” Thanks, I needed that!

I would like to thank, Dr. George Stanley, for offering his support, understanding, and guidance at a time when my world was changing more rapidly than I could cope with. I am thankful that you believed in me even when my work ethic was not the best that it should have and could have been.

To Dr. David Young, for his knowledgeable, enthusiastic, assistance, guidance, encouragement, and, his infinite patience with someone who had no idea what a Bohr magneton was.

To Dr. Frank Fronczek and Dr. Steven F. Watkins for all of the crystallography lessons that you both so graciously offered. Because of your excitement and enthusiasm about crystal chemistry, I have truly developed a greater respect for crystal chemistry and the people who choose to make it their life’s work.

I would also like to thank my colleagues who have all listened to me complain, encouraged me to continue, and provided support in a variety of ways. To my collaborators, at University of California-Davis: Professor Zachary Fisk and his students, Han-Oh Lee, Long Pham, and Sam Maquilon. To Dr. Monica Moldovan who has spent an overwhelming number of hours measuring the physical properties of so many of my samples, she has also been a supporting and encouraging friend.
I would like to thank my family and friends, who have encouraged and supported me in too many ways to name. Since I know they are waiting to read their names in this document here goes. I would like to thank: Dr. Shawn D. Llopis, Dr. Evan L. Thomas, Jasmine N. Millican, Dr. Robin Macaluso, and the Chan research group. 

I would also like to acknowledge the fiscal support of the grants that funded my work: the National Science Foundation Career Award, American Chemical Society, Petroleum Research Fund, and Alfred P. Sloan Research Foundation.
**TABLE OF CONTENTS**

ACKNOWLEDGEMENTS ................................................................................................................................. ii

ABSTRACT .................................................................................................................................................... vi

CHAPTER 1. INTRODUCTION ........................................................................................................................ 1
1.1 Intermetallic Compounds .................................................................................................................... 1
1.2 Synthetic Methods for Intermetallic Compounds ............................................................................. 5
1.3 Structure Determination of Intermetallic Compounds ...................................................................... 5
  1.3.1 X-ray Diffraction ....................................................................................................................... 5
  1.3.2 Bragg’s Law .............................................................................................................................. 5
  1.3.3 Principles of Diffraction .......................................................................................................... 6
  1.3.4 Powder X-ray Diffraction ...................................................................................................... 7
  1.3.5 Crystal Mounting .................................................................................................................... 7
  1.3.6 Instrumentation ....................................................................................................................... 7
  1.3.7 Unit Cell Determination ....................................................................................................... 8
  1.3.8 Data Reduction ...................................................................................................................... 9
  1.3.9 Structure Solution ................................................................................................................. 9
1.4 Magnetism .......................................................................................................................................... 10
  1.4.1 Curie-Weiss Law ................................................................................................................... 11
1.5 Resistivity ......................................................................................................................................... 15
  1.5.1 Kondo Effect ....................................................................................................................... 15
  1.5.2 RKKY .................................................................................................................................... 16
1.6 Magnetoresistance ............................................................................................................................ 17

CHAPTER 2 CRYSTAL GROWTH, STRUCTURE, MAGNETIC AND TRANSPORT PROPERTIES OF TbRhIn₅ .............................................................................................................. 19
2.1 Introduction .......................................................................................................................................... 19
2.2 Experimental .................................................................................................................................... 21
  2.2.1 Synthesis ............................................................................................................................... 21
  2.2.2 Single Crystal X-ray Diffraction .......................................................................................... 22
  2.2.3 Physical Property Measurements ....................................................................................... 23
2.3 Results and Discussion ..................................................................................................................... 23
  2.3.1 Crystal Structure .................................................................................................................. 23
  2.3.2 Physical Properties ............................................................................................................... 25
2.4 Conclusion ...................................................................................................................................... 29

CHAPTER 3 SYNTHESIS, STRUCTURE, AND MAGNETORESISTANCE OF SmPd₂Ga₂ ................................................................................................................................. 31
3.1 Introduction ...................................................................................................................................... 31
3.2 Experimental ................................................................................................................................... 32
  3.2.1 Synthesis .............................................................................................................................. 32
  3.2.2 Single Crystal X-ray Diffraction .......................................................................................... 33
  3.2.3 Physical Property Measurements ....................................................................................... 34
3.3 Results and Discussion ..................................................................................................................... 35
CHAPTER 4. SYNTHESIS, STRUCTURE, AND MAGNETISM OF Tb₄MGa₁₂ (M = Pd, Pt) .................................................................40
  4.1 Introduction ......................................................................................................................40
  4.2 Experimental ....................................................................................................................42
    4.2.1 Syntheses ..................................................................................................................42
    4.2.2 Single Crystal X-ray Diffraction .............................................................................42
    4.2.3 Physical Property Measurements ...........................................................................44
  4.3 Results and Discussion ....................................................................................................44
    4.3.1 Crystal Structure ....................................................................................................44
    4.3.2 Physical Properties .................................................................................................47

CHAPTER 5 CRYSTAL GROWTH, MAGNETIC AND TRANSPORT PROPERTIES OF Ln₄MGa₁₂ (Ln = Dy, Ho, Er; M = Pd, Pt) .................................................................51
  5.1 Introduction ......................................................................................................................51
  5.2 Experimental ....................................................................................................................52
    5.2.1 Synthesis ..................................................................................................................52
    5.2.2 Single Crystal X-ray Diffraction .............................................................................53
    5.2.3 Physical Property Measurements ...........................................................................53
  5.3 Results and Discussion ....................................................................................................54
    5.3.1 Single Crystal X-ray Diffraction .............................................................................54
    5.3.2 Physical Properties .................................................................................................59
  5.4 Conclusion .......................................................................................................................65

CHAPTER 6 FINAL REMARKS ............................................................................................. 66

REFERENCES ............................................................................................................................69

APPENDIX I: SINGLE CRYSTAL X-RAY DIFFRACTION DATA FOR Ln₄FeGa₁₂ (Tb, Er) .............................................................................................................................76

APPENDIX II: REPRINT PERMISSION FOR JOURNAL ARTICLES ...........................................79

VITA ...........................................................................................................................................83
ABSTRACT

This work focuses on the structural stability, magnetic and transport properties of ternary lanthanide compounds grown using indium and gallium flux. Single crystals of TbRhIn$_5$ were synthesized using indium flux. TbRhIn$_5$ is isostructural to the well known $Ln_nMIn_{3n+2}$ ($n = 1, 2, \infty$; $Ln =$ La, Ce; $M =$ Rh, Ir) and adopts the HoCoGa$_5$ structure type and crystallizes in the space group $P4/mmm$, $Z = 1$. Lattice parameters are $a = 4.6000(6)$ Å and $c = 7.4370(11)$ Å, $V = 157.29(6)$ Å$^3$. A sharp antiferromagnetic transition is observed at $T_N = 48$ K for TbRhIn$_5$.

Single crystals of SmPd$_2$Ga$_2$ have been synthesized by flux growth methods. SmPd$_2$Ga$_2$ adopts the tetragonal space group $I4/mmm$, $Z = 2$, with lattice parameters, $a = 4.2170(3)$ Å and $c = 10.4140(3)$ Å. This new material has physical properties similar to other Sm intermetallics and has, most notably, a large positive magnetoresistance at low temperatures. Magnetic measurements indicate that SmPd$_2$Ga$_2$ is ferromagnetic with $T_c \sim 5$ K.

Single crystals of Tb$_4M$Ga$_{12}$ ($M =$ Pd, Pt) have been synthesized. The isostructural compounds crystallized in the cubic space group, $I\bar{m}3m$ with $Z = 2$ and lattice parameters: $a = 8.5930(7)$ Å and $a = 8.5850(3)$ Å for Tb$_4$PdGa$_{12}$ and Tb$_4$PtGa$_{12}$, respectively. Magnetic measurements suggest that Tb$_4$PdGa$_{12}$ and Tb$_4$PtGa$_{12}$ order antiferromagnetically Néel temperatures of 16 K and 12 K, respectively.

Single crystals of $Ln_4M$Ga$_{12}$ ($Ln =$ Dy, Ho, Er; $M =$ Pd, Pt) were synthesized and characterized by single crystal X-ray diffraction. $Ln_4M$Ga$_{12}$ ($Ln =$ Dy, Ho, Er; $M =$ Pd, Pt) are isostructural to Tb$_4$PdGa$_{12}$. Magnetic measurements show that Dy$_4$PdGa$_{12}$ and Ho$_4$PdGa$_{12}$ do not show any magnetic ordering down to 2 K, while Er$_4$PdGa$_{12}$ shows an antiferromagnetic transition at $T_N = 3$ K, as well as, magnetic transitions at 13 K and 21 K. Dy$_4$PtGa$_{12}$ orders antiferromagnetically at $T_N = 11$ K and Ho$_4$PtGa$_{12}$ shows magnetic transitions at 26 K and 92 K. Er$_4$PtGa$_{12}$ shows an antiferromagnetic transition at $T_N = 5.5$ K and magnetic transitions at 25 K.
and 93 K. The structure, magnetic, and transport behavior of these phases are discussed and compared.
CHAPTER 1. INTRODUCTION

1.1 Intermetallic Compounds

An intermetallic compound consists of two or more metals and has a distinctive structure and composition. To date intermetallic compounds have found their niche in a range of applications from computer read-write heads, shape memory alloys, dentistry, and jewelry.\cite{1,2} Binary phase systems in which one metal of the periodic table is paired with another metal have been well studied with $\sim$80\% of all possible combinations studied which has lead the ability to predict the structures of binary compounds with $\sim$95\% confidence level.\cite{3,4} If a truncated periodic table is constructed using only the metals that are not radioactive or inert, we find that there about 85 usable elements. If we select three different elements with which to synthesize a compound, we obtain $\sim$83,000 possible ternary intermetallic compounds possible based on direct combination of elements.\cite{5} There are only $\sim$80 structure types known for binary compounds, a number which pales in comparison to the over 1000 structure types which are presently known for ternary intermetallic compounds.\cite{3,4} The primary interest in these phases is that many of them exhibit new phenomena or possess desirable properties, such as superconductivity, ferromagnetism, magnetic ordering, and unusual transport properties.

Predictive methods which are capable of determining the structure of binary compounds have proven to be sporadic when substitutions are made. It For Example, MgB$_2$\cite{6} crystallizes in the well known AlB$_2$-structure type. It was assumed that the substitution of beryllium on the Mg site would result in a compound isostructural to MgB$_2$ with similar physical properties. This assumption proved to be far from true as MgB$_2$ was discovered by Japanese researchers to have one of the highest recorded superconducting transition temperatures (39 K) reported to date.\cite{7} In addition, BeB$_{2.75}$ exhibits a very complex structure in comparison to the simple hexagonal honeycomb structure of MgB$_2$, and has a $T_c$ of 0.72 K.\cite{8} For this reason the importance of
developing predicting tools to assist in the determination suitable substitutions which would allow structure integrity to be maintained. There is evidence in lanthanide oxides that as structures become more complex, the physical properties may become enhanced.⁹

A large number of technologically significant intermetallic compounds contain lanthanide elements partnered with transition metals which exhibit interesting properties due to the interaction between the electrons of the lanthanide elements partially filled $f$ shells with the $d$ shells of the transition metal. This is especially true of compounds formed between rare earths and B, Be, Mg, Ru, Rh, Pd as well as, compounds formed between lanthanide elements and In, Ga, Tl, Pb, Cd and Zn. It is of interest to us to learn why compounds tend to favor certain structure types.¹⁰ The emphasis of this work is to synthesize large single crystals of new lanthanide ternary intermetallic compound for the purpose of full structural and physical property characterization.

1.2 Synthetic Methods for Intermetallic Compounds

Traditional synthetic methods for inorganic compounds are based almost on the concepts of solubility as it relates to acids, bases, salts of substances and reactions are carried out in solution at temperatures which rarely exceed 100 °C. However, more recently, new synthetic strategies which use solution chemistry techniques to synthesize intermetallic compounds have been discovered. Nanocrystals and nanowires of AuCu and AuCu₃ were recently synthesized using a direct solution synthetic method which uses the concept of water-based mixing of the solid state precursors.¹¹ The synthesis of intermetallic compounds is very different from traditional inorganic compounds. The preparation of intermetallic compounds has traditionally been limited to the combination of elements using an arc-melting apparatus or an induction furnace at high temperatures between 500 and 2500 °C.¹²,¹³ Arc melting takes place in a cold-wall system using an inert atmosphere at a reduced pressure. The apparatus consists of a cathode
(usually tungsten) and a copper anode. A stream of electrons emitted from the cathode are drawn through a plasma of ionized gas to the water cooled copper anode in the form of a crucible or hearth forms the arc. The reaction is presumed to reach thermodynamic equilibrium during an amount of time predetermined by the user. The thermodynamic equilibrium relationships can be represented by phase diagrams which show the phase condition in a system of constituents as a function of temperature and composition. Resulting compounds are usually polycrystalline as they are made from metals with high melting points which must be ground, re-heated, and pressed into pellets several times to expose new surface area to fully react. Crystal growth is often inhibited because the fast cooling creates a sharp temperature gradient which makes it difficult for the compounds to crystallize to yield large single crystals. Representative compounds formed exhibit some of the most frequently occurring crystal structure types known: CsCl, MgCu2, MoSi2, AuCu3, CaCu5, and AlB2. In the AuCu3 type, the rare-earth atoms may occupy the Au sites (ErAl3) or the Cu sites (La3In). As inherent to all intermetallic compounds, there is a fixed ratio between the number of atoms from each participating element for that structure type. It is not to be taken for granted that a combination of any two metals in the periodic table leads to the formation of an intermetallic compound. For example, no compounds are formed when lanthanide elements are melted together with Mo, Ta or W. The arc melting method is not suitable for the synthesis of compounds which contain elements with high vapor pressures as in Mg, Zn or Cd. In these cases, the compounds can be prepared by sealing the starting materials into tantalum or niobium capsules and heating at temperatures sufficiently high for the reaction to occur. Many of the compounds of technological importance have complex compositions and high temperature methods can be disadvantageous because the products are thermodynamically stable with high activation energy barriers therefore the synthesis result in the simplest of binary compounds. In an effort to circumvent the formation of polycrystalline
simple binary compounds for which full structural and physical characterization is laborious, a change to a synthetic method which allow for the formation of complex structures is needed. To this effect, common low temperature syntheses, solvothermal or flux methods which take place below 400°C can be used. Resulting compounds are often metastable compounds which can’t be made using other methods. Solvothermal methods use water or other solvents as media for crystal growth and are discussed in detail elsewhere. For the purpose of this dissertation, much attention is given to the use of the flux method as the synthetic method of choice for the growth of single crystals of the ternary intermetallic compounds discussed in the latter chapters. Flux growth is a low temperature (<1200 °C) method that is based on the theory that the activation energy barrier which exists in high temperature methods can be overcome by reacting soluble materials in a suitable solvent. A suitable solvent (flux) is defined as one which has a low melting point making it capable of forming a melt with a large difference between its melting and boiling points. In addition, a method has to exist that allow the resulting crystals to be extracted from the melt. Most importantly, the flux should not be reactive with any of the other reactants which would form any of the thermodynamically stable binary species. The availability of single crystals reduced the ambiguity associated with polycrystalline samples as physical properties can be studied as a function of crystallographic direction. A study of the magnetic properties in several directions has very often led to a better understanding of the magnetic anisotropy and its origin, the crystal field splitting of the lanthanide trivalent ground state. The availability of high quality single crystals also gives us the ability obtain information on crystalline field effects, which previously had to be derived from specific heat data and magnetic data obtained on polycrystalline materials obtained from inelastic neutron scattering experiments. This has led in several cases to a new insight into the factors that govern the magnetic interactions in these compounds.
1.3 Structure Determination of Intermetallic Compounds

The work presented in the preceding chapters focused on the growths of single crystals of new intermetallic phases characterized by X-ray diffraction.

1.3.1 X-ray Diffraction

X-rays are produced when high energy accelerated particles (electrons) collide with matter. The X-ray spectrum which results from this interaction consists of two components, white radiation (broad spectrum of wavelengths) and a number of monochromatic wavelengths. Monochromatic X-rays used for experimentation are produced by the collision of the high energy particles with a metal target (copper or molybdenum) which is partially ionized by the incident electrons. The energy released from the transition results in X-radiation. The transition energies have fixed values which result in a spectrum of characteristic X-rays. For example, in copper the $2p \rightarrow 1s$ transition called $K_\alpha$ has a wavelength of 1.5418 Å and the $3p \rightarrow 1s$ transition, $K_\beta$ has a value of 1.3922 Å.

1.3.2 Bragg’s Law

Crystals can be viewed as consisting of layers or planes which behave as semitransparent mirrors where the angle of reflection of the X-rays reflected off the plane is equal to the angle of incidence of the beam with the rest reflected by the succeeding planes. Figure 1.1 shows the

Figure 1.1 Diffraction of X-rays from lattice planes illustrating Bragg’s law.
derivation of Bragg’s law. Incident X-ray beams 1 and 2 are reflected from adjacent atomic planes within the crystal. Ray 1’ and ray 2’ are said to be in phase when the X-rays interact constructively to ensure that \( abc \) is equal to a whole number of wavelengths. This constructive interaction leads to Bragg’s law which states \( n \lambda = 2d \sin \theta \), where \( \theta \) is the Bragg angle, \( n \) is an integer, \( \lambda \) is the wavelength and \( d \) is the spacing between two adjacent planes.\(^{12}\)

1.3.3 Principles of Diffraction

Bragg’s law shows the conditions necessary for diffraction it tell us nothing about the scattering intensity from the atoms in each cell.\(^{19}\) The wave-particle duality of electromagnetic radiation allows the use of the wave-like component of this phenomenon to explain the scattering of radiation from a crystal. The X-ray beam can be thought of as a traveling plane wave which strikes an electron causing it to move. The scattering of the wave is because an accelerated electron radiates in all directions upon impact. Each scattered wave has an identical wavelength but different amplitudes and phases.\(^{19}\)

1.3.4 Powder X-ray Diffraction

In polycrystalline materials, a beam of X-rays passes through a sample of randomly-oriented microcrystals and produces a pattern of rings on a distant screen. Powder X-ray diffraction provides less information than single-crystal diffraction; however, it is much simpler and faster. Powder x-ray diffraction is useful for confirming the identity of a solid material, its crystallinity, and phase purity. Powder X-ray diffractometers consist of an X-ray source, a movable sample platform, an X-ray detector, and associated computer-controlled electronics. The sample is either packed into a shallow cup-shaped holder or deposited onto a quartz substrate. The x-ray source is usually the same as used in single-crystal diffractometers, Mo or Cu. The X-ray beam is fixed and the sample platform rotates with respect to the beam by an
angle theta. The detector rotates at twice the rate of the sample; at an angle of $2\theta$ with respect to the incoming X-ray beam.

1.3.5 Crystal Mounting

A glass fiber that is just thick enough to support a cut single crystal is inserted and glued inside a brass pin using a small quantity of epoxy resin as an adhesive and allowed to dry. Single crystals fragments of dimension less than 0.08 mm are cut with a razor blade and affixed to a glass fiber using more adhesive. The crystal axis of the mounted sample should be tilted ~30° away from the mounting support to minimize absorption effects and to minimize background scattering from the sample mount. The brass pin containing the mounted crystal is then inserted into the goniometer head. The crystal is centered in the beam of X-rays using a microscope with its view perpendicular to the phi rotation axis. The height of the crystal is adjusted and the view direction is adjusted parallel to the microscope to obtain a shaper image. The adjustments are repeated for the $x$, $y$, and $z$ directions.

1.3.6 Instrumentation

Single crystal experiments were performed using a Bruker Nonius Diffractometer equipped with a Kappa Charge Coupled Device (CCD). The KappaCCD consists of an enclosed Mo Ka ($\lambda = 0.71073\ \text{Å}$) X-ray source, a 3 axes goniometer (Omega, Kappa, and Phi) which is used to position the crystal and a Theta-axis which positions the detector. The optics of the instrument contains a main shutter and a fast shutter, a graphite monochromater (used to suppress brehmstralung radiation), and sealed fine focus collimators which eliminates stray radiation so that the desired radiation can be collected into a bundle. The CCD, a two-dimensional detector, measures the light signal which is produced when generated X-rays are converted into visible light through the use of phosphors (Gd,O,S). For each individual reflection
measured by the detector, the detector moves round one axis to the proper $2\theta$ angle. More than one axis of rotation is needed since the detector can only see reflections which occur in the horizontal plane. The KappaCCD equipped with its 3-axes goniometer is able to measure the individual positions and intensities of the reflections. Figure 1.2 shows schematic of a four circle diffractometer with the angles shown. The system is controlled by a host computer with data collecting and evaluation software that connects to the system.

![Diagram of a four-circle diffractometer](image)

**Figure 1.2** Schematic representation of a four-circle diffractometer showing the four rotations, three for the crystal denoted as $\phi, \chi, \omega$ and one for the detector ($2\theta$) adapted from pg. 30 *Crystal Structure Determination* by W. Clegg.\(^{17}\)

### 1.3.7 Unit Cell Determination

Once a crystal has been mounted and centered in the beam, a series of phi scans are performed to determine its singularity. The mastership of the host system is un-grabbed and remote computer interface on the server is used for unit cell determination. Computer software is used to assign $hkl$ indices and measure Bragg angles so that the six unit cell parameters are calculated using Bragg’s law.
1.3.8 Data Reduction

The process of converting intensities to observed structure amplitude and then applying certain corrections is called data reduction. The data was corrected for absorption and Lorenz-polarization factors which are observed because reflected radiation is partially polarized. The reflections obtained have varying degrees of differences in instrumental conditions therefore raw data is scaled using Denzo and Scalepack programs.\textsuperscript{20}

1.3.9 Structure Solution

The intensity $I(hkl)$ of the X-ray beam is proportional to the square of the wave amplitude $F(hkl)$ which consists of both an amplitude term and a phase term.\textsuperscript{19} The relative intensity $I$, the Bragg angle $\theta$, and the multiplicity factor $p$ is related to the relative structure factor by the following equation.\textsuperscript{17-19}

$$I = |F|^2 \frac{1 + \cos^2 2\theta}{\sin^2 \theta \cos \theta}$$  \hspace{1cm} (1.1)

Since intensity is known, the amplitude can be calculated but the structure factor can not be calculated because the phase is not known. Therefore, only the relative structure factor can be calculated which is done by trial and error by assuming of a set of atomic positions and calculating the intensity of the reflections ($|F_{\text{calc}}|$) and comparing them with the observed ones ($|F_{\text{obs}}|$), until there is sufficient agreement between the values.\textsuperscript{17-19} The residual factor or $R$-factor value adds together the difference between the observed and calculated reflections without attention given to sign and then dividing by the summation of all the observed amplitudes. The residual factor or $R$-factor is defined below.\textsuperscript{17-19}

$$R = \frac{\sum |F_{\text{obs}}| - |F_{\text{calc}}|}{\sum |F_{\text{obs}}|}$$  \hspace{1cm} (1.2)

When a weighting scheme $w$ is used, then the $R$-factor is defined as.\textsuperscript{17-19}
The data is then refined using the least squares method in which the two sets of data ($F_{\text{obs}}$ and $F_{\text{calc}}$) are compared to determine the best fit between the calculated diffraction pattern versus the observed diffraction pattern.$^{17-19}$

### 1.4 Magnetism

The last several decades have experienced a fervent interest in the magnetic properties of intermetallic compounds. Certain general features of the ordered magnetic states of intermetallic compounds have theoretical applications important to all magnetic materials and are explained briefly below. All materials exhibit magnetism when a sufficient magnetic field is applied. The flux density $B$, is related to the permeability $\mu$, and the applied field $H$ (1.4).$^{12,21}$ The concept of magnetic permeability is analogous to electrical conductivity, where the electrical conductivity is defined as the ratio of current density to electric field. Magnetic permeability is defined as the ratio of flux density to magnetic field strength and is generated in a material by electrons spinning around their own axes, which creates a magnetic moment in the material.$^{12,21}$

\[
B = \mu H 
\]  

(1.4)

Further,

\[
B = \mu_0 H + \mu_0 M 
\]  

(1.5)

where $\mu_0$ is the permeability of free space and $M$ is the magnetization which is the average field strength of these moments at any particular point. The response of the magnetic moments to an applied field is the magnetic susceptibility $\chi$, which is defined as.$^{12,21}$

\[
\chi = \frac{M}{H} 
\]  

(1.6)
Magnetic behavior exhibited in magnetic systems is ascribed to several types: diamagnetism, paramagnetism, ferromagnetism, antiferromagnetism, and ferrimagnetism. The temperature-dependent magnetic susceptibility $\chi$ versus $T$ can be used to differentiate between the different types of magnetism.\textsuperscript{12,21} Diamagnetism is the most common type of behavior as these systems contain spin paired moments and show a small, negative susceptibility. Thus a diamagnetic material slightly repels an applied field. Paramagnetic substances have random spin orientation which results from the competition between thermal vibration and the aligning effect of the applied field. Therefore, paramagnetic materials show a small positive susceptibility and a weak attraction to the external field.\textsuperscript{12} Ferromagnetic substances have magnetic domains in which the magnetic fields of the individual atoms align, but the orientation of the magnetic fields of the domains is random, giving rise to no net magnetic field. However, upon the application of an external magnetic field the individual domains tend to line up in the direction of this external field. For this reason, these materials are attracted to a magnetic field and the magnetic susceptibility is much greater than one.\textsuperscript{12} Antiferromagnetic materials have magnetic moments that align antiparallel upon the application of an external magnetic field, resulting in no net magnetic moment. The magnetic susceptibility for antiferromagnetic substances is positive and somewhat similar to that observed in paramagnetic substances.\textsuperscript{12} Ferrimagnetic substances have different types of atoms with different moments, which upon the application of an external magnetic field the moments align antiparallel, some of the moments cancel while others do not.\textsuperscript{12}

1.4.1 Curie-Weiss Law

Most paramagnetic materials in which there is no intrinsic magnetism due to cooperative interaction between neighboring spins can be described by the Curie Law (1.4) which states that the magnetic susceptibility is inversely proportional to temperature.\textsuperscript{12,21}
The Curie-Weiss law is used to describe the magnetic behavior of a material above its ordering temperature when there is cooperative interaction between neighboring spins which may induce ferromagnetic or antiferromagnetic behavior. The Curie-Weiss law states:

$$\chi = \frac{C}{T - \theta}$$  \hspace{1cm} (1.8)

where $C$ is the Curie constant and $\theta$ represents the Weiss constant. The values of $\theta$ can be obtained from plotting the inverse susceptibility versus temperature and extrapolating to a minimum. The slope of the line corresponds to the inverse Curie constant, $C^{-1}$.\textsuperscript{12,21}

Using this formulation, ferromagnetic substances have large $\chi$, with $\theta > 0$, $\theta$ for ferromagnetic substances usually coincides with the Curie temperature, $T_c$ which denotes temperature above which spontaneous magnetization vanishes. In antiferromagnetic substances, the extrapolated value of $\theta < 0$ and the susceptibility value $\chi$, is small. Negative $\theta$ temperatures cannot be observed, so a departure from Curie-Weiss behavior occurs.\textsuperscript{12,21} For this reason, upon cooling the behavior antiferromagnetic materials can be better described below the Néel temperature, $T_N$. The magnetic susceptibility of antiferromagnets is usually very small at low temperatures but increases rapidly with temperature until a maximum is reached at $T_N$.\textsuperscript{12,21} Curie-Weiss behavior is usually regained at temperatures above $T_N$.\textsuperscript{12,21} The use of $\theta$ to determine the magnetic character of compounds can be quite deceptive as there are in existence, compounds which order antiferromagnetically but have positive theta values such as $Ln_5Ge_3$\textsuperscript{22} ($Ln = $ lanthanide). The positive value of $\theta$ is indicative of weak antiferromagnetic interactions.
1.4.2 Determination of the Magnetic Moment

The magnetic properties can therefore be related to the number of unpaired spins present in a material. The magnetic properties of a material arise from the electron spin and the electron orbital motion. The magnetic moment of an atom or ion in free space is:\textsuperscript{21}

\[ \mu = \gamma \hbar J = -g \mu_B J \] \hspace{1cm} (1.9)

where $\hbar J$ is the total angular momentum obtained from the summation of the orbital momentum $\hbar L$ and spin momentum $\hbar S$; the constant $\gamma$, is the spectroscopic splitting factor or $g$ factor and is defined by:\textsuperscript{21}

\[ g \mu_B = -\gamma \hbar \] \hspace{1cm} (1.10)

The $g$ factor for a single electron is 2.0023, however for a free atom the $g$ factor for a free atom is calculated using the Landé equation:\textsuperscript{12,21}

\[ g = 1 + \left( \frac{J(J+1) + S(S+1) - L(L+1)}{2J(J+1)} \right) \] \hspace{1cm} (1.15)

The Bohr magneton is defined as:

\[ 1BM = \frac{e\hbar}{2\pi mc} \] \hspace{1cm} (1.11)

where $e$ is the electron charge, $\hbar$ is Planck's constant, $m$ is the mass of an electron, and $c$ is the speed of light. The value of a Bohr magneton, $\mu_B$ is $9.27410 \times 10^{-24} \text{ J/T}$ or $9.27410 \times 10^{-21} \text{ erg/G}$ and is closely equivalent to the electron spin moment $\mu_s$ which is given by

\[ \mu_s = g \sqrt{s(s+1)} \] \hspace{1cm} (1.12)

where $s$ is the spin quantum number, $\frac{1}{2}$; substituting for $s$ and $g$ gives $\mu_s = 1.73 \ \mu_B$.\textsuperscript{12,21} For atoms or ions where the spin moment is greater than 1, the electron spin moment is given by:

\[ \mu_s = g \sqrt{S(S+1)} \] \hspace{1cm} (1.13)
where \( S \) is the sum of the spin numbers from each unpaired electron.\(^{12,21}\) The susceptibility is related to equation 1.7 by the following relationship:

\[
\frac{M}{H} = \frac{NJ(J+1)g^2 \mu_B^2}{3k_B T} = \frac{Np^2 \mu_B^2}{3k_B T} = \frac{C}{T}
\]  

(1.14)

where \( p \), the effective number of Bohr magnetons is defined as\(^{21}\)

\[
p \equiv g \sqrt{J(J+1)}
\]  

(1.5)

1.4.2.1 Magnetism in Rare Earth Intermetallic Compounds

A well-known property of the rare-earth elements is their incomplete 4f shell, which becomes progressively filled in going from La to Lu. The shielding of the 4f shell leads to interesting physical properties which differ from one lanthanide ion to the next by the number of electrons compacted in the 4f shell. The unpaired electrons accommodated in this shell largely determine the physical properties of the lanthanide elements and compounds. The chemical properties of compounds which consist of lanthanide elements are predominantly determined by the valence electrons. The valence electrons are mostly unaffected as the 4f shell is progressively filled, this results in similar chemical properties for the lanthanides. As a general rule, the rare earths give rise to the same type of compound when combined with other metals. Exceptions to this rule are compounds which contain Ce, Eu and Yb. The rare-earth elements usually exist in a trivalent state in most metal systems, however, Ce, Eu and Yb may adopt a different valence. Cerium very often tends to be tetravalent, while Eu and Yb to be divalent.\(^{10,21}\)

The theory used above to calculate magnetic moment is based on each system having a \((2J+1)\) degenerate ground state. The theory can be applied for most of the rare earth ions by calculating \( g \)-factors using the Landé equation and Hund’s rules. Hund’s rule states that \( S \) is equal to the maximum allowed value in accordance with Pauli’s exclusion principle and that the maximum
value of the angular momentum $L$ is consistent with the value obtained for $S$. The total angular momentum $J$, is equal to the absolute value of $L-S$ when the shell is less than half full, $L+S$ if more than half full, and $L=S$ when half filled. For example, for Tb$^{3+}$, the g value calculated using equation 1.11, is 1.5. The angular momentum $L$, for the $f$-shell is equal to 3, $S$ is equal to 3, and since Tb$^{3+}$ has 8 $4f$ electrons the shell is more than half filled which gives a $J$ value of 6. Substituting this $J$ value into equation 1.16 gives an effective moment $\mu$, of 9.72 $\mu_B$ per Tb$^{3+}$ ion. The experimental values obtained for $\mu$ may have some disagreement from the calculated ones due to the influence of the higher states of the $L-S$ multiplet.

**1.5 Resistivity**

Electrical resistivity is the electrical resistance of a sample with a geometric correction for the sample thickness and area. At room temperature, the electrical resistivity of most metals is dominated by the collisions of conduction electrons with lattice phonons; however, as the temperature is lowered collisions with impurity ions and imperfections in the lattice become prevalent. The net resistivity is given by:

$$\rho = \rho_L + \rho_i$$

(1.21)

Where $\rho_L$ is the resistivity due to thermal phonons and $\rho_i$ is the resistivity due to static defects and imperfections which disturb the periodicity of the lattice.\(^{21}\) Since the number of thermal collisions decrease with temperature, the extrapolated resistivity, $\rho_i(0)$ is the residual resistivity. The residual resistivity ratio (RRR) is defined as the ratio of the resistivity at room temperature to the residual resistivity and is used as an approximation of the purity of a sample.

**1.5.1 Kondo Effect**

The Kondo effect is a low temperature phenomenon which is used to explain the effect on current flow due to the presence of magnetic impurities (local magnetic moments) in dilute solid solutions. The Kondo effect is based on calculations which predict the probability of spin-
flip scattering events in which the spin of delocalized electrons may flip.\textsuperscript{23} As the temperature approaches zero, the interaction between the conduction electron spin and the spin on the local moment becomes very strong suggesting that each magnetic moment is paired with a conduction electron with opposite spin.\textsuperscript{23} As a result, the spin resistivity deviates from normal metallic behavior and at a certain point, begins to increase with temperature. The temperature at which the electrical resistivity becomes independent of temperature is known as the Kondo coherence temperature, $T_K$.\textsuperscript{23} In Kondo systems, the total energy of the system is minimized if the spin of the conduction electron is aligned opposite to that of the magnetic ion. The effective magnetic moment in these materials is reduced due to the competition between the Kondo effect and the formation of local magnetic moments. As the temperature decreases towards $T_K$, itinerant electrons become increasingly spin polarized due to the oscillatory nature of the Ruderman-Kittel-Kasuya-Yosida mechanism which is described below.

1.5.2 RKKY

The Ruderman-Kittel-Kasuya-Yosida (RKKY) explains the indirect exchange interaction between the $f$-electrons of the rare earth ions and the conduction electrons and is responsible for cooperative phenomena such as magnetic ordering in compounds.\textsuperscript{21,24,25} The magnetic ions in intermetallic compounds are well separated from each other so that any direct exchange between two neighboring $f$ shells is negligible. Due to their metallic nature, the magnetic interaction between two such ions can take place via the polarization of the conduction band electrons as in the case of the elemental rare earth metals.\textsuperscript{21,24,25}

The RKKY interaction is determined by the electronic band structure and Fermi surface topology. In the case of elemental rare earths it is well established that nesting of the Fermi surface, enhances the indirect exchange interaction which is responsible for the magnetic ordering.\textsuperscript{21,24,25} The magnetic ion is able to spin polarize surrounding conduction electrons with
\( \lambda r \), facilitating the coupling of the spin polarized electrons to the spin of a nearby ion, creating a cooperative interaction between distant magnetic ions. By considering the response of a set of \( R \) ions, interacting via the RKKY exchange to a periodic field in the paramagnetic phase, it is found the antiferromagnetic ordering temperature, \( T_N \) typically scales with \((g_J - 1)^2 J(J + 1)\) which is the well-known de Gennes scaling for isostructural compounds where the ordering temperature is determined solely by RKKY exchange interactions.\(^{26,27}\)

### 1.6 Magnetoresistance

Magnetoresistance is defined as,

\[
\frac{\Delta \rho}{\rho_0} = \frac{\rho_H - \rho_0}{\rho_0}
\]

where \( \Delta \rho \) is defined as the ratio of field dependent resistivity, \( \rho_H \) minus the zero field resistivity, \( \rho_0 \), to the zero field resistivity.\(^{18,19}\) Since the discovery of giant magnetoresistance (GMR) in Fe/Cr multilayers, intensive research studies have been focused on the changes in resistivity which accompanies the reorientation of magnetic moments when they are exposed to a magnetic field. Presently, the concept of magnetoresistance is applicable to a wide range of magnetic sensory devices such as computer read heads which detect magnetic field strength through resistivity changes.\(^{21}\) Magnetoresistance has since been discovered in intermetallic compounds which exhibit large positive magnetoresistance at low temperatures. LaSb\(_2\) shows large positive magnetoresistance of up to 10,000 % at 45 Tesla.\(^{28}\) Magnetoresistance has also been observed in Ce\(_2\)PdGa\(_{10}\) which has an increase in resistance of over 200 % between zero field and 9 T.\(^{29}\) \( LnNi(1-x)Sb_2 \) (\( Ln = Y, Dy, Ho; x \sim 0.4 \)) also show large positive magnetoresistance of over 100 % at 3 K and 9 T.\(^{30}\) PrCo\(_2\)Si\(_2\) (3 K) also shows positive magnetoresistance of > 20 % at 4 T.\(^{31}\) The magnetoresistance of LaMn\(_2\)Ge\(_2\), which is ferromagnetic below 326 K is found to be positive.
below 70 K gradually increasing to an unusually large value \( \sim \) nearly 100\% at 4.2 K in the presence of a field of 0.7 T.
CHAPTER 2. CRYSTAL GROWTH, STRUCTURE, MAGNETIC AND TRANSPORT PROPERTIES OF TbRhIn₅

2.1 Introduction

Heavy fermion intermetallic compounds exhibit exotic physical properties due to the interactions between their \( f \)-electrons and conduction electrons.\(^{33-42} \) Heavy fermions show normal metallic behavior at room temperature, while at lower temperatures the conduction electrons begin to screen the magnetic moment, resulting in effective masses approximately two orders of magnitude higher than that of a free electron. Since the effective mass of an electron is proportional to the electronic specific heat (\( \gamma \)), a large Sommerfeld coefficient (> 100 mJ/mol K\(^2\)) may be observed.\(^{34} \) Recently, these compounds have been reviewed and summarized.\(^{43} \) Heavy fermion compounds are typically cerium, ytterbium, or uranium-based intermetallic compounds.\(^{37,44-46} \) The rare earth ions in intermetallic compounds are well separated, so that any direct exchange between two neighboring \( f \)-shells is negligible.\(^{21,47} \) Due to their metallic nature, however, the magnetic interaction between two such ions can take place via the polarization of the conduction band electrons as in the case of the elemental rare earth metals. This Ruderman-Kittel-Kasuya-Yoshida (RKKY) indirect exchange interaction is responsible for cooperative magnetic ordering.\(^{47} \) The competition between Ruderman-Kittel-Kasuya-Yoshida (RKKY) interactions and the Kondo effect (the progressive screening of the magnetic moments by the conduction electrons at low temperatures), is important because the heavy fermion state is formed when the Kondo effect overcomes the RKKY interaction.\(^{48} \)

\( \text{CeMIn}_5 \ (M = \text{Co, Rh, Ir}) \) is a special class of heavy fermion materials which show magnetic ordering and/or unconventional superconductivity at low temperatures.\(^{49,50} \) The

---

\(^{1}\) Reprinted from Inorg. Chem., 45, Williams, W. M.; Pham, L.; Maquilon, S.; Moldovan, M.; Young, D. P.; Chan, J. Y., Crystal Growth, Structure, Magnetic and Transport Properties of TbRhIn₅, 4367, Copyright (2006), with permission from the American Chemical Society.
co-existence of magnetism and superconductivity is quite unusual, and in fact is magnetically mediated. Heavy fermion intermetallic compounds which show both magnetic ordering and superconductivity are of interest as they present the opportunity to study the competition and/or coexistence between the two mechanisms.

The crystal structure of CeMIn$_5$ ($M = \text{Co, Rh, Ir}$)\textsuperscript{51,52} which adopts the HoCoGa$_5$-structure type\textsuperscript{53} consists of alternating layers of CeIn$_3$ and MIn$_2$ layers stacked along the $c$-axis. Bulk CeIn$_3$ is a heavy fermion antiferromagnet which exhibits pressure-induced superconductivity.\textsuperscript{54} CeCoIn$_5$ ($\gamma \approx 290 \text{ mJ/mol-Ce K}^2$)\textsuperscript{55} under ambient conditions, has the highest superconducting transition temperature ($T_c = 2.3$ K) reported for any heavy fermion compound.\textsuperscript{49} The magnetization of CeCoIn$_5$ is highly anisotropic, exhibiting a weak metamagnetic transition around 4.2 T along the $c$-axis, while it gradually increases along the $a$-$b$ plane.\textsuperscript{56} CeRhIn$_5$ orders antiferromagnetically at $T_N = 3.8$ K and becomes superconducting at 2 K upon the application of $>16$ kbar of pressure with a $\gamma \approx 420 \text{ mJ/mol-Ce K}^2$.\textsuperscript{49} CeIrIn$_5$, under ambient conditions, has the largest Sommerfeld coefficient for the series with $\gamma \approx 750 \text{ mJ/mol-Ce K}^2$.\textsuperscript{57} The superconducting temperature of CeIrIn$_5$ is 0.4 K, however there is a resistivity drop at 1.2 K, of which there is debate about the mechanism responsible for the decrease in resistivity.\textsuperscript{49} Upon the application of pressure, the transition temperature at 0.4 K increases to a maximum value of $\sim 1$ K at approximately 15 kbar. The highest ordering temperatures reported for this class of compounds are those observed in GdRhIn$_5$ and GdIrIn$_5$ which order antiferromagnetically at Néel temperatures of 40 K and 42 K, respectively.\textsuperscript{58,59} Reduced spatial dimensionality and magnetic anisotropy, as a function of rare earth element have been observed in LnRhIn$_5$ ($Ln= \text{Ce, Nd, Sm, Gd}$). In an effort to further study the effects of magnetic anisotropy in Kondo systems, we were prompted to study TbRhIn$_5$. In this chapter, we compare
the structure, transport, and physical properties of single crystals of TbRhIn$_5$ with other magnetic analogs, CeRhIn$_5$, SmRhIn$_5$, NdRhIn$_5$, and GdRhIn$_5$.

2.2 Experimental

2.2.1 Synthesis

Tb pieces, Rh powder, and In shot (Alfa Aesar), all with stated purities of $\geq 99.9\%$, were combined in an atomic ratio of 1:1:20. The starting materials were then placed into an alumina crucible and sealed in an evacuated fused silica tube. The sealed sample was then gradually heated from room temperature to 1373 K at a rate of 473 K/hr for 2 hrs, then slowly cooled at 281 K/hr to 923° C, at which point the excess flux was removed via centrifugation. Synthesis yielded aggregates of layered crystals exhibiting a metallic luster.

Table 2.1 Crystallographic Parameters for TbRhIn$_5$

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>$a$ (Å)</td>
<td>4.6000(6)</td>
</tr>
<tr>
<td>$c$ (Å)</td>
<td>7.4370(11)</td>
</tr>
<tr>
<td>$V$ (Å$^3$)</td>
<td>157.29(6)</td>
</tr>
<tr>
<td>Crystal System, Z</td>
<td>Tetragonal, 1</td>
</tr>
<tr>
<td>Crystal Dimension (mm$^3$)</td>
<td>0.075 x 0.025 x 0.025</td>
</tr>
<tr>
<td>Space Group</td>
<td>$P4/mmm$</td>
</tr>
<tr>
<td>$\theta$ range (°)</td>
<td>2.5 – 30.0</td>
</tr>
<tr>
<td>$\mu$(mm$^{-1}$)</td>
<td>31.481</td>
</tr>
<tr>
<td>Measured reflections</td>
<td>742</td>
</tr>
<tr>
<td>Independent reflections</td>
<td>244</td>
</tr>
<tr>
<td>$R_{int}$</td>
<td>0.097</td>
</tr>
<tr>
<td>$h, k, l$</td>
<td>±7, ±5, ±11</td>
</tr>
<tr>
<td>$^aR[F^2 &gt; 2\sigma(F^2)]$</td>
<td>0.0432</td>
</tr>
<tr>
<td>$^bW(R(F^2))$</td>
<td>0.0833</td>
</tr>
<tr>
<td>Parameters</td>
<td>12</td>
</tr>
<tr>
<td>$\Delta\rho_{max}$(e Å$^{-3}$), $\Delta\rho_{min}$(e Å$^{-3}$)</td>
<td>3.24, -4.52</td>
</tr>
</tbody>
</table>

[^a]: $R = \sum |F_o| - |F_c|/\sum |F_o|
[^b]: $W = \sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]]^{1/2}$
Table 2.2  Atomic Positions and Thermal Parameters of TbRhIn$_5$

<table>
<thead>
<tr>
<th></th>
<th>$x$</th>
<th>$y$</th>
<th>$Z$</th>
<th>$U_{eq}$ (Å$^2$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tb</td>
<td>1a</td>
<td>0</td>
<td>0</td>
<td>0.014(3)</td>
</tr>
<tr>
<td>Rh</td>
<td>1b</td>
<td>0</td>
<td>0.5</td>
<td>0.015(2)</td>
</tr>
<tr>
<td>In(1)</td>
<td>4i</td>
<td>0.5</td>
<td>0.5</td>
<td>0.018(4)</td>
</tr>
<tr>
<td>In(2)</td>
<td>1c</td>
<td>0</td>
<td>0.3015(8)</td>
<td>0.017(3)</td>
</tr>
</tbody>
</table>

$U_{eq}$ is defined as one-third of the trace of the orthogonalized $U_{ij}$ tensor.

Table 2.3  Selected inter-atomic distances and bond angles of TbRhIn$_5$

### Distances (Å)

**Within cuboctahedra**

- In1-In2: 3.2140(12)
- In1-In1: 3.2527(4)
- Tb-In1 (x 4): 3.2140(12)
- Tb-In2 (x 8): 3.2527(4)

### Angles (°)

- In1-Tb-In1: 90°
- In1-Tb-In2: 60.960(8)
- In1-Tb-In2: 119.040(8)
- In2-Tb-In2: 88.330(2)
- In2-Tb-In2: 59.520(4)
- In2-Tb-In2: 120.480(4)

### Distances (Å)

**Within rectangular polyhedron**

- In2-In2 (c-axis): 2.9470(3)
- In2-In2 ($a$-$b$ plane): 3.2562(7)
- Rh-In2 (x 8): 2.7316(9)

### Angles (°)

- In2-Rh-In2: 73.130(13)
- In2-Rh-In2: 65.200(2)

2.2.2  Single Crystal X-ray Diffraction
A 0.025 x 0.025 x 0.075 mm$^3$ single crystal fragment was placed on a glass fiber and mounted on the goniometer of a Nonius Kappa CCD diffractometer equipped with Mo $K_{\alpha}$ radiation ($\lambda = 0.71073$ Å). Data were collected at 293(2) K. Additional data collection and crystallographic parameters are presented in Table 2.1.

The structures were solved with the SHELXL software package$^{60}$ using CeRhIn$_5$ as a structural model. The atomic displacement parameters were treated anisotropically, and an extinction coefficient was applied to the data after a final least squares cycle. The atomic coordinates and displacement parameters are provided in Table 2.2, and selected interatomic distances are listed in Table 2.3.

2.2.3 Physical Property Measurements

Magnetic properties were measured on single crystals using a Quantum Design (SQUID) magnetometer. The temperature-dependent susceptibility was measured in an applied field of 1000 G up to room temperature after being cooled to 2 K under zero magnetic field. Field-dependent magnetization data were also collected from zero field to 10 Tesla at 2 K. The resistivity (down to 2 K) data were measured using a standard four-probe method with a Quantum Design Physical Property Measurement System (PPMS) at ambient pressure. Specific heat data was determined using the thermal transport option on the PPMS. The heat capacity of the TbRhIn$_5$ was measured at zero field in the temperature range of 300 K to 0.36 K. Single crystals of the nonmagnetic analog, LaRhIn$_5$ which were used for heat capacity measurements, were also grown using the flux method at Los Alamos National Lab (LANL).

2.3 Results and Discussion

2.3.1 Crystal Structure

TbRhIn$_5$ is isostructural to the CeMIn$_5$ ($M = \text{Co}, \text{Rh}, \text{Ir}$) compounds which adopt the HoCoGa$_5$-type ($P4/mnm$)$^{53}$ The structure consists of four atoms in the asymmetrical unit: Tb,
Rh, In1 and In2 atoms occupying the 1a, 1b, 1c, and 4i positions, respectively. Figure 2.1 shows the crystal structure of TbRhIn₅ which consists of alternating layers of TbIn₃ cuboctahedra and RhIn₂ rectangular prisms that contain two independent indium sites, In1 and In2.

![Diagram of TbRhIn₅ crystal structure](image)

**Figure 2.1** Layers of TbIn₃ cuboctahedra and RhIn₂ rectangular prisms alternate along the c-axis. Tb is coordinated to eight In1 atoms and four In2 atoms.

The coordination of Tb in the cuboctahedra is eight-fold to In1 and four-fold to In2 with distances of 3.2140(12) Å and 3.2527(4) Å, respectively. These distances are in good agreement with the Tb-In interatomic distances in the binary compounds, Tb₂In and TbIn₃, in which the Tb-In distances range from 3.025 Å to 3.359 Å.⁶¹ In CeCoIn₅, the cuboctahedra are elongated along the c-axis, whereas, a shortening of the c-axis is observed in the Ir analog. The ratio of Ce-In₂:Ce-In1 distance in CeRhIn₅ is close to unity, indicating that the cuboctahedra are not distorted.⁶² The ratio of Tb-In2 to Tb-In1 is 1.014, suggesting that the cuboctahedra in TbRhIn₅ are quite symmetrical. The Rh atom is coordinated to eight In2 atoms and forms the edge of the neighboring rectangular prism. The Rh-In2 distance in TbRhIn₅ is 2.7316(9) Å, is comparable to the Rh-In2 distances of 2.7572(3) Å observed in LaRhIn₅, as well as, the summation of the atomic radii for rhodium and indium.⁶² The In1-In2 and In1-In1 interatomic
distances in TbRhIn$_5$ are 3.2140 (12) Å and 3.2527(4) Å, respectively, which are in good agreement with the values observed in RhIn$^{63}$ and RhIn$_3^{64,65}$, ranging from 3.200 Å to 3.580 Å.

2.3.2 Physical Properties

The temperature dependence of the magnetic susceptibility of TbRhIn$_5$ is shown in Figure 2.2 for the field (1000 G) both along the $c$-axis and in the $a$-$b$ plane. A large anisotropy in the susceptibility data is observed. A sharp antiferromagnetic transition appears at 48 K. Above $T_N$, the inverse susceptibility obeys the Curie-Weiss law and is well fit by $[1/\chi(T) = (T-\theta) / C]$ in the temperature range of 80 – 300 K. We find an average effective moment of $\sim 9.72 \mu_B$/Tb$^{3+}$ ion along the $c$-axis and the $a$-$b$ plane with Weiss temperatures of $\theta = -75$ K and $\theta = -5$ K.

![Figure 2.2](image_url)  

**Figure 2.2** The temperature dependence of the magnetic susceptibility of TbRhIn$_5$ is shown under an applied field (1000 G) both along the $c$-axis and in the $a$-$b$ plane.
Figure 2.3  The field dependence of the magnetization of TbRhIn$_5$ at 2 K.

Figure 2.4  The temperature-dependent resistivity of TbRhIn$_5$.  

26
respectively. The effective moment is in agreement with the full Hund’s moment for Tb³⁺ which is 9.72 \( \mu_B \). The negative \( \theta \) values indicate antiferromagnetic correlations, which are quite strong along the c-axis.

The temperature dependence of the electrical resistivity of a single crystal of TbRhIn₅ is shown in Figure 2.4. TbRhIn₅ is metallic \((d\rho/dT > 0)\) and has a residual resistivity ratio \( (RRR) \) of 6. A kink in the resistivity is observed near the ordering temperature at 48 K, consistent with a reduction in the spin disorder scattering. Above \( T_N \), the resistivity increases linearly with temperature. The small downturn at 3.4 is due to some residual In flux in the sample.

Figure 2.5 shows the temperature-dependence of the specific heat \( C_p \) for TbRhIn₅. At zero field, a large cusp is observed at \( \sim 48 \) K which is consistent with the antiferromagnetic transition observed in the susceptibility. The specific heat can be described by the equation \( C_p = \gamma T + \alpha T^3 \), where \( \gamma \) is the Sommerfeld coefficient and \( \alpha \) is the phonon contribution to the total specific heat. The phonon contribution is negligible at low temperatures, which allows the electronic contribution to the specific heat to be determined experimentally. The \( f \)-electron contribution to the specific heat, \( C/T_{m} \), (Figure 2.5), is obtained by subtracting the phonon contribution \( C/T \) of LaRhIn₅. Since LaRhIn₅ does not contain any \( f \)-electrons, it is a good approximation of the lattice contribution to the specific heat. The specific data in TbRhIn₅ is similar to other antiferromagnetic LnMIn₅ materials. Several mechanisms act simultaneously to produce the specific heat data as shown in Figure 2.6. There is a large nuclear Schottky contribution at low temperatures (below 2K). It arises due to the hyperfine interaction between the 4\( f \) electrons and the Tb³⁺ nuclei, which carry a nuclear spin moment of \( I = 3/2 \). There is a possible Schottky anomaly due to the crystalline electric field (CEF) at 11 K as shown in Figure 2.6, and there is a large peak at 48 K due to the antiferromagnetic transition.
Figure 2.5 The specific heat of TbRhIn$_5$ (closed circles) and LaRhIn$_5$ (open circles). The f-electron contribution of Tb is denoted with open triangles.

Figure 2.6 The specific heat of TbRhIn$_5$ after subtracting the lattice contribution (closed triangles), Schottky (line), and nuclear Schottky contributions (open circles). The entropy of TbRhIn$_5$ is shown in the inset.
The entropy is obtained by integrating $C/T_m$ with respect to temperature. A value of $R \ln 3$ is recovered by the ordering temperature. Since the number of states $N$ is determined by the entropy as $R \ln N$, this confirms that Tb is in a triplet ground state ($N=3$).

### 2.4 Conclusion

In summary, TbRhIn$_5$ has been synthesized using flux methods and is isostructural to the well studied CeRhIn$_5$. The magnetic moments of CeRhIn$_5$ form an incommensurate spiral along the $c$-axis,$^{57,66}$ and although CEF anisotropy energetically favors the moments to point along the $c$-axis, the magnetic moments have been found to lie in the $a$-$b$ plane.$^{67}$ Thus there may be competition between the two magnetic interactions, since we observe a 50\% decrease in $T_N$ for CeRhIn$_5$ in comparison to the parent compound CeIn$_3$. In contrast, the easy axis of magnetization in TbRhIn$_5$ ($T_N = 47$ K) is along the $c$-axis, therefore $T_N$ is enhanced nearly 24\% relative to TbIn$_3$ ($T_N = 36$ K).$^{15}$ In addition, the enhanced $T_N$ indicates that RKKY interactions are more dominant than the Kondo effect in this compound as we observe more interaction between the uncompensated rare earth ions. The magnetic susceptibility of GdRhIn$_5$ is only significantly anisotropic below $T_N$ showing an easy axis of magnetization in the plane. Furthermore, CeRhIn$_5$ becomes superconducting less than 16 kbar of mechanical pressure, but the superconducting state diminishes at $\sim 25$ kbar. The size of the atomic radii of Ce$^{3+}$ vs. Tb$^{3+}$ decreases by $\sim 3.4$% due to lanthanide contraction. Multiplying 16 kbar by 3.4\% gives an estimated molecular pressure for TbRhIn$_5$ of $\sim 25$ kbar at which the superconducting state diminishes in CeRhIn$_5$.$^{52}$ The magnetic ordering temperature of TbRhIn$_5$ scale in accordance with the de Gennes factor $[(gJ^2 - 1)][J(J + 1)]$ of LnRhIn$_5$ ($Ln =$ Ce, Nd, Sm, Gd) for ground state multiplet $J$ through the rare earths, with $T_N$ of 3.8 K to 48 K for Ce and Tb analogs, respectively. Although TbRhIn$_5$ is not a heavy fermion superconductor, it does have strong antiferromagnetic correlations giving rise to an ordering temperature much higher than its heavy fermion analog.
CeRhIn$_5$. It would be interesting to do a doping study by substituting Ce for Tb in TbRhIn$_5$ to observe how the heavy fermion superconducting state develops out of a strong antiferromagnet.
CHAPTER 3. SYNTHESIS, STRUCTURE, AND MAGNETORESISTANCE OF SMPd$_2$Ga$_2$

3.1 Introduction

Compounds of the ThCr$_2$Si$_2$-structure type are abundant due to their robust structure and the interesting physical properties that result from the ability of this structure to adopt different elements with various atomic sizes.$^{68-71}$ A significant number of these compounds have been shown to exhibit superconductivity, including the well known $Ln$-Ni-B-C ($Ln$ = lanthanide), which are stuffed variants of the ThSi$_2$Cr$_2$-structure type.$^{72}$ Other compounds boast a wide range of magnetic properties. UCr$_2$Si$_2$$^{73}$ and PrNi$_2$Ge$_2$$^{74}$ order antiferromagnetically at $T_N = 27$ K and $T_N = 24$ K, respectively, and EuNi$_2$P$_2$ is an interesting compound because of the mixed valence states of Eu (2+/3+).$^{75}$ Several ternary $Ln$-Pd-Ga containing phases are known to adopt the BaAl$_4$ structure type which is related to the ThCr$_2$Si$_2$ structure type when $x = 2$ in $Ln$Pd$_x$Ga$_{4-x}$. Ternary gallides (La, Ce, Pr, Nd, Sm)Pd$_x$Ga$_{4-x}$ have been shown to exist as solid solutions in arc melted samples of $Ln$Pd$_x$Ga$_{4-x}$ at various compositions.$^{76}$

LaPd$_2$Ga$_2$ and CePd$_2$Ga$_2$ crystallize in the CaBe$_2$Ge$_2$ structure type and undergo a structural phase transition with decreasing temperature at 65 K and 125 K, respectively.$^{77}$ The physical properties of this family of materials are also quite interesting and often display strongly correlated electron behavior. LaPd$_2$Ga$_2$ is a superconductor with a critical temperature of 1.9 K, while the Ce-analog orders antiferromagnetically at 2.3 K.$^{77}$ Compounds of the ThCr$_2$Si$_2$ and CaBe$_2$Ge$_2$ structure types share similar structural features. Both structures are described by tetragonal unit cells with comparable lattice parameters ($\sim 4$ Å x 10 Å). The CaBe$_2$Ge$_2$-type (space group $P4/mmm$) is closely related to the ThCr$_2$Si$_2$-type (space group $I4/mmm$) and forms

---

$^1$Reprinted from Inorg. Chem, 42, Williams, W. M.; Macaluso, R. T.; Moldovan, M.; Young, D. P.; Chan, J. Y., Crystal Growth, Synthesis, Structure, and Magnetoresistance of SmPd$_2$Ga$_2$, 7315, Copyright (2002), with permission from the American Chemical Society.
in the temperature range of 1100 °C-1700 °C. In some cases, i.e. EuZn$_2$Ge$_2$, it is almost impossible to discriminate between the two structure types by X-ray diffraction. The structure type in $RT_2X_2$ compounds ($R$ = small atomic radius, $T$ = transition metal or main group, $X$ = main group element) is influenced by atomic radii and synthesis conditions of the constituent elements. The CaBe$_2$Ge$_2$-type is more prone to form when a sample is quenched at high temperatures. The CaBe$_2$Ge$_2$-type consists of layers of edge sharing BeGe$_4$ and GeBe$_4$ tetrahedra with alternating layers of isolated Ca atoms in a 1:1:1 ratio. In contrast, the ThCr$_2$Si$_2$-type consists of CrSi$_4$ edge sharing tetrahedra with alternating layers of isolated Th atoms in a 1:1 ratio. Band structure calculations have shown that the ThCr$_2$Si$_2$-type is more stable at room temperature due to its less dispersed filled band and its lower Fermi level. A Monte Carlo simulation study showed that at high temperatures entropic contributions become more important and thus can favor the CaBe$_2$Ge$_2$-type.

Intermetallic compounds containing Sm often exhibit unique magnetic behavior. This is often due to Sm ions existing in multiple electronic configurations ($4f^6$ and $4f^5$), which are referred to as mixed valence systems. SmPd$_2$Si$_2$ shows evidence of spontaneous magnetism at temperatures below 34 K. Gd$_{0.925}$La$_{0.075}$Mn$_2$Ge$_2$, which is isostructural to SmPd$_2$Ga$_2$, has been shown to exhibit negative magnetoresistance ($\Delta \rho/\rho_0 \sim 15\%$ at 145 K). In our search for novel ternary intermetallics, we have discovered SmPd$_2$Ga$_2$, which also crystallizes in the ThCr$_2$Si$_2$ structure type. In this chapter, we report the synthesis, crystal structure, and physical properties of SmPd$_2$Ga$_2$.

### 3.2 Experimental

#### 3.2.1 Synthesis

The samples were synthesized from small chunks of Sm (99.9+ %, Ames Lab), Pd powder (99.998%, Alfa Aesar), and Ga pieces (99.99999%, Alfa Aesar). Single crystals were
grown by placing the constituent elements in an aluminum oxide crucible in a molar ratio of 1:1:20. The sample was sealed in an evacuated quartz tube and heated to a temperature of 1170 °C for 7 hrs and slowly cooled to 350 °C, at which point the hot flux was removed by centrifugation. Large crystals of SmPd₂Ga₂ were obtained and showed no signs of instability or degradation when exposed to air.

Table 3.1. Crystallographic Parameters of SmPd₂Ga₂

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>a (Å)</td>
<td>4.2170(3)</td>
</tr>
<tr>
<td>c (Å)</td>
<td>10.4140(3)</td>
</tr>
<tr>
<td>V (Å³)</td>
<td>185.57</td>
</tr>
<tr>
<td>Crystal Dimension (mm³)</td>
<td>0.04 x 0.04 x 0.08</td>
</tr>
<tr>
<td>Crystal System, Z</td>
<td>Tetragonal, 2</td>
</tr>
<tr>
<td>Space Group</td>
<td>I4/mmm</td>
</tr>
<tr>
<td>θ range(°)</td>
<td>1.0-27.48</td>
</tr>
<tr>
<td>μ (mm⁻¹)</td>
<td>63.03</td>
</tr>
</tbody>
</table>

Data Collection

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Measured reflections</td>
<td>941</td>
</tr>
<tr>
<td>Independent reflections</td>
<td>144</td>
</tr>
<tr>
<td>Reflections with I &gt;2σ(I)</td>
<td>142</td>
</tr>
<tr>
<td>R_int</td>
<td>0.081</td>
</tr>
<tr>
<td>H, k, l</td>
<td>± 5, ± 5, ± 14</td>
</tr>
</tbody>
</table>

Refinement

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>aR₁ [F² &gt; 2σ(F²)]</td>
<td>0.0424</td>
</tr>
<tr>
<td>b_wR₂(F²)</td>
<td>0.1156</td>
</tr>
<tr>
<td>Reflections</td>
<td>144</td>
</tr>
<tr>
<td>Parameters</td>
<td>12</td>
</tr>
<tr>
<td>Δρ_max (e Å⁻³)</td>
<td>2.412</td>
</tr>
<tr>
<td>Δρ_min (e Å⁻³)</td>
<td>1.023</td>
</tr>
<tr>
<td>Extinction coefficient</td>
<td>0.008(9)</td>
</tr>
</tbody>
</table>

\[ aR₁ = \frac{\sum|F_o| - |F_c|/\sum|F|}{b_wR₂(F²) = \frac{\sum[w(F_o² - F_c²)]/\sum[w(F_o²)]^{1/2}}{1/2} \]

3.2.2 Single Crystal X-ray Diffraction

A suitable crystal of ~ 0.02 mm x 0.08 mm x 0.02 mm was mechanically extracted, placed on a glass fiber, and mounted on the goniometer of a Nonius Kappa CCD diffractometer equipped with monochromatic Mo Kα radiation (λ = 0.70173 Å). Additional data collection
parameters and crystallographic information are presented in Table 3.1.

Table 3.2. Atomic Positions and Thermal Parameters of SmPd$_2$Ga$_2$

<table>
<thead>
<tr>
<th>Atom</th>
<th>$x$</th>
<th>$y$</th>
<th>$z$</th>
<th>$U_{11}$</th>
<th>$U_{22}$</th>
<th>$U_{33}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sm1</td>
<td>2$a$</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0.0095(7)</td>
<td>0.0095(7)</td>
</tr>
<tr>
<td>Pd1</td>
<td>4$d$</td>
<td>0</td>
<td>1/2</td>
<td>1/4</td>
<td>0.0250(6)</td>
<td>0.0250(6)</td>
</tr>
<tr>
<td>Ga1</td>
<td>4$e$</td>
<td>0</td>
<td>0</td>
<td>0.38217(5)</td>
<td>0.0161(5)</td>
<td>0.0161(5)</td>
</tr>
</tbody>
</table>

Table 3.3. Selected Inter-atomic Distances and Bond Angles of SmPd$_2$Ga$_2$

<table>
<thead>
<tr>
<th>Inter-atomic Distances (Å)</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Sm1-Ga1 (x 12)</td>
<td>3.227(4)</td>
</tr>
<tr>
<td>Sm1-Pd1 (x 8)</td>
<td>3.350(2)</td>
</tr>
</tbody>
</table>

*Within the PdGa$_4$ tetrahedron*

<table>
<thead>
<tr>
<th>Inter-atomic Distances (Å)</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Ga1-Pd1 (x 4)</td>
<td>2.514(5)</td>
</tr>
<tr>
<td>Pd1-Pd1 (x 4)</td>
<td>2.981(9)</td>
</tr>
<tr>
<td>Ga1-Ga1</td>
<td>2.47(2)</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Angles (°)</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Ga1-Sm1-Ga1 (x 2)</td>
<td>107.3(9)</td>
</tr>
<tr>
<td>Ga1-Sm1-Ga1 (x 2)</td>
<td>113.7(3)</td>
</tr>
</tbody>
</table>

The structure was solved using direct methods (SHELXL97). Data were then corrected for extinction and refined with anisotropic displacement parameters. Atomic positions and related structural information is provided in Table 3.2. Selected inter-atomic distances and bond angles are given in Table 3.3.

3.2.3 Physical Property Measurements

The electrical resistivity of a single crystal of SmPd$_2$Ga$_2$ was measured by the standard 4-probe AC technique at 27 Hz with a current of 1 mA. 1-mil (0.001 in) Pt wires were attached to the sample with silver epoxy. The magnetoresistance and magnetic susceptibility were measured in a 9-Tesla PPMS system from Quantum Design.
3.3 Results and Discussion

3.3.1 Crystal Structure

The structure of SmPd$_2$Ga$_2$ is provided in Figure 3.1. SmPd$_2$Ga$_2$ is isostructural to ThCr$_2$Si$_2$ and crystallizes in the tetragonal *I*4/mm space group (No. 139) with Sm, Pd, and Ga occupying the 2a, 4d, and 4e sites, respectively.

![Crystal Structure Diagram](image)

Figure 3.1 The crystal structure of SmPd$_2$Ga$_2$ consists of isolated Sm atoms, and PdGa$_4$ tetrahedra with Sm, Pd, and Ga atoms represented as black, grey, and white circles, respectively.

The crystal structure consists of layers of PdGa$_4$ edge sharing tetrahedra alternating with layers of isolated Sm atoms in a 1:1 ratio along the c-axis. Each Pd atom is coordinated to 4 Ga atoms by a bond distance of 2.514 (5) Å, which is in agreement with the summation of the atomic radii of Ga (1.22 Å) and Pd (1.37 Å), as well as, the typical inter-atomic distances in Pd-Ga binaries. In Pd$_2$Ga, for example, Pd and Ga atoms are separated by 2.558 Å. The Pd-Ga distances in Pd$_5$Ga$_3$ range between 2.388 - 2.701 Å, and 2.501 - 2.691 Å in PdGa$_5$ and Pd$_2$Ga. Each layer of PdGa$_4$ tetrahedra is connected to the next layer of PdGa$_4$ tetrahedra by a 2.47(2) Å Ga-Ga bond along the c-axis. The Ga-Ga inter-atomic distance of 2.47(2) Å also agrees with the calculated value of 2.44 Å. The Ga-Ga inter atomic distances agree with interatomic distances reported in CeGa$_6$, CeGa$_2$, and PdGa$_5$ which fall within the range of 2.297
– 2.930 Å. Ga-Pd-Ga bond angles in the PdGa₄ tetrahedron are 107.3(9)° and 113.7(3)° which are slightly distorted. The layers of PdGa₄ tetrahedra form a cage-like structure, which encapsulates one Sm atom. In the samarium layer, the Sm-Sm inter-atomic distance of 4.2170(3) Å is too long to be considered as bonding.

3.3.2 Physical Properties

The in-plane (a-plane) resistivity of a single crystal of SmPd₂Ga₂ as a function of temperature from 1.8 – 300 K is shown in Figure 3.2. The sample is metallic (dρ/dT > 0) with a weak temperature dependence above 100 K. A broad shoulder occurs in the data near 60 K, and the resistivity decreases more rapidly below this temperature. This type of behavior is often observed in Kondo lattice systems in which the conduction electrons interact with local magnetic moments. The drop in the resistivity is usually associated with the onset of Kondo coherence. No superconductivity in SmPd₂Ga₂ was observed down to a temperature of 1.8 K.

The in-plane relative magnetoresistance (MR = Δρ/ρ₀) of SmPd₂Ga₂ at different temperatures is shown in Figure 3.3, where Δρ = ρ(H) - ρ₀, and ρ₀ = ρ(0). The MR is positive

![Figure 3.2](image-url)

**Figure 3.2** Shows the in-plane resistivity for a single crystal of SmPd₂Ga₂
and quite large at 2 K, increasing by over 100% at 9 Tesla. In fact, the 9-Tesla MR at 2 K is comparable to the zero-field resistivity at room temperature. The MR also appears to violate Kohler’s rule, as the MR does not scale as a function of $F(H/\rho_o)$. The MR decreases with increasing temperature, and is quickly suppressed above 50 K. This occurs in the same temperature range where the broad shoulder appears in the zero-field resistivity. The large MR could be related to topological features of the Fermi surface, or it may result from an increase in spin-disorder scattering as suggested by magnetization data presented. Measurements of the magnetization at low temperatures and high fields (de Haas van-Alphen effect) can be used to experimentally determine the Fermi surface, and such experiments are planned for the near future. The data are qualitatively consistent with a local moment system. However, the inverse susceptibility plotted versus temperature (not shown) is not linear at high temperatures, as would

**Figure 3.3** Relative in-plane magnetoresistance of a single crystal of SmPd$_2$Ga$_2$ at different temperatures with $H \parallel c$. 

```
Figure 3.4  Temperature dependent magnetic susceptibility ($\chi = M/H$) in a field of 1000 gauss with $H \parallel c$. Inset: Inverse susceptibility (with van Vleck term subtracted) versus temperature.

Figure 3.5. Magnetization versus applied field of a single crystal of SmPd$_2$Ga$_2$ for $H \parallel c$ and $T = 2$ K. The inset shows an expanded view of the low-field region, clearly showing hysteresis in the magnetization.
be expected for the Curie-Weiss law. The weaker than linear increase in the reciprocal susceptibility is consistent with Sm ions in the $3^+$ state in conjunction with a large temperature-independent van Vleck susceptibility. Such behavior is typical in Sm intermetallics. By using a modified Curie-Weiss law of the form: $\chi(T) = \chi_o + C/(T - \theta)$, we were able to fit the magnetic susceptibility data quite well down to \( \sim 8 \text{ K} \) (see solid line, main panel of Fig. 3.4). Here, $\chi_o$ represents the temperature-independent van Vleck term, $C$ is the Curie constant, and $\theta$ is the Weiss temperature. By plotting the inverse susceptibility versus temperature with $\chi_o$ subtracted from the raw data, we find linear behavior extending up to \( \sim 70 \text{ K} \) (see inset Fig.3.4). From a linear fit to this curve we obtain values of $1.2 \times 10^{-4}$ emu-K/gm and $5.2 \text{ K}$ for $C$ and $\theta$, respectively. The positive value of $\theta$ suggests ferromagnetic correlations, and from $C$ we calculate an effective magnetic moment $p = 0.70 \mu_B$/mol Sm. This is smaller than, but close to, the full Hund’s rule moment for Sm$^{3+}$. Further evidence for ferromagnetic ordering is shown in Figure 3.5, where we plot the magnetization versus applied field at 2 K. The magnetization is not saturated, even at a field of 9 Tesla, and the low-field data (inset Fig. 3.5) clearly show hysteresis in the magnetization – a clear sign of ferromagnetism. Given that the MR at 2 K tends to track the magnetization, we feel an increase in the spin-disorder scattering is a plausible explanation for the large MR at low temperature.

### 3.4 Conclusion

In conclusion, we have synthesized the new ternary intermetallic SmPd$_2$Ga$_2$ by metal flux techniques and determined its crystal structure. The material forms in the ThCr$_2$Si$_2$ structure which is common for many $RT_2X_2$ compounds, where $R$ is a lanthanide, $T$ is a transition metal, and $X$ is a group 3 or 4B element. SmPd$_2$Ga$_2$ is metallic and orders ferromagnetically at 5 K. It has an unusually large positive magnetoresistance at low temperatures that may be due to an increase in spin-disorder scattering. No superconductivity was observed down to 1.8 K.
CHAPTER 4. SYNTHESIS, STRUCTURE AND MAGNETISM OF Tb₄M₆Ga₁₂
(M = Pd, Pt)

4.1 Introduction

The ternary compounds Ceₙ₆MX₃n+2 (n = 1, 2; \( M = \text{Co, Rh, Ir}; X = \text{Ga, In} \))⁴⁹,⁵⁰,⁵³,⁵⁷,⁸¹ have received a great deal of attention within the last few years. This system possesses a very rich magnetic phase diagram that allows one to probe ground states with long-range magnetic order, superconductivity, and quantum criticality. Ce₆In₅ (\( M = \text{Co, Rh, Ir} \)) forms tetragonal structure composed of alternating layers of CeIn₃ cuboctahedra and “MIn2” rectangular prisms.³⁶,⁸² The quasi-two-dimensional layered structure is highly anisotropic. Ce₆In₅ (\( M = \text{Co, Ir} \)) exhibit heavy fermion superconductivity under ambient conditions at \( T_c = 2.3 \text{ K} \) and \( T_c = 0.4 \text{ K} \), respectively.³⁶ CeRhIn₅ superconducts at 2.1 K under applied pressures of 16 kbar.⁸³ CeRhIn₅, under ambient pressure, is a heavy-fermion antiferromagnet with \( T_N = 3.8 \text{ K} \).⁵⁷,⁸⁴ Similarly, Ce₆M₈In₈ (\( n = 2; M = \text{Rh, Ir} \)) consists of one layer of MIn2 rectangular prisms alternating with two layers of CeIn₃ cuboctahedra.⁸⁵ Ce₂RhIn₈ orders antiferromagnetically at \( T_N = 2.8 \text{ K} \) at ambient pressure and superconducts at 2.1 K under a pressure of 25 kbar.⁸⁵ CeIn₃ (\( n = \infty \)) is antiferromagnetic (\( T_N = 10 \text{ K} \)) and superconducts (\( T_c = 0.25 \text{ K} \)) under a pressure of 25 kbar.⁸⁶

In our search for Pd and Pt containing intermetallics, we have discovered several Ce-Pd-Ga phases. CePdGa₆ is a heavy fermion metamagnet (\( \gamma \sim 230-360 \text{ mJ/mol K}^2 \)), in which the Ce \( f \)-moments order antiferromagnetically along the \( c \)-axis at \( T_N = 5.5 \text{ K} \). A reconfiguration of spins induces a ferromagnetic moment in the \( ab \)-plane.⁸⁵ Ce₂PdGa₁₂ orders antiferromagnetically at \( T_N \sim 11 \text{ K} \) with a spin reconfiguration transition at 5 K and has recently been compared to Ce₂PdG₁₀ which exhibits large positive magneto-resistance of over 200% at 9 Tesla.²⁹

¹Reprinted from J. Solid State Chem., 178, Williams, W. M.; Moldovan, M.; Young, D. P.; Chan, J. Y., Synthesis, Structure and Magnetism of Tb₄M₆Ga₁₂ (\( M = \text{Pd, Pt} \)), 4367, Copyright (2004), with permission from Elsevier.
Other Ce-Pd-Ga phases have also been reported. Ce₈Pd₂₄Ga orders antiferromagnetically at \( T_N = 3.6 \) K and exhibits an enhanced electronic specific heat at \( T = 10 \) K. CePdGa exhibits an antiferromagnetic transition at \( T_N = 1.8 \) K. CePd₂Ga₃ orders ferromagnetically at \( T_c = 6 \) K. CePd₂Ga (YPd₂Si-type) order antiferromagnetically at a Néel temperatures of. Rare earth intermetallics containing Sm or Tb were also investigated because of the possibility of mixed valency or other unusual magnetic or electronic behavior. SmPd₂Ga₂, of the ThCr₂Si₂ structure type, has been discovered to exhibit large positive magnetoresistance which increases by almost 100% at low temperature.

Magnetic ordering is also found in terbium intermetallics. A study by neutron diffraction shows that orthorhombic TbNiGa orders antiferromagnetically at \( T_N = 23 \) K. TbNi₃Ga₂ (YCo₃Ga₂-type) orders ferromagnetically below 14 K. Tb₂CoGa₃ orders ferromagnetically below 28 K. TbPdGa exhibits a complicated magnetic structure which undergoes a magnetic transformation at 26 K. TbPtGa and TbRhGa of the orthorhombic TiNiSi-structure type are antiferromagnetic with Néel temperatures of 34 K and 22 K, respectively. Finally, TbGa₂ exhibits a multi-step metamagnetic transition at \( T_N = 18 \) K when the field is applied perpendicular to the \( c \)-axis, while TbGa₆ (PuGa₆-type), exhibits pressure-induced superconductivity (\( T_c = 6 \) K) at ~10 kbar.

Neutron and Single crystal X-ray studies of RE₄FeGa₁₂₋ₓGeₓ (RE = Sm, Tb) reveal that these compounds crystallize in the cubic U₄Re₇Si₆-type (\( I m \bar{3} m \)) with lattice parameters \( a = 8.657(4) \) Å and 8.5620(9) Å for Sm and Tb analogs, respectively. Tb₄FeGa₁₂₋ₓGeₓ orders antiferromagnetically at a Néel temperature of 13 K, while the isostructural Sm analog does not exhibit any magnetic ordering.

The crystal structure and transport measurements on polycrystalline \( R_4MGa_{12} \) (\( R = \) Gd-Lu; \( M = \) Ni, Pd) were reported. The structure of \( R_4MGa_{12} \) (\( R = \) Gd-Lu; \( M = \) Ni, Pd) is cubic.
and can be viewed as a redistributed homolog of \( \text{U}_{4}\text{Re}_{7}\text{Si}_6 \)-type\(^9\) or alternatively, the structure can be regarded as the result of partially filling the octahedral voids in the cubic close packed \( \text{AuCu}_3 \)-type.\(^{29}\) The electrical resistivity of \( R_4M\text{Ga}_{12} \) (\( R = \text{Gd-Lu}; M = \text{Ni, Pd} \)) shows metallic behavior.\(^{100}\) In this chapter, we report the crystal structure, transport and magnetic properties of single crystals of \( \text{Tb}_4\text{PdGa}_{12} \) and \( \text{Tb}_4\text{PtGa}_{12} \).

4.2 Experimental

4.2.1 Syntheses

The samples were synthesized from small pieces of Tb metal (99.9\%, Alfa Aesar), Pd and Pt powder (99.998\%, Alfa Aesar), and Ga pieces (99.99999\%, Alfa Aesar). Single crystals were grown by placing constituent elements in an aluminum oxide crucible in a molar ratio of 1:1:20. The sample was sealed in an evacuated fused silica tube and heated to a temperature of 1150 °C for 7 h and then cooled at a rate of 15°C/h to 530 °C, at which point the excess Ga flux was removed by centrifugation. The synthesis yielded cuboidal-shaped crystals which ranged in size from 0.02 mm\(^3\) to 0.5 mm\(^3\).

4.2.2 Single Crystal X-ray Diffraction

A single crystal fragment of \( \sim 0.02 \text{ mm} \times 0.04 \text{ mm} \times 0.06 \text{ mm} \) (\( \text{Tb}_4\text{PdGa}_{12} \)) and \( \sim 0.02 \text{ mm} \times 0.04 \text{ mm} \times 0.08 \text{ mm} \) (\( \text{Tb}_4\text{PtGa}_{12} \)) were mechanically extracted, placed on a glass fiber and mounted on the goniometer of a Nonius Kappa CCD diffractometer equipped with Mo \( K\alpha \) radiation (\( \lambda = 0.71073 \text{ Å} \)). Additional data collection and crystallographic parameters are presented in Table 4.1.

To ensure sample homogeneity several single crystals from several different sample growths were characterized by single crystal X-ray diffraction. Crushed single crystals were also characterized by powder X-ray diffraction to confirm sample homogeneity.
Table 4.1 Crystallographic Parameters

<table>
<thead>
<tr>
<th></th>
<th>Tb₄PtGa₁₂</th>
<th>Tb₄PtGa₁₂</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Formula</strong></td>
<td>Tb₄PtGa₁₂</td>
<td>Tb₄PtGa₁₂</td>
</tr>
<tr>
<td><em>a</em> (Å)</td>
<td>8.5930(7)</td>
<td>8.5850(3)</td>
</tr>
<tr>
<td>V (Å³)</td>
<td>634.73(6)</td>
<td>632.73(4)</td>
</tr>
<tr>
<td>Z</td>
<td>2</td>
<td>2</td>
</tr>
<tr>
<td>Crystal Dimension (mm³)</td>
<td>0.02 x 0.04 x 0.06</td>
<td>0.02 x 0.04 x 0.08</td>
</tr>
<tr>
<td>Crystal System</td>
<td>Cubic</td>
<td>Cubic</td>
</tr>
<tr>
<td>Space Group</td>
<td>Im 3m</td>
<td>Im 3m</td>
</tr>
<tr>
<td>θ range (°)</td>
<td>3.5-30.0</td>
<td>3.36-30.0</td>
</tr>
<tr>
<td>μ (mm⁻¹)</td>
<td>48.260</td>
<td>58.034</td>
</tr>
</tbody>
</table>

**Data Collection**

<p>| | | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Measured reflections</td>
<td>718</td>
<td>715</td>
</tr>
<tr>
<td>Independent reflections</td>
<td>117</td>
<td>118</td>
</tr>
<tr>
<td>Reflections with I &gt; 2σ(I)</td>
<td>109</td>
<td>100</td>
</tr>
<tr>
<td>Rint</td>
<td>0.1060</td>
<td>0.0914</td>
</tr>
<tr>
<td>h</td>
<td>-12 → 12</td>
<td>-12 → 12</td>
</tr>
<tr>
<td>k</td>
<td>-8 → 8</td>
<td>-8 → 8</td>
</tr>
<tr>
<td>l</td>
<td>-8 → 8</td>
<td>-8 → 8</td>
</tr>
</tbody>
</table>

**Refinement**

<p>| | | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td><em>R</em>[F² &gt; 2σ(F²)]</td>
<td>0.0454</td>
<td>0.0257</td>
</tr>
<tr>
<td>$b_w$(F²)</td>
<td>0.1189</td>
<td>0.0512</td>
</tr>
<tr>
<td>Reflections</td>
<td>109</td>
<td>116</td>
</tr>
<tr>
<td>Parameters</td>
<td>10</td>
<td>10</td>
</tr>
<tr>
<td>Δρₘₐₓ (e Å⁻³)</td>
<td>2.809</td>
<td>2.077</td>
</tr>
<tr>
<td>Δρₘᵟᵣ (e Å⁻³)</td>
<td>-3.319</td>
<td>-2.010</td>
</tr>
<tr>
<td>Extinction coefficient</td>
<td>0.00433(8)</td>
<td>0.00378(6)</td>
</tr>
</tbody>
</table>

The structures were solved using direct methods (SHELXL97). Data were then corrected for extinction and refined with anisotropic displacement parameters. Atomic coordinates and related structural information is provided in Table 4.2. Selected interatomic distances are given in Table 4.3. The stoichiometries of the samples were determined by dividing the site multiplicity of each atomic position by the multiplicity of the atomic position with the smallest coefficient.

Elemental analysis was performed using a Hitachi S-3600N Variable Pressure Scanning Electron Microscope (VP-SEM) with integrated energy dispersive spectroscopy (EDS) capabilities.
Table 4.2. Atomic Positions and Thermal Parameters of \( \text{Tb}_4\text{MGa}_{12} \) (\( \text{M} = \text{Pd}, \text{Pt} \))

<table>
<thead>
<tr>
<th></th>
<th>( x )</th>
<th>( y )</th>
<th>( z )</th>
<th>( U_{eq}^{a} ) (( \text{Å}^2 ))</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{Tb}<em>4\text{PdGa}</em>{12} )</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>( \text{Tb} ) 8c</td>
<td>3/4</td>
<td>3/4</td>
<td>3/4</td>
<td>0.0082(1)</td>
</tr>
<tr>
<td>( \text{Pd} ) 2a</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0.0057(7)</td>
</tr>
<tr>
<td>( \text{Ga} ) 12e</td>
<td>1/2</td>
<td>0.204366(3)</td>
<td>¼</td>
<td>0.0073(8)</td>
</tr>
<tr>
<td>( \text{Ga} ) 12d</td>
<td>1/2</td>
<td>0</td>
<td>0</td>
<td>0.0060(1)</td>
</tr>
<tr>
<td>( \text{Tb}<em>4\text{PtGa}</em>{12} )</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>( \text{Tb} ) 8c</td>
<td>3/4</td>
<td>3/4</td>
<td>3/4</td>
<td>0.0084(3)</td>
</tr>
<tr>
<td>( \text{Pt} ) 2a</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0.0072(3)</td>
</tr>
<tr>
<td>( \text{Ga} ) 12e</td>
<td>1/2</td>
<td>0.203989(2)</td>
<td>¼</td>
<td>0.0089(4)</td>
</tr>
<tr>
<td>( \text{Ga} ) 12d</td>
<td>1/2</td>
<td>0</td>
<td>0</td>
<td>0.0070(4)</td>
</tr>
</tbody>
</table>

\( ^a U_{eq} \) is defined as one-third of the trace of the orthogonalized \( U_{ij} \) tensor.

4.2.3 Physical Property Measurements

Transport and magnetic measurements were performed on single crystals of \( \text{Tb}_4\text{MGa}_{12} \). The electrical resistance was measured by the standard 4-probe AC technique at 27 Hz with a current of 1 mA. 1-mil (0.001 in) Pt wires were attached to the sample with silver epoxy. The magnetic susceptibility measurements were made using a commercial magnetometer (Quantum Design). The samples were zero-field-cooled (ZFC) to 2 K and then warmed to room temperature in a constant DC field of 1000 Gauss.

4.3 Results and Discussion

4.3.1 Crystal Structure

The structure of \( \text{Tb}_4\text{PdGa}_{12} \) is shown in Figure 4.1. \( \text{Tb}_4\text{MGa}_{12} \), (\( \text{M} = \text{Pd}, \text{Pt} \)) of the Y\(_4\text{PdGa}_{12}\)-structure type\(^{27}\) crystallizes in the cubic \( \text{Im}\overline{3}m \) space group (No. 229) with Tb, Pd, Ga1, and Ga2 occupying the 8c, 2a, 12d and 12e sites, respectively. The crystal structure consists of corner-sharing \( \text{MGa}_6 \) octahedra and \( \text{TbGa}_3 \) cuboctahedra. The bonding distances in the cuboctahedra are listed in Table 4.3.
Table 4.3  Selected Inter-atomic Distances and Angles of Tb₄MGa₁₂ (M = Pd, Pt)

<table>
<thead>
<tr>
<th>Cuboctahedra</th>
<th>Tb₄PdGa₁₂</th>
<th>Tb₄PtGa₁₂</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tb₁-Ga₁ (x 6)</td>
<td>3.03844(18)</td>
<td>3.0526(11)</td>
</tr>
<tr>
<td>Tb₁-Ga₂ (x 6)</td>
<td>3.0641(4)</td>
<td>3.05994(11)</td>
</tr>
<tr>
<td>Ga₁-Ga₂</td>
<td>2.7730(19)</td>
<td>2.7746(2)</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Cuboctahedra</th>
<th>Angles (°)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ga₁-Tb-Ga₂ (x 4)</td>
<td>54.05(4)</td>
</tr>
<tr>
<td>Ga₁-Tb-Ga₂ (x 4)</td>
<td>90.0</td>
</tr>
<tr>
<td>Ga₁-Tb-Ga₂ (x 4)</td>
<td>125.959(4)</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Octahedra</th>
<th>Tb₄Ga₁₂ (x 6)</th>
<th>Tb₄PdGa₁₂</th>
</tr>
</thead>
<tbody>
<tr>
<td>M-Ga₂</td>
<td>2.544(3)</td>
<td>2.5341(3)</td>
</tr>
</tbody>
</table>

Figure 4.1. The crystal structure of Tb₄PdGa₁₂ is shown above. TbGa₃ cuboctahedra are shown in dark gray and PdGa₆ octahedra are shown light gray. Ga atoms are shown as white circles.
The $M\text{Ga}_6$ octahedron in $Tb_4M\text{Ga}_{12}$ ($M = \text{Pd, Pt}$) is isostructural to the AgCa$_6$ octahedron in the Ag$_8$Ca$_3$ structure type, a body centered cubic cell.  The Pd-Ga interatomic distance in the octahedra in $Tb_4\text{PdGa}_{12}$ is 2.5444(3) Å, which is shorter than the summation of the covalent radii for Pd (1.31 Å) and Ga (1.26 Å). The Pt-Ga interatomic distance in the octahedra in $Tb_4\text{PtGa}_{12}$ is 2.5341(3) Å, which is smaller than the expected interatomic distance of 2.54 Å from the summation of the covalent radii of Pt (1.28 Å) and Ga (1.26 Å). The experimental interatomic distances in $Tb_4M\text{Ga}_{12}$ ($M = \text{Pd, Pt}$) are comparable to $M$-Ga ($M = \text{transition metal}$) interatomic distances in the $M$-Ga octahedra of Ce$_8\text{Pd}_{24}\text{Ga}$ which range from 2.633-2.927 Å. The Pd-Ga distance is 2.5609(4) Å, 2.635(7) Å, and 2.623(5) Å in CePdGa$_6$, TbPdGa, and ErPdGa, respectively.

Similar to $\text{RE}_4\text{FeGa}_{12-x}\text{Ge}_x$ and $\text{R}_4\text{MGa}_{12}$ ($\text{R} = \text{Gd-Lu}; \ M = \text{Ni, Pd}$), the transition metal in $Tb_4M\text{Ga}_{12}$ ($M = \text{Pd, Pt}$) occupy a unique crystallographic site (2a). However, in $\text{RE}_4M_7\text{Ge}_6$ ($M = \text{Ru, Os, Rh, Ir}$), $M_4\text{Co}_7\text{Ge}_6$ ($M = \text{Zr, Hf}$), Np$_4\text{Ru}_7\text{Ge}_6$, Sc$_4M_7\text{Ge}_6$, and U$_4\text{Re}_7\text{Si}_6$, the transition metal occupies two crystallographic sites (2a and 12d). The transition metal in gallium containing compounds tends to occupy the 2a crystallographic site, as is the case in $Tb_4M\text{Ga}_{12}$. Indeed, when gallium is present the transition metal occupies the crystallographic site with the lowest multiplicity, while the higher multiplicity site is stabilized with gallium.

The Tb cuboctahedra in $Tb_4\text{PdGa}_{12}$ is composed of six Tb-Ga(1) distances of 3.03844(18) Å and six Tb-Ga(2) distances of 3.0641(4) Å. These distances are comparable to the interatomic distances expected from the summation of the atomic radii for Tb (1.75 Å) and Ga (1.26 Å), as well as, the typical interatomic distances in TbGa$_2$ and TbGa$_6$ however, the cuboctahedra found in La$M$In$_5$ are composed of 4 x La-In(1) and 8 x La-In(2). The La-In2/La-In1 ratio of distances in the cuboctahedra is 1.0110, 1.0000, and 0.99720 for LaCoIn$_5$, respectively.
LaRhIn$_5$, and LaIrIn$_5$, respectively indicating the Rh compound is the least distorted.\textsuperscript{111} The ratio between the Tb-Ga and Tb-Ga\textsubscript{1} distances in Tb$_4$PdGa$_{12}$ is 1.000845 and 1.00813 in Tb$_4$PtGa$_{12}$, indicating that the cuboctahedra in these phases are highly symmetric. The Ga-Ga interatomic distance is 2.7730(19) Å and 2.7746(2) Å for Tb$_4$PdGa$_{12}$ and Tb$_4$PtGa$_{12}$, respectively. Both of these are longer than the interatomic distances expected by the summation of the covalent radii previously mentioned, but they are well within the range of 2.297(5) - 2.830(7) Å distances reported in CeGa$_6$,\textsuperscript{41} CeGa$_2$,\textsuperscript{64} and CePdGa$_6$.\textsuperscript{85}

### 4.3.2 Physical Properties

Figure 4.2 shows the temperature dependence of the susceptibility for Tb$_4$PdGa$_{12}$ taken in a constant field of 1000 Gauss. The antiferromagnetic transition with a Néel temperature at $T_N = 16$ K is very sharp, and a second transition is observed near 2.1 K. Above $T_N$ the susceptibility obeys the Curie-Weiss law, and the linear behavior expected in $1/\chi$ vs. $T$ is shown in the inset of Figure 4.2.

Figure 4.3 shows the temperature dependence of the magnetic susceptibility of Tb$_4$PdGa$_{12}$.. Fitting the data to the following form: $\chi(T) = C/(T - \theta)$, we find an effective magnetic moment of 7.6 $\mu_B$ per Tb ion and a Weiss temperature $\theta = -31.5$ K, indicating strong antiferromagnetic correlations. The effective moment is somewhat smaller than that expected for Tb$^{3+}$ (9.7 $\mu_B$) but is close to the value for Tb$^{4+}$ (7.9 $\mu_B$).or Tb$_4$PtGa$_{12}$. A sharp antiferromagnetic transition takes place at $T_N = 12$ K, and, as in the Pd compound, a smaller transition appears near 2 K. From the Curie-Weiss fit (inset Fig. 4.3) we obtain an effective magnetic moment of 6.2 $\mu_B$ per Tb ion and a Weiss temperature $\theta = -25.8$ K. In this case, the effective moment is smaller than what is expected for either Tb$^{3+}$ or Tb$^{4+}$. Therefore, the Tb valence in Tb$_4$PtGa$_{12}$ cannot be deduced from the susceptibility measurements. Experimentally measuring an effective moment below the full Hund’s rule value is not uncommon in Tb
compounds. Neutron diffraction and specific heat measurements in magnetic field will be useful in determining the magnetic structure of these two compounds and are planned for the near future.

Figure 4.2 The susceptibility of Tb$_4$PdGa$_{12}$ as a function of $T$ measured at 1000 G. The inset figure shows the inverse susceptibility versus temperature of Tb$_4$PdGa$_{12}$.

Figure 4.3 The susceptibility of Tb$_4$PtGa$_{12}$ as a function of $T$, measured at 1000 G. The inset figure shows the inverse susceptibility versus temperature of Tb$_4$PtGa$_{12}$. 
The magnetization has not saturated at 9 T, and a non-hysteretic metamagnetic transition is observed at ±5 T. For Tb₄PtGa₁₂ the field-dependent magnetization is shown in Figure 4.5. Again, the magnetization is not saturated at 9 T and metamagnetic transitions can be seen at ±3000 Gauss. This transition is hysteretic in field. Similar hysteresis loops have been observed in other Tb compounds, such as TbGa₂.

The electrical resistivity of single crystals of Tb₄PdGa₁₂ and Tb₄PtGa₁₂ is shown as a function of temperature in Figure 4.6. The samples are metallic \( (d\rho/dT > 0) \), with residual resistance ratios (RRR) of 4 and 7 for Tb₄PtGa₁₂ and Tb₄PdGa₁₂, respectively. A kink in the resistivity is observed for each compound near its antiferromagnetic ordering temperature, indicating a decrease in the spin-disorder scattering.

The structure and preliminary magnetization studies warrant further investigation. It would be of interest to grow the high temperature polymorph of TbGa₃ which is isostructural to the antiferromagnetic heavy fermion CeIn₃. Compounds of the \( LnMGa₁₂ \) structure type can

\[ \text{Figure 4.4} \quad \text{The magnetization } M \text{ of } Tb₄PdGa₁₂ \text{ as a function of field, measured at 2 K.} \]
provide the opportunity to compare the influence of the rare earth atom in the cuboctahedra coordination. High pressure and ambient pressure heat capacity experiments are in progress.

**Figure 4.5** The magnetization $M$ of Tb$_4$PtGa$_{12}$ as a function of field, measured at 2 K.

**Figure 4.6** The electrical resistivity of Tb$_4$PdGa$_{12}$ (solid circle) and Tb$_4$PtGa$_{12}$ (open circle) as a function of temperature.
CHAPTER 5. CRYSTAL GROWTH, MAGNETIC AND TRANSPORT PROPERTIES OF $Ln_4MGa_{12}$ ($Ln = Dy, Ho, Er; M = Pd, Pt$)

5.1 Introduction

Ternary intermetallic compounds consisting of $Ln-M-Ga$ ($Ln =$ lanthanide; $M =$ transition metal) are interesting to study due to the wide range of structural features and physical properties they exhibit.\textsuperscript{29,53,113-117} CePd$_2$Ga crystallizes in the YPd$_2$Ga-type (space group, \textit{Pnma}) and orders antiferromagnetically at 2.9 K.\textsuperscript{91} CePd$_3$Ga$_x$ ($x = 0.0, 0.05, 0.10, 0.15,$ and $0.20$) with increasing $x$, transforms from a nonmagnetic Kondo lattice to a magnetic Kondo (short range order) system which is accompanied by a change from an intermediate valence state for cerium towards a Ce$^{+3}$ state.\textsuperscript{118} CePdGa$_6$ is a heavy fermion antiferromagnet with $\gamma \sim 230$-360 mJ/mol K$^2$ and $T_N = 5.5$ K, where $\gamma$ is the Sommerfeld coefficient and is proportional to the effective mass of the electron.\textsuperscript{85} Ce$_2$PdGa$_{12}$ orders antiferromagnetically at $T_N \sim 11$ K, with a spin reconfiguration transition at 5 K.\textsuperscript{119} Ce$_8$Pd$_{24}$Ga is antiferromagnetic below 3.1 K and studies show that the magnetic properties of this compound are governed by a balance between crystal-field, Kondo (short range order), and Ruderman Kittel Kosuya Yoshida (RKKY) interactions which are responsible for long range order between the magnetic moments of the rare earth ions.\textsuperscript{120-122}

Large positive magnetoresistance have also been found in other $Ln$-Pd-Ga compounds. SmPd$_2$Ga$_2$, of the ThCr$_2$Si$_2$-type is composed of layers of isolated Sm atoms and layers of PdGa$_4$ edge sharing tetrahedral alternating along the $c$-axis orders ferromagnetically at 5 K. The low temperature (2 K) field dependent resistivity shows large positive magnetoresistance of over 100 % at 9 T.\textsuperscript{92} The low temperature (2 K) magnetoresistance of Ce$_2$PdGa$_{10}$, a layered structure consisting of alternating Ce-Ga bilayers and Ga-Pd layers, increases by over 200 % at 9 T.\textsuperscript{29}

$Ln_4MGa_{12}$ ($Ln =$ Ho, Tm; $M =$ Ni, Pd) crystallizes in the cubic $Im\bar{3}m$ (No.229) space group and has been described as a redistributed homolog of the U$_4$Re$_7$Si$_6$\textsuperscript{99} structure type. The
transport properties of polycrystalline $Ln_4MGa_{12}$ ($Ln = \text{Ho, Tm}; M = \text{Ni, Pd}$) show metallic behavior.\textsuperscript{100} Single crystals of $Ln_4\text{FeGa}_6\text{Ge}_6$ ($Ln = \text{Sm, Tb}$), grown using molten gallium as a flux are isostructural to $Y_4\text{PdGa}_{12}$.\textsuperscript{100} Transport measurements for the isostructural $Ln_4\text{FeGa}_6\text{Ge}_6$ ($Ln = \text{Sm, Tb}$) show metallic behavior.\textsuperscript{98} $\text{Sm}_4\text{FeGa}_6\text{Ge}_6$ does not show any magnetic ordering down to 2 K, while the Tb-analog orders antiferromagnetically at $T_N = 13$ K.\textsuperscript{98} Magnetic measurements show the rare earth ions in these compounds to be in a +3 magnetic state while the Fe atoms are in a nonmagnetic state.\textsuperscript{98}

We have recently reported the crystal growth of $\text{Tb}_4MGa_{12}$ ($M = \text{Pd, Pt}$) from gallium flux. Transport property measurements show that the compounds are metallic. $\text{Tb}_4\text{PdGa}_{12}$ and $\text{Tb}_4\text{PtGa}_{12}$ order antiferromagnetically with Néel temperatures of 16 K and 12 K, respectively.\textsuperscript{114} In this chapter, we discuss the crystal growth, transport, and magnetic properties of single crystals of $Ln_4MGa_{12}$ ($Ln = \text{Dy, Ho, Er}; M = \text{Pd, Pt}$).

### 5.2 Experimental

#### 5.2.1 Syntheses

The samples were synthesized from lanthanide (Dy, Ho, Er) pieces, palladium or platinum powder, and gallium shot which were obtained from Alfa Aesar, all with purities greater than 99.9 %. The lanthanide (Dy, Ho, Er) pieces were combined with palladium or platinum powder and gallium pellets in a molar ratio of 1: 1: 20. The samples were then placed in alumina crucibles and sealed in a fused silica tube and gradually heated (200° C/hr) to 1150° C for 7 hrs, then slow cooled (10° C/hr) to 530° C at which point the excess flux was removed via centrifugation. The synthesis yielded metallic single crystals which ranged in size from 0.02 to 1 mm$^3$. Polycrystalline samples of $\text{Ho}_4MGa_{12}$ ($M = \text{Pd, Pt}$) were synthesized by arc melting stoichiometric amounts of Ho, Pd, and Ga on a water-cooled copper hearth under an argon
atmosphere. The arc melted samples were then annealed in an evacuated quartz tube for 2 weeks at 850 °C. The qualities of the annealed samples were examined by powder X-ray diffraction.

5.2.2 Single Crystal X-ray Diffraction

Single crystal fragments of an average size of ~0.02 mm x 0.02 mm x 0.04 mm were mechanically extracted, placed on a glass fiber and mounted on the goniometer of a Nonius Kappa CCD diffractometer equipped with Mo $K_{\alpha}$ radiation ($\lambda = 0.71073$ Å). The data was then corrected, reduced, and scaled using the SHELXL software package. Systematic absences led to the following possible space groups: $I\bar{2}3$, $I\bar{2}13$, $Im\bar{3}$, $I432$, and $Im\bar{3}m$. Space group (No. 229) $Im\bar{3}m$, was chosen due to the fact that it was the space group of highest symmetry. The structures were solved using Tb$_4$PtGa$_{12}$ as a structural model. The structure consists of four atomic positions in which the lanthanide ($Ln$) occupies the 8c (1/4, 1/4,1/4) site, transition metal (Pd, Pt), occupies the 2a (0,0,0) site, Ga1 the 12e (0, $y$, 0; where $y = \sim 0.2000$) site, and Ga2 the 12d (1/4,0,1/2) site. Additional data collection and crystallographic parameters are presented in Table 5.1. Atomic positions and thermal displacement parameters are given in Table 5.2. Selected interatomic distances are listed in Table 5.3

5.2.3 Physical Property Measurements

Transport and magnetic measurements were performed on single crystals of $Ln_4MGa_{12}$ ($Ln = $ Dy, Ho, Er; $M = $ Pd, Pt). The electrical resistance was measured by the standard 4-probe AC technique at 27 Hz with a current of 1 mA. 1-mil (0.001 in) Pt wires were attached to the sample with silver epoxy. The magnetic susceptibility measurements were performed using a commercial magnetometer (Quantum Design). The samples were zero-field-cooled (ZFC) to 2 K and then warmed to room temperature in a constant DC field of 1000 Gauss (0.1 T).
5.3 Results and Discussion

5.3.1 Synthesis and Structure

The use of metallic fluxes for crystal growth has increased in recent years because it is an inexpensive, effective technique for growing single crystals at relatively low temperatures.\textsuperscript{13,98,123}

\begin{table}[h]
\centering
\begin{tabular}{lcccccc}
\hline
 & $Z=2$ & \text{Dy$_4$PdGa$_{12}$} & \text{Dy$_4$PtGa$_{12}$} & \text{Ho$_4$PdGa$_{12}$} & \text{Ho$_4$PtGa$_{12}$} & \text{Er$_4$PdGa$_{12}$} & \text{Er$_4$PtGa$_{12}$} \\
\hline
Space Group & $\text{Im}\bar{3}m$ & $\text{Im}\bar{3}m$ & $\text{Im}\bar{3}m$ & $\text{Im}\bar{3}m$ & $\text{Im}\bar{3}m$ & $\text{Im}\bar{3}m$ & $\text{Im}\bar{3}m$ \\
\hline
$a$ (Å) & 8.5930(5) & 8.5710(6) & 8.5500(4) & 8.5460(7) & 8.5330(7) & 8.5260(6) & 8.5260(6) \\
$V$ (Å$^3$) & 634.50(9) & 629.64(8) & 625.03(7) & 624.15(9) & 621.31(9) & 619.78(8) & 619.78(8) \\
Temperature (°C) & 25 & 23 & 25 & 25 & 23 & 25 & 25 \\
$\mu$ (mm$^{-1}$) & 44.368 & 89.384 & 20.306 & 61.524 & 80.328 & 95.260 & \\
Collected reflections & 2170 & 1431 & 4136 & 1436 & 610 & 2166 & \\
Unique reflections & 878 & 529 & 1049 & 678 & 181 & 879 & \\
$R_{int}$ & 0.0601 & 0.0311 & 0.0237 & 0.0368 & 0.0352 & 0.0495 & \\
\hline
$R(F)^a$ & 0.0595 & 0.0312 & 0.0245 & 0.0380 & 0.0271 & 0.0520 & \\
$R_w(F_o^2)^b$ & 0.0731 & 0.0626 & 0.0564 & 0.1168 & 0.0725 & 0.0602 & \\
\hline
\end{tabular}
\caption{Crystallographic Data for Ln$_4$MGa$_{12}$ ($Ln = \text{Dy, Ho, Er;}\ M = \text{Pd, Pt}$)}
\end{table}

\textsuperscript{a} $R(F) = \sum | F_o | - | F_c | / \sum | F_o |$

\textsuperscript{b} $R_w(F_o^2) = \sum w(F_o^2 - F_c^2)^2 / \sum w(F_o^2)^2$
Table 5.2  Atomic Positions and $U_{eq}$ Values for $Ln_4MGa_{12}$ ($Ln =$ Dy, Ho, Er; $M =$ Pd, Pt)

<table>
<thead>
<tr>
<th>Atom</th>
<th>Wyckoff</th>
<th>$x$</th>
<th>$y$</th>
<th>$z$</th>
<th>$U_{eq}$($\AA^2$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dy$<em>4$PdGa$</em>{12}$</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Dy</td>
<td>8c</td>
<td>$\frac{1}{4}$</td>
<td>$\frac{1}{4}$</td>
<td>$\frac{1}{4}$</td>
<td>0.0083(4)</td>
</tr>
<tr>
<td>Pd</td>
<td>2a</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0.0103(4)</td>
</tr>
<tr>
<td>Ga1</td>
<td>12d</td>
<td>0</td>
<td>0.20404(2)</td>
<td>0</td>
<td>0.0101(4)</td>
</tr>
<tr>
<td>Ga2</td>
<td>12e</td>
<td>$\frac{1}{2}$</td>
<td>0</td>
<td>$\frac{1}{4}$</td>
<td>0.0096(4)</td>
</tr>
<tr>
<td>Dy$<em>4$PtGa$</em>{12}$</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Dy</td>
<td>8c</td>
<td>$\frac{1}{4}$</td>
<td>$\frac{1}{4}$</td>
<td>$\frac{1}{4}$</td>
<td>0.00495(4)</td>
</tr>
<tr>
<td>Pt</td>
<td>2a</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0.00739(3)</td>
</tr>
<tr>
<td>Ga1</td>
<td>12d</td>
<td>0</td>
<td>0.2037(2)</td>
<td>0</td>
<td>0.00968(6)</td>
</tr>
<tr>
<td>Ga2</td>
<td>12e</td>
<td>$\frac{1}{2}$</td>
<td>0</td>
<td>$\frac{1}{4}$</td>
<td>0.00713(6)</td>
</tr>
<tr>
<td>Ho$<em>4$PdGa$</em>{12}$</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ho</td>
<td>8c</td>
<td>$\frac{1}{4}$</td>
<td>$\frac{1}{4}$</td>
<td>$\frac{1}{4}$</td>
<td>0.0164(6)</td>
</tr>
<tr>
<td>Pt</td>
<td>2a</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0.0148(4)</td>
</tr>
<tr>
<td>Ga1</td>
<td>12d</td>
<td>0</td>
<td>0.2037(2)</td>
<td>0</td>
<td>0.00968(6)</td>
</tr>
<tr>
<td>Ga2</td>
<td>12e</td>
<td>$\frac{1}{2}$</td>
<td>0</td>
<td>$\frac{1}{4}$</td>
<td>0.00713(6)</td>
</tr>
<tr>
<td>Er$<em>4$PdGa$</em>{12}$</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Er</td>
<td>8c</td>
<td>$\frac{1}{4}$</td>
<td>$\frac{1}{4}$</td>
<td>$\frac{1}{4}$</td>
<td>0.0104(4)</td>
</tr>
<tr>
<td>Pd</td>
<td>2a</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0.0105(4)</td>
</tr>
<tr>
<td>Ga1</td>
<td>12d</td>
<td>0</td>
<td>0.20407(2)</td>
<td>0</td>
<td>0.0107(4)</td>
</tr>
<tr>
<td>Ga2</td>
<td>12e</td>
<td>$\frac{1}{2}$</td>
<td>0</td>
<td>$\frac{1}{4}$</td>
<td>0.0095(1)</td>
</tr>
<tr>
<td>Dy$<em>4$PtGa$</em>{12}$</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Dy</td>
<td>8c</td>
<td>$\frac{1}{4}$</td>
<td>$\frac{1}{4}$</td>
<td>$\frac{1}{4}$</td>
<td>0.0104(4)</td>
</tr>
<tr>
<td>Pt</td>
<td>2a</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0.0105(4)</td>
</tr>
<tr>
<td>Ga1</td>
<td>12d</td>
<td>0</td>
<td>0.20407(2)</td>
<td>0</td>
<td>0.0107(4)</td>
</tr>
<tr>
<td>Ga2</td>
<td>12e</td>
<td>$\frac{1}{2}$</td>
<td>0</td>
<td>$\frac{1}{4}$</td>
<td>0.0095(1)</td>
</tr>
<tr>
<td>Ho$<em>4$PtGa$</em>{12}$</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ho</td>
<td>8c</td>
<td>$\frac{1}{4}$</td>
<td>$\frac{1}{4}$</td>
<td>$\frac{1}{4}$</td>
<td>0.0133(8)</td>
</tr>
<tr>
<td>Pt</td>
<td>2a</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0.0100(5)</td>
</tr>
<tr>
<td>Ga1</td>
<td>12d</td>
<td>0</td>
<td>0.20408(5)</td>
<td>0</td>
<td>0.0117(7)</td>
</tr>
<tr>
<td>Ga2</td>
<td>12e</td>
<td>$\frac{1}{2}$</td>
<td>0</td>
<td>$\frac{1}{4}$</td>
<td>0.0109(7)</td>
</tr>
<tr>
<td>Er$<em>4$PtGa$</em>{12}$</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Er1</td>
<td>8c</td>
<td>$\frac{1}{4}$</td>
<td>$\frac{1}{4}$</td>
<td>$\frac{1}{4}$</td>
<td>0.0104(4)</td>
</tr>
<tr>
<td>Pt</td>
<td>2a</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0.0105(4)</td>
</tr>
<tr>
<td>Ga1</td>
<td>12d</td>
<td>0</td>
<td>0.20410(2)</td>
<td>0</td>
<td>0.0107(4)</td>
</tr>
<tr>
<td>Ga2</td>
<td>12e</td>
<td>$\frac{1}{2}$</td>
<td>0</td>
<td>$\frac{1}{4}$</td>
<td>0.0095(1)</td>
</tr>
</tbody>
</table>

$U_{eq}$ is defined as one-third of the trace of the orthogonalized $U_{ij}$ tensor.
Single crystals of $Ln_4MGa_{12}$ ($Ln = Dy$, Ho, Er; $M = Pd, Pt$) were synthesized using molten gallium as a flux. Similar to Zharaleva et al, we find a shorter isothermal ($\leq 3$ days) step for the growth of these phases leads to the formation of the cubic phase. In addition, upon the substitution of early rare earths such as cerium and praseodymium in the synthesis at 500 °C, we find that $Ln_2PdGa_{10}$ ($Ln = Ce, Pr$) is formed.\textsuperscript{29}

The crystal structure of $Ln_4MGa_{12}$ ($Ln = Dy$, Ho, Er; $M = Pd, Pt$) which can be viewed either as a homolog of the $U_4Re_7Si_{16}$\textsuperscript{99} structure type or the $Y_4PdGa_{12}$\textsuperscript{100} structure type, both with space group (No. 229), $Im\bar{3}m$ is shown in Figure 5.1. The $U_4Re_7Si_{16}$ structure type is a robust structure type with representative analogues consisting of intermetallic compounds which contain rare earth and actinide metals including yttrium-lutetium.\textsuperscript{76,98,99,105,108,124-129} The $Dy_4PdGa_{12}$ consists of corner-sharing $PdGa_6$ octahedra and $DyGa_3$ cuboctahedra. The lattice parameters of $Ln_4MGa_{12}$ ($Ln = Dy$, Ho, Er; $M = Pd, Pt$) are shown to decreases linearly with the

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{fig5_1.png}
\caption{The crystal structure of $Dy_4PdGa_{12}$ is shown. Dysprosium, palladium, and gallium atoms are represented as gray (large spheres), black, and white circles respectively.}
\end{figure}
decrease in the rare earth atomic radii due to lanthanide contraction. The lattice parameters for the $Ln_4\text{PdGa}_{12}$ ($Ln = \text{Dy, Ho, Er}$) are in agreement with those reported for polycrystalline data for $Ln_4\text{PdGa}_{12}$ ($Ln = \text{Gd-Tm, Lu}$).\textsuperscript{100} Six Ga1 atoms and six Ga2 atoms are coordinated to each lanthanide atom as shown in Figure 5.1b. The interatomic distances in the cuboctahedra of $Ln_4M\text{Ga}_{12}$ ($Ln = \text{Dy, Ho, Er}; M = \text{Pd, Pt}$) are listed in Table 5.3. The interatomic distances scale well with the summation of the values for the atomic radii of Ga (1.26 Å) and Dy (1.59 Å), Ho (1.58 Å), or Er (1.57 Å).\textsuperscript{130} The $Ln$-Ga1 interatomic distance in $Ln_4M\text{Ga}_{12}$ ($Ln = \text{Dy, Ho, Er}; M = \text{Pd, Pt}$) are in agreement with the $Ln$-Ga1 interatomic distances found in $Ln\text{Ga}_6$ (La - Yb)\textsuperscript{131} range from 3.188 Å to 3.307 Å.

![Figure 5.1b: Six Ga1 (black circles) and six Ga2 atoms (white circles) are coordinated to Dy (gray circles).](image)

Similarly, the $Ln$-Ga2 interatomic distances are also in agreement with those found in $Ln\text{Ga}_6$ (La - Yb) which range from 3.077 Å to 3.138 Å.\textsuperscript{131} The $Ln$-Ga interatomic distances in $Ln_4M\text{Ga}_{12}$ ($Ln = \text{Dy, Ho, Er}; M = \text{Pd, Pt}$) are slightly larger than those found in the cuboctahedra of $Ln\text{Ga}_3$ (La-Tm)\textsuperscript{112} which range from 2.101 Å to 2.830 Å. The ratio of $Ln$-Ga(1) to $Ln$-Ga(2) in each cuboctahedron is ~1, which indicates that the cuboctahedra are highly symmetrical.
Table 5.3  Selected Interatomic Distances (Å)

<table>
<thead>
<tr>
<th></th>
<th>$M = \text{Pd}$</th>
<th>$M = \text{Pt}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dy$<em>4$MGa$</em>{12}$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Dy-Ga1 (x6)</td>
<td>3.0278(2)</td>
<td>3.0303(2)</td>
</tr>
<tr>
<td>Dy-Ga2 (x6)</td>
<td>3.0532(2)</td>
<td>3.0549(2)</td>
</tr>
<tr>
<td>M-Ga2 (x6)</td>
<td>2.5258(2)</td>
<td>2.53000(18)</td>
</tr>
<tr>
<td>Ho$<em>4$MGa$</em>{12}$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ho-Ga1 (x6)</td>
<td>3.0229(2)</td>
<td>3.0215(2)</td>
</tr>
<tr>
<td>Ho-Ga2 (x6)</td>
<td>3.0487(3)</td>
<td>3.0460(3)</td>
</tr>
<tr>
<td>M-Ga2 (x6)</td>
<td>2.5226(2)</td>
<td>2.533(2)</td>
</tr>
<tr>
<td>Er$<em>4$Mga$</em>{12}$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Er-Ga1 (x6)</td>
<td>3.0169(2)</td>
<td>3.0144(2)</td>
</tr>
<tr>
<td>Er-Ga2 (x6)</td>
<td>3.0414(2)</td>
<td>3.0397(5)</td>
</tr>
<tr>
<td>M-Ga2 (x6)</td>
<td>2.5188(2)</td>
<td>2.533(3)</td>
</tr>
</tbody>
</table>

The transition metal environment in $Ln_4MGa_{12}$ ($Ln = \text{Dy, Ho, Er; } M = \text{Pd, Pt}$) is six coordinate to gallium and forms $MGa_6$ octahedra. The interatomic distances are listed in Table 5.3. The (Pd, Pt)-Ga interatomic distances which range from 2.5188(2) Å to 2.533(3) Å are smaller than the interatomic distances reported for the PdGa$_6$ octahedra of Ce$_8$PdGa$_{24}$ (2.633 Å - 2.927 Å).$^{121,132}$ The (Pd, Pt)-Ga interatomic distance in the octahedra of Tb$_4$PdGa$_{12}$ and Tb$_4$PdGa$_{12}$ is 2.5444(3) Å and 2.5341(3) Å, respectively.$^{114}$ The (Pd, Pt)-Ga interatomic distances in $Ln_4MGa_{12}$ ($Ln = \text{Dy, Ho, Er; } M = \text{Pd, Pt}$) are also comparable to Pd-Ga interatomic distances found in CePdGa and TbPdGa which range from 2.5609 Å – 2.6350 Å.$^{96}$ The distinction between the $U_4Re_7Si_6$ and $Y_4PdGa_{12}$ structure types is dependent on the site occupancy of the transition metal. The transition metal in Yb$_4$Rh$_7$Ge$_6$,$^{15}$ Yb$_4$Ir$_7$Ge$_6$,$^{23}$ Lu$_4$Rh$_7$Ge$_6$,$^{25}$ Np$_4$Ru$_7$Ge$_6$,$^{25}$ and $M_4Co_7Ge_6$ ($M = \text{Zr, Hf}$)$^{26}$ occupies the 2$a$ and 12$d$ sites. However, when gallium is present, the transition metal prefers to occupy the 2$a$ Wyckoff site, as found in $Ln_4MGa_{12}$ ($Ln = \text{Gd-Tm, Lu; } M = \text{Ni, Pd}$),$^{100}$ $Ln_4FeGa_6Ge_6$ ($Ln = \text{Sm, Tb}$),$^{98}$ and Tb$_4$MGa$_{12}$ ($M = \text{Pd, Pt}$).$^{114}$ The Ga1 and Ga2 atoms in these compounds occupy the 12$d$ and 12$e$ sites.
5.3.2 Physical Properties

Figure 5.2 shows the temperature-dependent magnetic susceptibility of aggregates of single crystals of $Ln_4PdGa_{12}$ ($Ln =$ Dy, Ho, Er) measured at an applied field of 0.1 Tesla. Dy$_4$PdGa$_{12}$ shows no magnetic ordering down to 2 K, however kinks are observed in the susceptibility at 5 and 9 K (inset). Fitting the inverse susceptibility data to a Curie-Weiss fit of the following form: $\chi(T) = C/(T - \theta)$, an effective moment of 9.41 $\mu_B$ was obtained and a Weiss constant, $\theta = -18$, indicative of antiferromagnetic correlations. No magnetic ordering is observed down to 2 K for Ho$_4$PdGa$_{12}$ (open circles). The magnetic susceptibility of Er$_4$PdGa$_{12}$ (closed triangles) shows an antiferromagnetic transition at $T_N \sim 3$ K, and magnetic transitions at 13 K and 21 K. An effective moment of 8.93 $\mu_B$ is obtained from the inverse magnetic susceptibility data with a $\theta = -8.5$. The experimental moments for Dy$_4$PdGa$_{12}$ and Er$_4$PdGa$_{12}$ are slightly smaller than the calculated values 10.65 $\mu_B$ and 9.58 $\mu_B$ for Dy$^{3+}$ and Er$^{3+}$. The experimental magnetic moment of 9.33 $\mu_B$ and $\theta = 0.2$, obtained for Ho$_4$PdGa$_{12}$ is smaller than the full Hund’s value for Ho$^{3+}$ of 10.61 $\mu_B$.

![Figure 5.2](image.png)

**Figure 5.2** Magnetic susceptibility of $Ln_4PdGa_{12}$ ($Ln =$ Dy, Ho, Er) at 0.1 T is shown.
Figure 5.3 The magnetization of $Ln_4PdGa_{12}$ ($Ln$ = Dy, Ho, Er) at 2 K is shown.

Figure 5.3 shows the field-dependent magnetization of $Ln_4PdGa_{12}$ ($Ln$ = Dy, Ho, Er) measured at a constant temperature of 2 K. The magnetization for Dy$_4PdGa_{12}$ (closed circles) increases linearly with field. The inset shows the field-dependent magnetization for Ho$_4PdGa_{12}$. Since no magnetic ordering was observed down to 2 K, it is possible that a transition exists below 2 K which would account for the ferromagnetic-like field dependent feature observed at 2 K. The magnetization of Er$_4PdGa_{12}$ (open triangles) increases linearly to $\sim$ 0.5 T after which a field induced step-wise metamagnetic transition is observed at 0.6 T, followed by a subsequent increase in the magnetization up to 1.5 T where another stepwise metamagnetic transition is observed. The magnetization begins to saturate above 2 T. Similar metamagnetic transitions are seen in the magnetization of TbGa$_2$ and Tb$_4PdGa_{12}$ with $T_N \sim$ 18 K and 11 K, respectively.

The temperature-dependent magnetic susceptibility of $Ln_4PtGa_{12}$ ($Ln$ = Dy, Ho, Er) is shown in Figure 5.4 measured at 0.1 Tesla. Dy$_4PtGa_{12}$ (closed circles) orders antiferromagnetically at $T_N = 11$ K. Fitting the data to the Curie-Weiss law, we find an effective magnetic moment of $9.69 \mu_B$ and a Weiss constant $\theta$ of -14 K. The magnetic susceptibility of
Ho$_4$PtGa$_{12}$ (open circles) shows magnetic transitions at 26 K and 92 K and the experimental effective moment obtained from the Curie-Weiss fit (9.91 $\mu_B$ and $\theta = 0.1$), is smaller than what is calculated moment. The susceptibility of Er$_4$PtGa$_{12}$ shows an antiferromagnetic transition at $T_N = 5.5$ K, as well as, magnetic transitions at 25 K, and 93 K. An effective moment of 8.73 $\mu_B$ and $\theta = -26$ is obtained for Er$_4$PtGa$_{12}$, consistent with antiferromagnetic correlations at low temperatures. The effective magnetic moments obtained for Dy$_4$PtGa$_{12}$ and Er$_4$PtGa$_{12}$ are both slightly lower than the expected values for Dy$^{3+}$ (10.65 $\mu_B$) and Er$^{3+}$ (9.58 $\mu_B$).

The field dependent magnetization of $Ln_4PtGa_{12}$ ($Ln = Dy$, Ho, Er) measured at a constant temperature of 2 K shown in Figure 5.5. Similar to the Pd-analog, the magnetization for Dy$_4$PtGa$_{12}$ (closed circles) increases linearly with temperature and is typical in antiferromagnetic systems, shows no sign of saturation at 9 Tesla. A small hysteresis is observed in the magnetization curve of Ho$_4$PtGa$_{12}$. Akin to the Pd-analog, it is possible that the 2 K magnetization is measured near a magnetic transition. The magnetization of Er$_4$PtGa$_{12}$ (inset) increases linearly up to 2.5 T, then begins to saturate above 3 T. A summary of the magnetic properties of $Ln_4MGa_{12}$ ($Ln = Dy$, Ho, Er; $M = Pd$, Pt) is shown in Table 5.4.

The electrical resistivity of single crystals of $Ln_4PdGa_{12}$ ($Ln = Dy$, Ho, Er) and $Ln_4PtGa_{12}$ ($Ln = Dy$, Ho, Er) as a function of temperature is shown in Figures 5.6 and 5.7 respectively. The samples show metallic behavior with $(d\rho/dT > 0)$ with RRR (residual resistivity ratio) values of 5.67, 5.79 and 9.27 for Dy$_4$PdGa$_{12}$, Ho$_4$PdGa$_{12}$ and Er$_4$PdGa$_{12}$, respectively. RRR values for the Pt analogues are 8.92, 7.84, and 7.76 for Dy$_4$PtGa$_{12}$ Ho$_4$PtGa$_{12}$, and Er$_4$PtGa$_{12}$, respectively. The magnetoresistance of $Ln_4PdGa_{12}$ ($Ln = Dy$, Ho, Er) is shown in figure 5.8. The MR is positive with values of 87%, 45%, and 79% for Dy$_4$PtGa$_{12}$ Ho$_4$PtGa$_{12}$, and Er$_4$PtGa$_{12}$, respectively at 3K.
and 9 T. The Magnetoresistance of $Ln_4PtGa_{12}$ ($Ln = \text{Dy}, \text{Ho}, \text{Er}$) is shown in figure 5.9. Dy$_4$PtGa$_{12}$ and Ho$_4$PtGa$_{12}$ is positive, increasing by over 46% and 8%, respectively at 9 T. Er$_4$PdGa$_{12}$ shows a negative magnetoresistance of 6% at 3 K and 9T.

**Figure 5.4** Magnetic susceptibility of $Ln_4PtGa_{12}$ ($Ln = \text{Dy}, \text{Ho}, \text{Er}$) at 0.1 T is shown.

**Figure 5.5** The magnetization of $Ln_4PdGa_{12}$ ($Ln = \text{Dy}, \text{Ho}, \text{Er}$) at 2 K is shown.
Table 5.4  Magnetic Properties of $Ln_4$MGa$_{12}$ ($Ln = $ Dy, Ho, Er; $M = $ Pd, Pt) Compounds

<table>
<thead>
<tr>
<th></th>
<th>$C$</th>
<th>$\theta$ (K)</th>
<th>$\mu_{\text{calc}}$ ($\mu_\text{B}$)</th>
<th>$\mu_{\text{eff}}$ ($\mu_\text{B}$)</th>
<th>Fit Range (K)</th>
<th>Ordering T (K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dy$<em>4$PdGa$</em>{12}$</td>
<td>11.06</td>
<td>-18</td>
<td>10.65</td>
<td>9.41</td>
<td>50-250</td>
<td>N/A</td>
</tr>
<tr>
<td>Ho$<em>4$PdGa$</em>{12}$</td>
<td>10.97</td>
<td>0.2</td>
<td>10.61</td>
<td>9.33</td>
<td>50-250</td>
<td>N/A</td>
</tr>
<tr>
<td>Er$<em>4$PdGa$</em>{12}$</td>
<td>9.96</td>
<td>-8.5</td>
<td>9.58</td>
<td>8.93</td>
<td>50-250</td>
<td>3; 13; 21</td>
</tr>
<tr>
<td>Dy$<em>4$PtGa$</em>{12}$</td>
<td>11.74</td>
<td>-14</td>
<td>10.65</td>
<td>9.69</td>
<td>50-250</td>
<td>11</td>
</tr>
<tr>
<td>Ho$<em>4$PtGa$</em>{12}$</td>
<td>12.67</td>
<td>0.1</td>
<td>10.61</td>
<td>9.91</td>
<td>150-250</td>
<td>26; 92</td>
</tr>
<tr>
<td>Er$<em>4$PtGa$</em>{12}$</td>
<td>9.54</td>
<td>-26</td>
<td>9.58</td>
<td>8.73</td>
<td>150-250</td>
<td>5.5; 25; 93</td>
</tr>
</tbody>
</table>

Figure 5.6  The resistivity of single crystals of $Ln_4$PdGa$_{12}$ ($Ln = $ Dy, Ho, Er) is shown.
Figure 5.7  The resistivity of single crystals of $Ln_4PtGa_{12}$ ($Ln = Dy, Ho, Er$) is shown.

Figure 5.8  The magnetoresistance of $Ln_4PdGa_{12}$ ($Ln = Dy, Ho, Er$) is shown.
Figure 5.9  The magnetoresistance of $Ln_4PtGa_{12}$ ($Ln = Dy, Ho, Er$) is shown

5.4 Conclusion

Single crystals of $Ln_4MGa_{12}$ ($Ln = Tb, Dy, Ho, Er; M = Pd, Pt$) were synthesized and characterized by single crystal X-ray diffraction. $Ln_4MGa_{12}$ ($Ln = Tb, Dy, Ho, Er; M = Pd, Pt$) are isostructural to $Y_4PdGa_{12}$, which crystallizes in the cubic, $Im\bar{3}m$ space group with lattice parameters $a \approx 8.5$ Å, $Z = 2$. $Ln_4MGa_{12}$ ($Ln = Dy, Ho, Er; M = Pd, Pt$) has proven to be a robust structure type with the possibility of incorporating a variety of transition metals.
CHAPTER 6 FINAL REMARKS

This work started with the purpose of synthesizing large single crystals of ternary intermetallic compounds using the flux growth method in order to study structural motifs and physical properties. Much thought was given to which systems would be advantageous to study. The highest considerations given to systems in which gallium and indium could be utilized as a reactant flux. The crystal chemistry of the ternary, \( LnT\text{In} \) (\( Ln = \) lanthanide metal, \( T = \) transition metal) systems have intensively been investigated in recent years and have been shown to exhibit a range of magnetic and electrical properties. When this work began, our group was doing much work with an emphasis on the highly correlated electron systems, mainly materials which were heavy fermions. In an effort to further understand, heavy fermion behavior, synthesis of single crystals of a homologous series of compounds Ce\( M\text{In}_5 \) (Co, Rh, Ir) had been synthesized to study the interplay of superconductivity and magnetism which were observed in these compounds.\(^{49,50}\)

Not having a definitive theory as to the mechanism responsible for heavy electron behavior, synthesis of analogs which did not exhibit heavy fermion behavior was important for use as a comparative tool. As such, \( \text{TbRhIn}_5 \) was a suitable candidate as to date, there are no known terbium intermetallic compounds which are heavy fermions. The compound exhibited similar properties to other known members of the homologous series, as well as, exhibiting the highest magnetic ordering temperature (\( T_N = 48 \text{ K} \)) found in the series.\(^{133}\)

Concurrently, we began to study compounds which contained lanthanide elements in a mixed valent state. Since there were not many examples in the literature of ternary intermetallic lanthanide compounds which used gallium as a flux, this appeared to be a rich area of research to explore. Samarium was chosen as the lanthanide for the first synthesis as it has a tendency to form compounds which exhibit mixed valence or valence fluctuation. Congruently, our synthetic efforts began with studying the well known \( \text{ThCr}_2\text{Si}_2 \) –type since there were already in existence
several hundred germanides and silicides. In addition, it appeared that many of the existing lanthanide intermetallic compounds were in which enhanced or exotic physical properties were reported crystallized in the ThCr$_2$Si$_2$–type (1-2-2) or some structural derivative.

Gallium should be a suitable replacement for the main group element. The literature revealed two gallides with 1-2-2 stoichiometry: LaPd$_2$Ga$_2$ and CePd$_2$Ga$_2$, both of which were formed by arc melting and crystallize in the structurally similar CaBe$_2$Ge$_2$-type.$^{134}$ Using the flux method, large single crystals of the new ternary intermetallic compound, SmPd$_2$Ga$_2$ were grown making it one of the few known ferromagnetic intermetallic compounds. In addition, we have observed large positive MR in this compound of over 100 % at 9 T.$^{135}$ In an effort to study the interplay of long range order and single ion anisotropy as a function of lanthanide element, synthesis which involved the use of terbium onto the lanthanide site began. Following a similar temperature profile, we were unable to form the 1-2-2 stoichiometry. However, we were able to grow $Ln_4MGa_{12}$ ($Ln =$ Tb, Dy, Ho, Er; $M =$ Pd, Pt) hence referred to as 4-1-12, which appear to be more robust structurally.$^{114}$ Since we know that in intermetallic compounds, chemical composition to a great extent is determined by the crystal chemistry. It is also well known that most lanthanide metals prefer arrangements with higher coordination numbers as illustrated by the frequency in which metals form cubic and hexagonal close packed structures. Another geometrical principle which plays a role in the formation of structures is the connectivity principle which is the tendency of atoms to form three dimensional structures. Rather than allowing the incorporation of the smaller latter rare earth elements into a tetragonal structure which would exhibit unsymmetrical coordination spheres, the atoms instead form the more symmetrical 4-1-12 composition in which the lanthanide atoms adopt a symmetrical cuboctahedral formation. Preliminary data for single crystals of $Ln_4FeGa_{12}$ ($Ln =$Tb, Er) show that the compounds are isostructural to Y$_4$PdGa$_{12}$ with similar lattice parameters. Detailed
crystallographic information, magnetic and transport data for $Ln_4$FeGa$_{12}$ ($Ln =$Tb, Er) is given in Appendix 1. Preliminary magnetic measurements show that Tb$_4$FeGa$_{12}$ and Er$_4$FeGa$_{12}$ order antiferromagnetically at $T_N = 2.5$ K and $T_N = 5.5$ K, respectively. Fitting the magnetic data from 100-250 K to a Curie-Weiss fit, an effective moment of 9.3 $\mu_B$ is obtained for Er$_4$FeGa$_{12}$. Due to the non-linearity of the high temperature magnetic data for Tb$_4$FeGa$_{12}$, an effective moment could not be determined at this time. The temperature dependent electrical resistivity of single crystals of $Ln_4$FeGa$_{12}$ ($Ln =$Tb, Er) taken at a field of 0.1 T shows that the compounds exhibit metallic behavior. The field dependent resistivity (2 K) shows that Tb$_4$FeGa$_{12}$ shows 35% change in magnetoresistance (MR) at 9 T while the MR for Er$_4$FeGa$_{12}$ is quite large increasing by over 200 % at 9 T.
REFERENCES

(1) Masumoto, K.; McGahan, W. A. MRS Bull 1996, 21, 44.
(2) Schetky, L. M. MRS Bull 1996, 21, 50.
(5) Villars, P. J. Less-Common Met. 1984, 102, 199.


(60) Sheldrick, G. M.; "SHELXL97" University of Göttingen, Germany 1997.


(64) Schubert, K.; Lukas, H.; Meissner, H.; Bhan, S. Z. Metallkunde 1959, 50, 534.


(94) Schobinger-Papamantellos, P.; Fauth, T.; Middleton, D. P.; Buschow, K. H. J. **1997**.


APPENDIX I SINGLE CRYSTALS X-RAY DIFFRACTION DATA FOR Er₄FeGa₁₂

Table AI.1 provides the atomic positions and displacement parameters found for Er₄FeGa₁₂ obtained from single crystal X-ray diffraction. A fragment of Er₄FeGa₁₂ was mounted onto the goniometer of a Nonius KappaCCD diffractometer equipped with MoKα radiation (λ = 0.71073 Å). Data was collected at 293 K and then corrected for extinction and refined with anisotropic displacement parameters. Er₄FeGa₁₂ is isostructural to Ln₄MGa₁₂ (Ln = Tb, Dy, Ho, Er; M = Pd, Pt) which are discussed in Chapters 4 and 5.

Table AI.1 Crystallographic Information for Ln₄FeGa₁₂ (Ln = lanthanide)

<table>
<thead>
<tr>
<th>Formula</th>
<th>Er₄FeGa₁₂</th>
</tr>
</thead>
<tbody>
<tr>
<td>a (Å)</td>
<td>8.470(16)</td>
</tr>
<tr>
<td>V (Å³)</td>
<td>608(2)</td>
</tr>
<tr>
<td>Z</td>
<td>2</td>
</tr>
<tr>
<td>Crystal Dimension (mm³)</td>
<td>0.02 x 0.04 x 0.06</td>
</tr>
<tr>
<td>Crystal System</td>
<td>Cubic</td>
</tr>
<tr>
<td>Space Group</td>
<td>I m 3 m</td>
</tr>
<tr>
<td>θ range(°)</td>
<td>23.0-30.0</td>
</tr>
<tr>
<td>μ (mm⁻¹)</td>
<td>58.034</td>
</tr>
<tr>
<td>Measured reflections</td>
<td>131</td>
</tr>
<tr>
<td>Independent reflections</td>
<td>65</td>
</tr>
<tr>
<td>Reflections with I &gt; 2σ(I)</td>
<td>43</td>
</tr>
<tr>
<td>R_{int}</td>
<td>0.0914</td>
</tr>
<tr>
<td>h</td>
<td>-10 → 10</td>
</tr>
<tr>
<td>k</td>
<td>-7 → 7</td>
</tr>
<tr>
<td>l</td>
<td>-7 → 7</td>
</tr>
<tr>
<td>aR</td>
<td>0.0366</td>
</tr>
<tr>
<td>b_{wR}(F²)</td>
<td>0.1269</td>
</tr>
<tr>
<td>Reflections</td>
<td>116</td>
</tr>
<tr>
<td>Parameters</td>
<td>10</td>
</tr>
<tr>
<td>Δρ_{max} (e Å⁻³)</td>
<td>2.077</td>
</tr>
<tr>
<td>Δρ_{min} (e Å⁻³)</td>
<td>-2.010</td>
</tr>
<tr>
<td>Extinction coefficient</td>
<td>0.0028(12)</td>
</tr>
</tbody>
</table>

\[ aR(F) = \frac{\sum |F_o| - |F_c|}{\sum |F_o|} \]

\[ b_{wR}(F²) = \sum [w(F_o^² - F_c^²)]/\sum [w(F_o^²)]^{1/2} \]
Table AII.1  Atomic Positions and Displacement Parameters for \( \text{Er}_4\text{FeGa}_{12} \)

<table>
<thead>
<tr>
<th>Atom</th>
<th>Wyckoff</th>
<th>( x )</th>
<th>( y )</th>
<th>( z )</th>
<th>( U_{eq}(\AA^2) )^( a )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{Er}<em>4\text{FeGa}</em>{12} )</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Er</td>
<td>8c</td>
<td>( \frac{1}{4} )</td>
<td>( \frac{1}{4} )</td>
<td>( \frac{1}{4} )</td>
<td>0.0097(1)</td>
</tr>
<tr>
<td>Fe</td>
<td>2a</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0.007(4)</td>
</tr>
<tr>
<td>Ga1</td>
<td>12d</td>
<td>0</td>
<td>0.2040(2)</td>
<td>0</td>
<td>0.0097(2)</td>
</tr>
<tr>
<td>Ga2</td>
<td>12e</td>
<td>( \frac{1}{2} )</td>
<td>0</td>
<td>( \frac{1}{4} )</td>
<td>0.0113(2)</td>
</tr>
</tbody>
</table>

\( ^a \)\( U_{eq} \) is defined as one-third of the trace of the orthogonalized \( U_{ij} \) tensor.

Table AIII.3  Selected Interatomic Distances

<table>
<thead>
<tr>
<th>( \text{Er}<em>4\text{FeGa}</em>{12} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Er-Ga1  (x6)</td>
</tr>
<tr>
<td>Er-Ga2  (x6)</td>
</tr>
<tr>
<td>Fe-Ga1</td>
</tr>
</tbody>
</table>

Figure AI.1A  The magnetic susceptibility of \( \text{Er}_4\text{FeGa}_{12} \) is shown.
Figure A1.2A  The temperature dependent resistivity of $Ln_4FeGa_{12}$ ($Ln = Tb, Er$) measured at a field of 0.1 T is shown.

Figure A1.2B shows the field dependent resistivity of $Ln_4FeGa_{12}$ ($Ln = Tb, Er$) measured at 2 K.
Dear Willa M Williams

We hereby grant you permission to reproduce the material detailed below at no charge in your thesis subject to the following conditions:

1. If any part of the material to be used (for example, figures) has appeared in our publication with credit or acknowledgement to another source, permission must also be sought from that source. If such permission is not obtained then that material may not be included in your publication/copies.

2. Suitable acknowledgment to the source must be made, either as a footnote or in a reference list at the end of your publication, as follows:

"Reprinted from Publication title, Vol number, Author(s), Title of article, Pages No., Copyright (Year), with permission from Elsevier”.

3. Reproduction of this material is confined to the purpose for which permission is hereby given.

4. This permission is granted for non-exclusive world English rights only. For other languages please reapply separately for each one required. Permission excludes use in an electronic form. Should you have a specific electronic project in mind please reapply for permission.

5. This includes permission for UMI to supply single copies, on demand, of the complete thesis. Should your thesis be published commercially, please reapply for permission.

Yours sincerely

Jennifer Jones
Rights Assistant
Dear Willa M Williams

We hereby grant you permission to reproduce the material detailed below at no charge in your thesis subject to the following conditions:

1. If any part of the material to be used (for example, figures) has appeared in our publication with credit or acknowledgement to another source, permission must also be sought from that source. If such permission is not obtained then that material may not be included in your publication/copies.

2. Suitable acknowledgment to the source must be made, either as a footnote or in a reference list at the end of your publication, as follows:
   "Reprinted from Publication title, Vol number, Author(s), Title of article, Pages No., Copyright (Year), with permission from Elsevier".

3. Reproduction of this material is confined to the purpose for which permission is hereby given.

4. This permission is granted for non-exclusive world English rights only. For other languages please reapply separately for each one required. Permission excludes use in an electronic form. Should you have a specific electronic project in mind please reapply for permission.

5. This includes permission for UMI to supply single copies, on demand, of the complete thesis. Should your thesis be published commercially, please reapply for permission.

Yours sincerely

Jennifer Jones
Rights Assistant
MEMORANDUM

TO: Willa M. Williams
FROM: C. Arleen Courtney, Copyright Associate

Thank you for your request for permission to include your paper(s) or portions of text from your paper(s) in your thesis. Permission is now automatically granted; please pay special attention to the implications paragraph below. The Copyright Subcommittee of the Joint Board/Council Committees on Publications approved the following:

Copyright permission for published and submitted material from theses and dissertations
ACS extends blanket permission to students to include in their theses and dissertations their own articles, or portions thereof, that have been published in ACS journals or submitted to ACS journals for publication, provided that the ACS copyright credit line is noted on the appropriate page(s).

Publishing implications of electronic publication of theses and dissertation material
Students and their mentors should be aware that posting of theses and dissertation material on the Web prior to submission of material from that thesis or dissertation to an ACS journal may affect publication in that journal. Whether Web posting is considered prior publication may be evaluated on a case-by-case basis by the journal’s editor. If an ACS journal editor considers Web posting to be “prior publication”, the paper will not be accepted for publication in that journal. If you intend to submit your unpublished paper to ACS for publication, check with the appropriate editor prior to posting your manuscript electronically.

If your paper has not yet been published by ACS, we have no objection to your including the text or portions of the text in your thesis/dissertation in print and microfilm formats; please note, however, that electronic distribution or Web posting of the unpublished paper as part of your thesis in electronic formats might jeopardize publication of your paper by ACS. Please print the following credit line on the first page of your article: "Reproduced (or 'Reproduced in part') with permission from [JOURNAL NAME], in press (or 'submitted for publication'). Unpublished work copyright [CURRENT YEAR] American Chemical Society." Include appropriate information.

If your paper has already been published by ACS and you want to include the text or portions of the text in your thesis/dissertation in print or microfilm formats, please print the ACS copyright credit line on the first page of your article: "Reproduced (or 'Reproduced in part') with permission from [FULL REFERENCE CITATION.] Copyright [YEAR] American Chemical Society." Include appropriate information.

Submission to a Dissertation Distributor: If you plan to submit your thesis to UMI or to another dissertation distributor, you should not include the unpublished ACS paper in your thesis if the thesis will be disseminated electronically, until ACS has published your paper. After publication of the paper by ACS, you may release the entire thesis (not the individual ACS article by itself) for electronic dissemination through the distributor; ACS’s copyright credit line should be printed on the first page of the ACS paper.
Use on an Intranet: The inclusion of your ACS unpublished or published manuscript is permitted in your thesis in print and microfilm formats. If ACS has published your paper you may include the manuscript in your thesis on an intranet that is not publicly available. Your ACS article cannot be posted electronically on a publicly available medium (i.e. one that is not password protected), such as but not limited to, electronic archives, Internet, library server, etc. The only material from your paper that can be posted on a public electronic medium is the article abstract, figures, and tables, and you may link to the article’s DOI. This paragraph does not pertain to the dissertation distributor paragraph above.

Thank you for writing. Questions? Please call me at 202/872-4368 or send e-mail to copyright@acs.org.
VITA

Willa Williams was born 8 September 1975, to the late Willie Williams, Jr., and Minnie Smith-Williams in Lexington, Mississippi. Willa is the mother of one son, Conja Rule, Jr., and sister to five sisters and three brothers: Mary (deceased), James, Thelma, Jerry, Earthie, Robert (deceased), Lucinda, Wilma, and Beverly.

Willa began her education in the public schools of Holmes County, Mississippi. In middle school, Willa became Co-Author of “Minds Stayed on Freedom: Holmes County Youth Speaks”, an oral history project which detailed the life of African Americans in rural Mississippi during the civil rights era. It was during this time that Willa developed a love for history and wanted to pursue a career as a historian.

Willa attended Jacob J. McClain High school where she was an active student participated in track and as member of the marching, concert and jazz bands. Upon graduation from high school, Willa received academic and music scholarships to several universities. In the summer of 1993, Willa enrolled at Mississippi Valley State University where she majored in biology. In her junior year of undergraduate study, Willa was advised that she only needed three more classes to receive a dual degree in biology and chemistry.

Willa received her Bachelor of Science (magna cum laude) in biology/chemistry in May, 1998 and began graduate study in analytical chemistry at Jackson State University until 2001 when she transferred to Louisiana State University. While at LSU, Willa has been a member of the American Chemical Society and has attended and presented at several national conferences.