Physical properties of $\text{RE}_3\text{TM}\text{Sb}_5$
($\text{RE} = \text{La, Ce}; \text{TM} = \text{Ti, Zr, Hf}$)

by

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B.Sc., University of British Columbia, 2014

Dissertation Submitted in Partial Fulfillment of the
Requirements for the Degree of
Master of Science

in the
Department of Physics
Faculty of Science

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SIMON FRASER UNIVERSITY
Fall 2019

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Abstract

Single crystals of RE$_3$TMSb$_5$ (RE = La, Ce; TM = Ti, Zr, Hf) have been grown by Sn flux and characterized by magnetization, electrical resistivity, and specific heat measurements. Powder X-ray diffraction analysis indicates that the title compounds crystallize into the hexagonal Hf$_5$Sn$_3$Cu-type structure (P6$_3$/mcm). The physical property measurements for Ce-containing compounds clearly indicate an antiferromagnetic ordering around 5 K. The effective magnetic moment estimated from magnetic susceptibility measurements is close to the theoretical value, indicating the 4f-electrons of Ce$^{3+}$ ions are well localized. Magnetization isotherms at $T = 2$ K show anisotropic behaviour between $H \parallel ab$ and $H \parallel c$. The temperature-dependent electrical resistivity follows a typical Kondo lattice behavior associated with thermal population of crystalline electric field (CEF) levels. The specific heat measurement for Ce-containing compounds reveals a large $C_m/T$ value at low temperatures, which is much bigger than that of La-containing samples. At high temperatures, the CEF energy level scheme is analyzed by fitting to the Schottky peak observed in specific heat, from which the energy level splitting between the three doublet states are found to be 165 and 380 K for all three Ce-containing samples. The resistivity measurements for all La-containing samples indicate an anomalous broad peak structure at high temperatures. We also investigate the previously reported superconductivity observed in La$_3$TiSb$_5$ and Ce$_3$TiSb$_5$ below 4 K. Our resistivity and specific heat measurements show that the superconductivity is not an intrinsic property of the single crystals, and is attributed to residual Sn flux.

Keywords: Rare-earth Intermetallic Compound, Kondo Effect, RKKY Interaction
Dedication

I dedicate this thesis to my sisters and dogs.
Acknowledgements

I would like to use this section as an opportunity to thank my senior supervisor, Eundeok Mun, for all the support throughout the years. His patient guidance is what allowed me to keep advancing through the program. I would also like to thank Steve Dodge for the support and understanding of topics, as well as the completion of this writing. Lastly, to all of the professors I was fortunately able to associate with through graduate level courses and teaching assisting, 'Thank you!'

We would like to acknowledge H. Park for initial sample growth. This work was supported by the Canada Research Chairs, Natural Sciences and Engineering Research Council of Canada, and Canada Foundation for Innovation program.
# Table of Contents

Approval ii  
Abstract iii  
Dedication iv  
Acknowledgements v  
Table of Contents vi  
List of Tables viii  
List of Figures ix  

1 Introduction 1  
1.1 Heavy Fermion Systems . . . . . . . . . . . . . . . . . . . . . . . . . . . 1  
1.1.1 Kondo Effect and RKKY Interaction . . . . . . . . . . . . . . . . . . 2  
1.2 Theoretical Background . . . . . . . . . . . . . . . . . . . . . . . . . . . 4  
1.2.1 Magnetic susceptibility . . . . . . . . . . . . . . . . . . . . . . . . . . 4  
1.2.2 Resistivity . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . 5  
1.2.3 Specific Heat . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . 6  
1.3 Previous Studies of RE₃TMSb₅ . . . . . . . . . . . . . . . . . . . . . . . . 7  
1.4 Motivation . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . 8  

2 Experimentals 10  

3 Results 14  
3.1 Magnetic Susceptibility and Magnetization . . . . . . . . . . . . . . . . 14  
3.1.1 La₃TMSb₅ . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . 14  
3.1.2 Ce₃TiSb₅ . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . 16  
3.1.3 Ce₃ZrSb₅ . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . 20  
3.1.4 Ce₃HfSb₅ . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . 22  
3.2 Resistivity . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . 26  
3.2.1 La₃TMSb₅ (TM = Ti, Zr, Hf) . . . . . . . . . . . . . . . . . . . . . . 26
3.2.2 Ce₃TMSb₅ (TM = Ti, Zr, Hf) ........................................... 26
3.3 Specific Heat ................................................................. 28
  3.3.1 La₃TiSb₅ and Ce₃TiSb₅ .................................................. 28
  3.3.2 La₃ZrSb₅ and Ce₃ZrSb₅ ............................................... 28
  3.3.3 La₃HfSb₅ and Ce₃HfSb₅ ............................................... 28

4 Discussion ........................................................................ 31

5 Summary ........................................................................... 37

Bibliography ....................................................................... 38
List of Tables

Table 1.1  $p(calc)$ and $\mu_{sat}$ for Lanthanide Ions  . . . . . . . . . . . . . . . . . . . . 5

Table 2.1  Lattice Parameters of Grown RE$_3$TMSb$_5$ Samples  . . . . . . . . . . . 11

Table 3.1  $\mu_{eff}$ and $\theta_p$ of Ce$_3$TMSb$_5$  . . . . . . . . . . . . . . . . . . . . 17

Table 3.2  $\gamma$, $\theta_D$, and $T_N$ of RE$_3$TMSb$_5$  . . . . . . . . . . . . . . . . . . 30
## List of Figures

| Figure 2.1 | Temperature Profile of Single Crystal RE$_3$TMSb$_5$ Growth | 10 |
| Figure 2.2 | Lattice Parameters of RE$_3$TMSb$_5$ | 11 |
| Figure 2.3 | Temperature Dependence of Electrical Resistivity $\rho$ of Ce$_3$TiSb$_5$ | 13 |
| Figure 3.1 | Magnetic Susceptibility $\chi$ and magnetization $M$ of La$_3$TiSb$_5$ | 15 |
| Figure 3.2 | Magnetic Susceptibility $\chi$ and magnetization $M$ of La$_3$ZrSb$_5$ | 15 |
| Figure 3.3 | Magnetic Susceptibility $\chi$ and magnetization $M$ of La$_3$HfSb$_5$ | 16 |
| Figure 3.4 | Inverse Magnetic Susceptibility $\chi^{-1}$ of Ce$_3$TiSb$_5$ | 17 |
| Figure 3.5 | Temperature Dependence of Magnetic Susceptibility $\chi$ for Ce$_3$TiSb$_5$ | 18 |
| Figure 3.6 | Magnetization $M$ of Ce$_3$TiSb$_5$ | 19 |
| Figure 3.7 | Inverse Magnetic Susceptibility $\chi^{-1}$ of Ce$_3$ZrSb$_5$ | 20 |
| Figure 3.8 | Temperature Dependence of Magnetic Susceptibility $\chi$ for Ce$_3$ZrSb$_5$ | 21 |
| Figure 3.9 | Magnetization $M$ of Ce$_3$ZrSb$_5$ | 21 |
| Figure 3.10 | Inverse Magnetic Susceptibility $\chi^{-1}$ of Ce$_3$HfSb$_5$ | 22 |
| Figure 3.11 | Temperature Dependence of Magnetic Susceptibility $\chi$ for Ce$_3$HfSb$_5$ | 23 |
| Figure 3.12 | Magnetization $M$ of Ce$_3$HfSb$_5$ | 24 |
| Figure 3.13 | Electrical Resistivity $\rho$ of La$_3$TMSb$_5$ (TM = Ti, Zr, Hf) | 25 |
| Figure 3.14 | Electrical Resistivity $\rho$ of Ce$_3$TMSb$_5$ (TM = Ti, Zr, Hf) | 26 |
| Figure 3.15 | Specific Heat $C_P$ of La$_3$TiSb$_5$ and Ce$_3$TiSb$_5$ | 27 |
| Figure 3.16 | Specific Heat $C_P$ of La$_3$ZrSb$_5$ and Ce$_3$ZrSb$_5$ | 29 |
| Figure 3.17 | Specific Heat $C_P$ of La$_3$HfSb$_5$ and Ce$_3$HfSb$_5$ | 29 |
| Figure 4.1 | Ordering Temperature $T_N$ in $d\rho(T)/dT$, $d\chi_{ab}(T)/dT$, and $C_m(T)$ | 32 |
| Figure 4.2 | Magnetic Contribution to Specific Heat Divided by Temperature $C_m/T$ | 33 |
| Figure 4.3 | Magnetic Contribution to Specific Heat $C_m$ of Ce$_3$TMSb$_5$ | 34 |
| Figure 4.4 | Magnetic Entropy $S_m(T)$ of Ce$_3$TiSb$_5$ | 35 |
Chapter 1

Introduction

1.1 Heavy Fermion Systems

Through specific heat and resistivity measurements, the first heavy fermion system, CeAl$_3$, was discovered [1]. A large, linear specific heat coefficient of $\gamma \sim 1620$ mJ/mol K$^2$ and the $T^2$ term in the electrical resistivity $A \sim 35 \mu\Omega$ cm/K$^2$ ($\rho = \rho_0 + AT^2$) was found in the low temperature range. Heavy fermion systems were originally defined as a collection of intermetallic compounds containing lanthanides (mainly Ce and Yb) or actinides (mainly U and Np). More compounds have been observed to exhibit such behaviour since then [2]. Heavy fermion systems gained great interest with the discovery of superconductivity in CeCu$_2$Si$_2$ compound [3]. The jump in specific heat at the superconducting transition temperature clearly indicates the characteristics of heavy fermion behavior. Prior to this discovery, magnetism and superconducting behaviour were believed to be contradictory phenomena. The $4f$-electrons in CeCu$_2$Si$_2$ are responsible for both the localized magnetic moments at high temperatures (following the Curie-Weiss law) and for superconductivity below the critical temperature $T_c$. A high-$T_c$ superconductor discovered in 1986 also demonstrated that the magnetism is responsible for the superconducting phase [4]. The traditional BCS theory of superconductivity generally does not apply to these two, strongly correlated systems.

As the name suggests, heavy fermion systems are characterized by the presence of large effective mass $m^*$ (50-1000 times greater than the mass of a free electron) below a characteristic temperature (coherence temperature) $T^*$ [2], where the effective mass can be obtained through specific heat measurements. In the temperature range much lower than the Debye temperature and Fermi energy, the specific heat $C$ can be expressed as $C/T = \gamma + \beta T^2$, where $\gamma$ is the electronic contribution and $\beta$ is the phonon contribution to the specific heat. Here, $\gamma = V_m k_F^2 k_F^2 m^*/3\hbar^2$, $V_m$ is the molar volume, $m^*$ the effective mass of the electron, $k_F$ the Fermi vector, and $T$ is the absolute temperature. $\gamma$ is on the order of 1 mJ/mol K$^2$ at the low temperature range for normal metals (like copper), but $\gamma$ approaches very large values below the $T^*$ for heavy fermion systems. The generally accepted definition of heavy
fermions are systems with $\gamma > 400 \text{ mJ/mol K}^2$. $\gamma$ is typically normalized to a mole of $f$-electron atoms, so comparisons between systems with different structure can be made. Some other characteristics of heavy fermion systems include (i) an enhanced Pauli spin susceptibility, indicating a large effective mass, (ii) a very large $T^2$ term in the electrical resistivity, (iii) the Wilson ratio between magnetic susceptibility and specific heat coefficient which is approximately one, and (iv) the Kadowaki-Wood ratio $A/\gamma^2 \sim 1 \times 10^{-5} \mu\Omega \text{ cm mol}^{-2} \text{K}^2/\text{mJ}^2$.

Ce- and Yb-based compounds at low temperatures show various ground states, such as antiferromagnetic and ferromagnetic ordering with weak moments, narrow-gap semiconductors with large effective masses, Fermi liquids with no long range magnetic ordering, or superconductivity [5]. Heavy fermions are Fermi liquids with no ordering while some others are non-Fermi liquids (NFL). The experimental result of Kondo alloy $Y_{1-x}U_xPd_3$ has led to intense theoretical and experimental activity in the general area of NFL behavior in $d$- and $f$-electron metals [6]. Originally, NFL behavior in $d$- and $f$-electron systems was discovered for doped systems. However, such behavior can be achieved in a variety of ways [7, 8]. The NFL state in many systems is related to a magnetic instability arising at $T = 0$, since the NFL behavior in those systems is found near a magnetically ordered phase. The NFL behaviours have been considered theoretically in the special case of a quantum phase transition (QPT) [7, 8]. A QPT is driven by a control parameter other than temperature (in contrast to classical phase transition) such as the applied magnetic field, pressure, or doping at $T = 0$. Since the experimental results can be obtained only for $T > 0$, the quantum critical point (QCP) in the phase diagram relies on the findings of the scaling behavior. Several QCP models exist for the NFL behavior of antiferromagnetic heavy fermion metals [9–17]. These models can be grouped into two categories: spin density wave quantum criticality invokes the fluctuations of the antiferromagnetic order parameter, whereas local quantum criticality involves a breakdown of the Kondo effect, changing the Fermi surface volume through the QCP. Although several theories have been proposed, there is no clear consensus about whether any particular theory explains the wide range of NFL properties.

### 1.1.1 Kondo Effect and RKKY Interaction

The ground state of Ce-based compounds is governed by two main interaction mechanisms, the Kondo effect and RKKY interaction. The temperature dependence of the electrical resistivity in some classes of materials showed a resistivity minimum, followed by a $-\log(T)$ dependence with decreasing temperature and saturating at low temperatures. Jun Kondo first explained the presence of a minimum in the resistivity of compounds containing $d$- and $f$-electron spins using a third-order perturbation method on a single spin-$1/2$ magnetic impurity (single-ion Kondo model) in 1964 [18]. The Kondo effect, named after Jun Kondo, is the screening of localized magnetic moments by the spins associated with the conduction electrons, giving rise to the $-\log(T)$ dependence above a characteristic temperature (Kondo
temperature $T_K$) and saturates below $T_K$. The resistivity minimum can be understood as a result of the decreasing phonon contribution and increasing Kondo contribution as the temperature is lowered. The Kondo contribution to the magnetic susceptibility and specific heat were derived later [19, 20]: At high temperatures, such a system follows a Curie-Weiss law, whereas at lower temperatures, the magnetic susceptibility $\chi(T)$ becomes finite with highly enhanced value; an important characteristic of heavy fermions is a large Sommerfeld coefficient $\gamma$ in the specific heat $C_P$.

A system with a high occupancy of magnetic moments cannot be explained by the single-ion, Kondo model. Such a system is called a Kondo lattice, where the resistivity develops a local maximum at another characteristic temperature (coherence temperature $T_{coh}$), and often follows the $T^2$ dependence (Fermi-liquid behavior) at even lower temperatures [21, 22]. Above $T_{coh}$, the interaction between the localized magnetic moments are weak, so they behave like incoherent magnetic impurities. In this range, the minimum and the $-\log(T)$ dependence occurs, much like the single-ion model. Below $T_{coh}$, the Kondo lattice has fully screened $f$-electron spins, exhibiting Fermi-liquid behaviour.

The term RKKY interaction stands for Ruderman-Kittel-Kasuya-Yosida interaction and describes the indirect magnetic exchange interactions of localized magnetic moments, mediated by the conduction electrons [23–25].

Localized magnetic moments $\langle S(x') \rangle$ of an $f$-electron located at $x'$ creates Friedel oscillations in the conduction spin density $\langle \sigma(x) \rangle$ such that:

$$\langle \sigma(x) \rangle = J \chi(x - x') \langle S(x') \rangle \quad (1.1)$$

$\chi(x - x')$ represents the non-local magnetic susceptibility and $J$ is the antiferromagnetic coupling. The spin density oscillation originates from the discontinuities in the occupancies $f(\epsilon_k)$ at the Fermi surface, and decays radially.

$$\langle \sigma(x) \rangle \approx -JD \frac{\cos(2k_Fx)}{|k_F x|^3} \quad (1.2)$$

$D$ represents the conduction electron density of states and $x$ is the distance from the magnetic moment. When a second local moment $\langle S(X) \rangle$ is positioned at $x$, it couples to the Friedel oscillation with energy $J\langle S(x) \cdot \sigma(x) \rangle$. The RKKY Hamiltonian is given by:

$$H_{RKKY} = K \langle S(x) \cdot \sigma(x) \rangle = -J^2 \chi(x - x') S(x) \cdot S(x') = J_{RKKY}(x - x') S(x) \cdot S(x') \quad (1.3)$$

$$J_{RKKY}(x - x') = J_{RKKY}(r) \approx -J^2 \frac{\cos(2k_Fr)}{k_F r} \quad (1.4)$$

The sign of the interaction is dependent on the distance between the magnetic moments, resulting in an interaction that can either be antiferromagnetic or ferromagnetic.
The ground state of Ce-based compounds can be understood by considering the RKKY interaction and Kondo screening [22]. When the RKKY coupling energy exceeds the energy required for the formation of Kondo singlets, the magnetic ordering is induced. If the Kondo screening is dominant, the ground state is a paramagnetic state. Alloys containing dilute concentrations of magnetic rare-earth or transition metal ions can demonstrate a random distribution of antiferromagnetic and ferromagnetic interactions. The magnetic state arising from such a disorder and frustration is called a "spin glass" system [26]. In this state, localized spins are frozen into random orientations. On the other hand, a dense system of magnetic ions may exhibit an antiferromagnetic or ferromagnetic state with a ordering temperature on the order of $J^2D$.

1.2 Theoretical Background

1.2.1 Magnetic susceptibility

The magnetic susceptibility is defined as the ratio of the magnetization $M$ and the intensity of the applied magnetic field $H$ [27].

$$\chi(H) = \frac{M(H)}{H}$$

(1.5)

Materials with $\chi$ greater than zero are said to be paramagnetic, which aligns spins in the same direction as the applied magnetic field, whereas materials with $\chi$ less than zero are said to be diamagnetic, aligning spins in the opposite direction as the applied magnetic field.

The magnetic susceptibility of local moment systems follows a Curie-Weiss Law:

$$\frac{M}{H} = \frac{C}{T - \theta_p}$$

(1.6)

Here, $\theta_p$ is the Weiss temperature and the Curie constant $C$ is defined as:

$$C = \frac{Np^2\mu_B^2}{3k_B}.$$  

(1.7)

The $\mu_B$ is the Bohr magneton, $k_B$ is the Boltzmann constant and $p$ denotes the effective moment.

Starting with lanthanum, the ions of the rare earth elements are trivalent and demonstrates similar chemical properties. Lanthanum has zero electrons in the 4$f$ shell, and the number of 4$f$ electrons increases by one for each element in the rare earth group. The radii of the rare earth ions decrease through the group (this is known as the "lanthanide contraction").

From the Hund’s rules, the maximum value of total spin $S$, the maximum value of the orbital angular momentum $L$, and the total angular momentum $J$ can be determined for the
Table 1.1: The calculated effective moment and saturated moment of each ion in the lanthanide group.

<table>
<thead>
<tr>
<th>Rare-Earth Ion</th>
<th>Configuration</th>
<th>$p(calc)$</th>
<th>$\mu_{sat}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ce$^{3+}$</td>
<td>$4f^{15}5s^2p^6$</td>
<td>2.54</td>
<td>2.14</td>
</tr>
<tr>
<td>Pr$^{3+}$</td>
<td>$4f^{2}5s^2p^6$</td>
<td>3.58</td>
<td>3.20</td>
</tr>
<tr>
<td>Nd$^{3+}$</td>
<td>$4f^{3}5s^2p^6$</td>
<td>3.62</td>
<td>3.27</td>
</tr>
<tr>
<td>Pm$^{3+}$</td>
<td>$4f^{4}5s^2p^6$</td>
<td>2.68</td>
<td>2.40</td>
</tr>
<tr>
<td>Sm$^{3+}$</td>
<td>$4f^{5}5s^2p^6$</td>
<td>0.84</td>
<td>0.71</td>
</tr>
<tr>
<td>Eu$^{3+}$</td>
<td>$4f^{6}5s^2p^6$</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Gd$^{3+}$</td>
<td>$4f^{7}5s^2p^6$</td>
<td>7.94</td>
<td>7.00</td>
</tr>
<tr>
<td>Tb$^{3+}$</td>
<td>$4f^{8}5s^2p^6$</td>
<td>9.72</td>
<td>9.00</td>
</tr>
<tr>
<td>Dy$^{3+}$</td>
<td>$4f^{9}5s^2p^6$</td>
<td>10.63</td>
<td>10.00</td>
</tr>
<tr>
<td>Ho$^{3+}$</td>
<td>$4f^{10}5s^2p^6$</td>
<td>10.60</td>
<td>10.00</td>
</tr>
<tr>
<td>Er$^{3+}$</td>
<td>$4f^{11}5s^2p^6$</td>
<td>9.59</td>
<td>9.00</td>
</tr>
<tr>
<td>Tm$^{3+}$</td>
<td>$4f^{12}5s^2p^6$</td>
<td>7.57</td>
<td>7.00</td>
</tr>
<tr>
<td>Yb$^{3+}$</td>
<td>$4f^{13}5s^2p^6$</td>
<td>4.54</td>
<td>4.00</td>
</tr>
</tbody>
</table>

The effective moment $p(calc) = g[J(J+1)]^{1/2}$ and saturated moment $\mu_{sat} = gJ$ can be calculated by using the $g$ factor from the Landé equation for each ion:

$$g = 1 + \frac{J(J+1) + S(S+1) - L(L+1)}{2J(J+1)}.$$  \hspace{1cm} (1.8)

Table 1.1 summarizes the $p(calc)$ and $\mu_{sat}$ for each of the trivalent ions in the lanthanide group. Experimentally, the effective moment and Weiss temperature of rare-earth-based compounds can be extracted from a linear fit to the inverse of the magnetic susceptibility. The $\mu_{sat}$ value can be determined from the magnetization measurement as a function of external magnetic fields. Comparison of the experimental determinations of the effective moment and saturated moment with the theoretical values are useful in the analysis of new compounds, since it allows the theoretical value to be compared to the measured value. The sign of $\theta_p$ tells us where the ferromagnetic or antiferromagnetic interactions dominate - if $\theta_p$ is greater than zero, ferromagnetic, and if $\theta_p$ is less than zero, antiferromagnetic.

1.2.2 Resistivity

The electrical resistance $R$ of an object is a quantity representing how strongly the object opposes the flow of electrical current through it. The resistance of given materials is dependent on the dimensions of the object as well as the resistivity $\rho$, which is a physical property of the material itself. The resistance is given by:
Here, \( L \) and \( A \) represents the length and cross-sectional area of the resistor, respectively. The resistivity is temperature-dependent, and every material has a characteristic resistivity. For simple metals at low temperatures, the electrical resistivity is quadratic in temperature \( \rho(T) = \rho_0 + \alpha T^2 \). In general, the resistivity will not decrease all the way to zero, even at \( T = 0 \) K, due to the lattice imperfection, dislocation, disorder, and impurities. The residual resistivity \( \rho_0 \) reflects all these contributions. A material is called a superconductor if the electrical resistivity becomes zero below a specific, non-zero temperature, known as the critical temperature \( T_C \).

### 1.2.3 Specific Heat

The specific heat \( C_P \) at constant pressure of a material is the energy required to raise the temperature of the material by 1 K per unit of mass. Specific heat measurements provide information about the electronic and magnetic properties of a material. It may also provide information about structural, magnetic, and superconducting phase transitions. Specific heat may also tell us about unwanted phases in a crystal. The heat capacity under fixed pressure is:

\[
C_P = \left( \frac{dQ}{dT} \right)_P \quad (1.10)
\]

In an ordinary metal at low temperatures, the \( C_P \) is characterized as a sum of the conduction electron contribution and a phonon contribution from the crystal lattice vibrations.

\[
C_P = \gamma T + \beta T^3 \quad (1.11)
\]

\( \gamma \) is known as the Sommerfeld coefficient, while the cubic term originates from the Debye \( T^3 \) approximation. By performing a linear fit on the plot of \( \frac{C}{T} \) against \( T^2 \), the two parameters, \( \gamma \) and \( \beta \), can be extracted. The Debye temperature \( \theta_D \) can be estimated from \( \beta = 12\pi^4 k_B/5\theta_D^3 \). The linear term reflects the effective mass of electrons. Heavy fermion materials containing elements with 4\( f \) or 5\( f \) valence electrons are characterized by \( \gamma \) values much larger than what is predicted by the free electron theory, as their effective masses are much larger.

In the higher temperature regime, the \( C_P(T) \) approaches a constant value. This value is predicted to be \( 3R \) where \( R \) is the gas constant, given by the Dulong-Petit law.

The specific heat is closely related to the entropy, which is a measure of the number of available configurations. Materials containing localized magnetic moments will exhibit an additional contribution to the specific heat. To obtain the magnetic part of the specific heat, the total specific heat of a non-magnetic reference compound such as the La-based
analogue can be subtracted from the total specific heat of the magnetic compound. The magnetic specific heat $C_m$ can be used to obtain the magnetic entropy associated with the magnetic moments of a material. The magnetic entropy $S_m$ be found using the following integral:

$$S_m = \int_0^T dT \frac{C_m}{T}. \tag{1.12}$$

An isolated rare-earth ion with angular momentum $J$ has $(2J + 1)$ degenerate levels. The degeneracy is lifted if an electric or magnetic field is applied. A Schottky peak in the magnetic specific heat is generally observed when the crystalline electric field levels become populated. The general expression for the Schottky contribution to the specific heat is given by:

$$C_{Sch}(T) = k_B \beta^2 \sum_{i,j} g_i g_j E_i (E_i - E_j) e^{-\beta (E_i + E_j)} \left( \sum_i g_i e^{-\beta E_i} \right)^2, \tag{1.13}$$

$\beta$ is defined as $1/k_BT$ and $g_i$ represents the degeneracies and the $E_i$’s represent the energy of the i-th level. For a simple two-level system, the $C_{Sch}$ becomes:

$$C_{Sch}(T) = k_B (\beta \Delta)^2 \frac{g_0}{g_1} \frac{e^{\beta \Delta}}{1 + (g_0/g_1)e^{\beta \Delta}}. \tag{1.14}$$

$\Delta$ is the energy difference between $g_0$ and $g_1$. An applied magnetic field also lifts the degeneracy due to the Zeeman effect.

### 1.3 Previous Studies of RE$_3$TMSb$_5$

In 1995, a new group of ternary rare-earth transition-metal antimonides of the form RE$_3$TMSb$_5$ (RE = La, Ce, Pr, Nd, Sm; TM=Ti, Zr, Hf, Nb) were grown for the first time [28]. The compounds were prepared by reactions of pure powders of the rare-earth metals, transition-metals, and antimony, resulting in thin, needle-shaped crystals. Initially, this phase was discovered by analyzing arc-melted samples with diverse stoichiometric ratios of elements, where excess antimony was used to compensate vaporization of Sb. The major phase grown from this method is indeed RE$_3$TMSb$_5$ (determined by the crystal structure), but some binary antimonide phases could not be eliminated, and Sm$_3$NbSb$_5$ was unable to be grown.

The structure and lattice parameters determined from x-ray diffraction were given for the first time on the newly grown title compounds. The sensitivity of the samples in air is discussed, "they begin to degrade over 1 day and completely decompose within 1 week." One of the main purposes behind the paper was "to search for new magnetic materials and to test the validity of bonding models" [28].

In 2002, the detailed characteristics of the crystal structure of the RE$_3$TiSb$_5$ family were reported [29]. Previously, only the detailed crystal structure of La$_3$TiSb$_5$ was determined.
from single-crystal X-ray diffraction, with only cell parameters for the remaining members in the RE$_3$TiSb$_5$ group [28]. The samples were prepared by using powdered elements combined in stoichiometric mixtures with a total weight of 0.250 g with 0.5 g of Sn flux. The mixture was heated at 570 °C for 1 day and at 950 °C for 2 days in an evacuated fused-silica tube. The Sn flux was centrifuged, and the remaining Sn was dissolved using 6 M HCl. The lattice parameters were all determined using powder x-ray diffraction, where the hexagonal P6$_3$/mcm space group was chosen with initial atomic positions taken from the earlier La$_3$TiSb$_5$ result.

The RE$_3$TiSb$_5$ samples were characterized by electrical resistivity and magnetization measurements [29]. Electrical resistivity from 2 to 300 K was measured along the needle axis, with an applied magnetic field perpendicular to the direction of the current. A broad structure was visible in the resistivity plots of the RE$_3$TiSb$_5$ compounds, with the curvature becoming less pronounced as the rare-earth metal is changed from La, Ce, Pr, Nd, to Sm. The compounds with La, Ce, and Nd become superconducting below 4 K, where the resistivity drop to 0 at $T = 3.7 - 4.1$ K was visible. The characterization of magnetic properties was made difficult as the samples were only 70-90% phase-pure. The main impurity was found to be elemental Sb, but no elemental Sn was detected.

More recently in 2017, detailed physical property measurements were conducted on Ce$_3$TiSb$_5$ [30]. Single crystals of La$_3$TiSb$_5$ and Ce$_3$TiSb$_5$ were grown using a Sn flux method. A high-purity, stoichiometric mixture of the elements of total 5 g were combined in an alumina crucible along with 10 g of Sn, then sealed in a quartz ampoule under a vacuum of $10^{-6}$ mbar. The mixture was heated to 1100 °C and kept there for 1 day, then cooled down to 550 °C for three weeks. The Sn flux was centrifuged out, but the formation of CeSb$_2$ was unavoidable. The specific heat measurement of a Ce$_3$TiSb$_5$ sample showed a large $\gamma$ value of $\sim$598 mJ/mol K$^2$, which is over 60 times larger than the $\gamma$ for La$_3$TiSb$_5$. Electrical resistivity Ce$_3$TiSb$_5$ clearly indicated a $-\log(T)$ dependence on temperature, demonstrating the presence of Kondo effect. The magnetization, electrical resistivity, and specific heat measurements of Ce$_3$TiSb$_5$ suggested that RKKY interaction is dominant over the Kondo interaction in the temperature range of less than 5.5 K, where the compound is in an antiferromagnetic ground state. The superconducting transition observed in both La and Ce compounds at $T = 3.7$ K were concluded to originate from the Sn flux in the samples.

1.4 Motivation

As far as we know, no single crystals of RE$_3$TMSb$_5$ (RE = La and Ce, TM = Zr and Hf) compounds have been previously grown and no detailed physical property measurements have been conducted on these compounds. Thus, we grew single crystals of La$_3$TMSb$_5$ and Ce$_3$TMSb$_5$ with TM = Ti, Zr, and Hf. The samples grown are indeed crystallized in the
hexagonal Hf₅Sn₃Cu-type structure (P6₃/mcm), confirmed from the x-ray diffraction data, which is consistent with earlier report [28]. Both La- and Ce-based samples are grown, in order to study 4f-electron magnetism offered by the Ce³⁺ ion in the compounds. The Ti group of transition metals are chosen to observe the changes in physical properties by varying the distance between Ce-ions as we replace the Ti with Zr and Hf.
Chapter 2

Experimental

All six of the compounds discussed in this thesis were grown using a Sn flux, where stoichiometric ratios of the elements in the target compound are placed along with Sn in an alumina crucible for growth, sealed in a silica tube. The ampoules were first heated to 1100 °C over a period of 2 hours, left to stay at 1100 °C for 4 hours, and followed by a cooling period of 198 hours down to 600 °C. The temperature profile of the furnace is shown in 2.1. The crucibles are taken out and centrifuged immediately in order to remove the Sn flux as much as possible. The grown RE₃TMSb₅ compounds form with needle-like morphology and the crystallographic c-axis is parallel to the needle axis.

In order to confirm the phase and determine lattice parameters, powder X-ray diffraction is performed on all six of the compounds in a Rigaku MiniFlex diffractometer at room temperature. Figure 2.2 summarizes the lattice parameters for all six of the grown RE₃TMSb₅ compounds along the a-axis and c-axis directions. Referenced lattice parameters are also shown for comparison [28, 29, 31]. The obtained lattice parameters and unit cell volumes are summarized in table 2.1. The DC magnetization M was measured on the samples in a Quantum Design Magnetic Property Measurement System (MPMS) in the temperature

![Figure 2.1: The temperature profile for the growth of single crystal RE₃TMSb₅ compounds.](image)
Table 2.1: The lattice parameters for the grown RE₃TMSb₅ compounds.

<table>
<thead>
<tr>
<th>Compound</th>
<th>a (Å)</th>
<th>c (Å)</th>
<th>V (Å³)</th>
</tr>
</thead>
<tbody>
<tr>
<td>La₃TiSb₅</td>
<td>9.532</td>
<td>6.278</td>
<td>494.7</td>
</tr>
<tr>
<td>La₃ZrSb₅</td>
<td>9.583</td>
<td>6.359</td>
<td>505.7</td>
</tr>
<tr>
<td>La₃HfSb₅</td>
<td>9.577</td>
<td>6.348</td>
<td>504.2</td>
</tr>
<tr>
<td>Ce₃TiSb₅</td>
<td>9.425</td>
<td>6.228</td>
<td>479.1</td>
</tr>
<tr>
<td>Ce₃ZrSb₅</td>
<td>9.494</td>
<td>6.313</td>
<td>492.8</td>
</tr>
<tr>
<td>Ce₃HfSb₅</td>
<td>9.477</td>
<td>6.300</td>
<td>490.0</td>
</tr>
</tbody>
</table>

Figure 2.2: The lattice parameters of the RE₃TMSb₅ compounds.
range of 1.8 to 300 K and an applied magnetic field up to 70 kOe. The samples were mounted on clear drinking straws and measurements were taken for both $H \parallel ab$ and $H \parallel c$. The specific heat of the samples was measured by the relaxation method in a Quantum Design Physical Property Measurement System (PPMS). The electrical resistivity of the samples were measured in a Quantum Design PPMS with a temperature range of 1.8 to 300 K and applied magnetic field up to 90 kOe, measured with the current directed along the $c$-axis. A four probe method was used, where four platinum leads with a radius of 50 $\mu$m were attached to the needle-shaped sample using Epotek H20E silver epoxy.

Previously, RE$_3$TMSb$_5$ (RE = La, Ce, Nd) compounds were reported to undergo a superconducting phase transition below 4 K [29]. We measured the electrical resistivity of as-grown samples, which also displayed superconducting phase transitions below 4 K. This behavior is most likely associated with the Sn flux remains trapped inside, or remaining on the surface. However, after etching the samples in HCl, the phase transition disappeared in all compounds, except the Ce$_3$TiSb$_5$ sample. Figure 2.3 shows the electrical resistivity of the HCl-etched Ce$_3$TiSb$_5$ sample below $T = 10$ K with an applied field of $H = 0$ or 1 kOe. The zero-field data displays a drop below 4 K, but does not go to 0 resistivity. The resistivity not decreasing all the way to zero suggests that the superconducting behaviour is not a bulk property of Ce$_3$TiSb$_5$. Although the sample is etched in one molar HCl prior to the measurements, all of the Sn could not be thoroughly removed. The critical field of Sn is only about $H = 300$ Oe, which explains the absence of the sudden decrease in resistivity in a magnetic field of 1 kOe. As such, we think the Sn flux was embedded inside Ce$_3$TiSb$_5$ sample chosen for measurement. In addition, the specific heat measurements of all six compounds indicate no anomaly corresponding to the resistivity drop, also confirming that the phase transition is not bulk in nature. The electrical resistivity at $H = 1$ kOe for Ce$_3$TiSb$_5$ will be treated as the zero field data in the low temperature region. Our results are consistent with a recent study on RE$_3$TiSb$_5$ (RE = La and Ce), which concluded that the superconductivity is an extrinsic property arising from the Sn flux [30].
Figure 2.3: The temperature dependence of the electrical resistivity $\rho$ for Ce$_3$TiSb$_5$ below 10 K.
Results

3.1 Magnetic Susceptibility and Magnetization

3.1.1 La$_3$TMSb$_5$

The magnetic susceptibility, $\chi \equiv M/H$, for La compounds is measured in an applied magnetic field of 70 kOe along the $c$-axis ($\chi_c$) and in the $ab$-plane ($\chi_{ab}$) from $T = 1.8$ to 300 K. Figure 3.1 (a) presents the temperature dependence of the magnetic susceptibility for La$_3$TiSb$_5$. As the temperature increases, $\chi_c$ displays a gradual decrease between $T = 1.8$ and 50 K, where it passes a minima, then proceeds to increase gradually, approaching around $-5 \times 10^{-6}$ emu/f.u. at $T = 300$ K. On the other hand, $\chi_{ab}$ is decreasing in the entire, measured temperature range, approaching $-3 \times 10^{-5}$ emu/f.u. at $T = 300$ K. It is noted that the $\chi_{ab}$ starts above the value of $\chi_c$ in the low temperature region, but is exceeded by $\chi_c$ at $T = 100$ K where a crossover occurs.

The magnetic field dependence of magnetization, $M(H)$, along the $c$-axis ($M_c$) and in the $ab$-plane ($M_{ab}$) for La$_3$TiSb$_5$ are presented in Fig. 3.1 (b). As magnetic field increases, $M_c$ decreases linearly to $-7.5 \times 10^{-5}$ $\mu_B$/f.u. at $H = 70$ kOe. On the other hand, $M_{ab}$ starts with a gradually increasing behaviour up to $\sim 20$ kOe, but slightly decreases as further increasing magnetic field. The anisotropy is pronounced in the $M$ plot, as $M_{ab}$ is always higher than the values of $M_c$.

Figure 3.2 (a) presents the temperature dependence of the magnetic susceptibility for La$_3$ZrSb$_5$ in an applied field of 70 kOe. A gradual decrease between $T = 1.8$ and 225 K is seen in $\chi_c$, then increases gradually, finally reaching around $-4 \times 10^{-5}$ emu/f.u. at $T = 300$ K. $\chi_{ab}$ decreases for the entire measurement range, approaching $-1.1 \times 10^{-4}$ emu/f.u. at $T = 300$ K. $\chi_{ab}$ begins above the value of $\chi_c$, but is exceeded by $\chi_c$ at $T = 60$ K. This phenomena where the value of $\chi_c$ eventually exceeds the value of $\chi_{ab}$ is also observed in La$_3$TiSb$_5$.

Figure 3.2 (b) presents $M(H)$ along the $c$-axis and in the $ab$-plane for La$_3$ZrSb$_5$. $M_c$ for La$_3$ZrSb$_5$ is similar to La$_3$TiSb$_5$. On the other hand, $M_{ab}$ displays a broad hump from
Figure 3.1: (a) The temperature dependence of the magnetic susceptibility $\chi$ for $\text{La}_3\text{TiSb}_5$. (b) The field dependence of the magnetization $M$ of $\text{La}_3\text{TiSb}_5$.

Figure 3.2: (a) The temperature dependence of the magnetic susceptibility $\chi$ for $\text{La}_3\text{ZrSb}_5$. (b) The field dependence of the magnetization $M$ of $\text{La}_3\text{ZrSb}_5$. 
Figure 3.3: (a) The temperature dependence of the magnetic susceptibility $\chi$ for La$_3$HfSb$_5$. (b) The field dependence of the magnetization $M$ of La$_3$HfSb$_5$.

$H = 0$ to $40 \text{ kOe}$, and a smooth decrease above $H = 40 \text{ kOe}$ to $-4 \times 10^{-5} \mu_B/\text{f.u.}$ at $H = 70 \text{ kOe}$. $M_{ab}$ is always greater than the values of $M_c$. This behaviour in $M$ for La$_3$ZrSb$_5$ is similar to what is seen in La$_3$TiSb$_5$.

$\chi_c$ and $\chi_{ab}$ for La$_3$HfSb$_5$ measured in an applied field of $70 \text{ kOe}$ are shown in figure 3.3 (a). $\chi_c$ displays a subtle, gradual increase for the entire temperature range of $T = 1.8$ to $300 \text{ K}$, which is almost flat on the scale shown in figure 3.3. On the other hand, $\chi_{ab}$ displays a gradual decrease until around $T = 200 \text{ K}$, where it begins to flatten, reaching a value of $-2.2 \times 10^{-4} \text{ emu/f.u.}$ at $T = 300 \text{ K}$. In La$_3$TiSb$_5$ and La$_3$ZrSb$_5$, $\chi_{ab}$ began lower than $\chi_c$, and eventually exceeded $\chi_c$ at some temperature, whereas $\chi_c$ is greater than $\chi_{ab}$ for the temperature range of $T = 1.8$ to $300 \text{ K}$ for La$_3$HfSb$_5$.

$M(H)$ for La$_3$HfSb$_5$ along the $c$-axis and in the $ab$-plane are presented in figure 3.3 (b). $M_c$ decreases linearly to $-2 \times 10^{-4} \mu_B/\text{f.u.}$ at $H = 70 \text{ kOe}$. This behaviour of $M_c$ for La$_3$HfSb$_5$ is similar to La$_3$TiSb$_5$ and La$_3$ZrSb$_5$. Somewhat similarly to $M_c$, $M_{ab}$ displays a linear decrease from 0 and approaching $-7 \times 10^{-4} \mu_B/\text{f.u.}$ at $H = 70 \text{ kOe}$. In La$_3$TiSb$_5$ and La$_3$ZrSb$_5$, $M_{ab}$ did not demonstrate a linearly decreasing behaviour throughout the applied field range of $H = 0$ to $70 \text{ kOe}$, like what is seen in the La$_3$HfSb$_5$. It is noted that $M_{ab}$ is greater than $M_c$ for La$_3$HfSb$_5$ between $H = 0$ to $70 \text{ kOe}$, but this is not the case for La$_3$TiSb$_5$ and La$_3$ZrSb$_5$.

### 3.1.2 Ce$_3$TiSb$_5$

Figure 3.4 presents the temperature dependence of the inverse magnetic susceptibility, $\chi_c^{-1}$ and $\chi_{ab}^{-1}$, measured in an applied field of $1 \text{ kOe}$ for Ce$_3$TiSb$_5$, which is consistent with earlier report [30]. The inverse magnetic susceptibility curves increase linearly above $175 \text{ K}$ for $\chi_c$ and above $150 \text{ K}$ for $\chi_{ab}$. The solid lines represents fits to the Curie-Weiss law: $\chi = C/(T - \theta_p)$, where $C$ is the Curie constant and $\theta_p$ is the Weiss temperature. From the
Figure 3.4: The temperature dependence of the inverse magnetic susceptibility $\chi^{-1}$ for Ce$_3$TiSb$_5$. The solid lines represent fits to the Curie-Weiss law. The open circular, square, and triangular symbols represent $\chi_c$, $\chi_{ab}$, and the polycrystalline average, respectively.

<table>
<thead>
<tr>
<th></th>
<th>$\mu_{eff}$ ($\mu_B$/Ce)</th>
<th>$\theta_p$ (K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ce$_3$TiSb$_5$</td>
<td>$\chi_c$</td>
<td>2.81</td>
</tr>
<tr>
<td></td>
<td>$\chi_{ab}$</td>
<td>2.58</td>
</tr>
<tr>
<td></td>
<td>$\chi_{poly}$</td>
<td>2.59</td>
</tr>
<tr>
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</tr>
<tr>
<td></td>
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<td>2.58</td>
</tr>
<tr>
<td></td>
<td>$\chi_{poly}$</td>
<td>2.60</td>
</tr>
<tr>
<td>Ce$_3$HfSb$_5$</td>
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<td>2.79</td>
</tr>
<tr>
<td></td>
<td>$\chi_{ab}$</td>
<td>2.60</td>
</tr>
<tr>
<td></td>
<td>$\chi_{poly}$</td>
<td>2.59</td>
</tr>
</tbody>
</table>

Table 3.1: The effective moment $\mu_{eff}$ and Curie-Weiss temperature $\theta_p$ for the Ce$_3$TMSb$_5$ (TM = Ti, Zr, Hf) samples. The values are obtained from a linear fit performed on the inverse magnetic susceptibility plot, $\chi_c^{-1}$, $\chi_{ab}^{-1}$, and $\chi_{poly}^{-1}$. 

17
fit, the effective moment $\mu_{\text{eff}}$ and Weiss temperature are estimated to be $\mu_{\text{eff}} = 2.81 \, \mu_B$/Ce and $\theta_p = -168 \, \text{K}$ for $H \parallel c$ and $\mu_{\text{eff}} = 2.58 \, \mu_B$/Ce and $\theta_p = 0 \, \text{K}$ for $H \parallel ab$. The $\mu_{\text{eff}}$ and $\theta_p$ values for the Ce-containing compounds are summarized in table 3.1. The significant difference between the obtained $\theta_p$ for $H \parallel c$ and $H \parallel ab$ is most likely associated with the crystalline electric field effect. The $\mu_{\text{eff}}$ and $\theta_p$ are also estimated from the polycrystalline average of the magnetic susceptibility, $\chi_{\text{poly}} \equiv \frac{1}{3} \chi_c + \frac{2}{3} \chi_{ab}$. The obtained value of $\mu_{\text{eff}} = 2.59 \, \mu_B$ for $\chi_{\text{poly}}$ is close to the theoretical value $\mu_{\text{eff}} = 2.54 \, \mu_B$ for the free Ce$^{3+}$ ion, indicating that the Ce atoms in the Ce$_3$TiSb$_5$ compound are in the Ce$^{3+}$ state. For $\chi_{\text{poly}}$, the Weiss temperature is found to be a negative value of $\theta_p = -27 \, \text{K}$, indicating antiferromagnetic exchange interactions between the Ce$^{3+}$ ions.

The magnetic susceptibility curves along the $c$-axis and in the $ab$-plane are shown in figure 3.5 in a semi-log scale. The magnitude of both $\chi_c$ and $\chi_{ab}$ for Ce$_3$TiSb$_5$ is about four orders of magnitude greater than the values measured for La$_3$TiSb$_5$. In the low temperature regime, below 100 K, a large anisotropy is observed between $\chi_c$ and $\chi_{ab}$. $\chi_{ab}$ indicates a
Figure 3.6: (a) The field dependence of the magnetization $M$ of Ce$_3$TiSb$_5$. The data displayed with open symbols and solid lines represents measurements conducted under an increasing magnetic field and a decreasing magnetic field, respectively. (b) The $M_{ab}$ data for Ce$_3$TiSb$_5$ is presented for temperatures $T = 2$, 3, 4, and 10 K.

peak at $T = 5.6$ K, whereas $\chi_c$ shows a kink at the same temperature. The peak in $\chi_{ab}$ suggests that there is an antiferromagnetic ordering below $T_N \sim 5$ K, determined by the peak position in $d(\chi T)/dT$ analysis. The inset of figure 3.5 displays the temperature dependence of $\chi_{ab}$ for $H = 1, 5, 10, 15, 20, 25$, and $30$ kOe. As the applied magnetic field is increased, the peak observed at $H = 1$ kOe shifts to a lower temperature, and is eventually suppressed below $T = 2$ K. The $\chi_{ab}(T)$ behaviour changes for applied fields above $H = 15$ kOe. For the $H = 15, 20$, and $25$ kOe data, no peak is detected, but a broad hump is seen instead. Broad humps are observed in the $H = 15$ kOe data at $T \sim 3$ and $5$ K. Similarly, a broad structure is seen in the $H = 20$ kOe data at $T \sim 4.5$ K, while a very subtle change in slope can be seen in the $H = 25$ kOe data around $T \sim 4.5$ K. As the applied field is further increased to $H = 30$ kOe, no broad structures are observed, indicating that the antiferromagnetic ordering is completely suppressed below $2$ K.

Figure 3.6 (a) shows the field dependence of magnetization, $M_c$ and $M_{ab}$, for Ce$_3$TiSb$_5$. A large anisotropy in the magnetization $M$ is observed. $M_c$ increases linearly, up to almost $0.2 \mu_B$/Ce at $H = 70$ kOe, whereas $M_{ab}$ shows steps involving metamagnetic transitions at $H = 7, 11, 21$ kOe, which are determined by $dM/dH$ analysis. This result is consistent with earlier study [30]. It is noted that $M_{ab}$ approaches a value around $0.85 \mu_B$/Ce at $H = 70$ kOe, which is only 40% of the theoretical, free ion saturation moment of Ce$^{3+}$ (2.14 $\mu_B$/Ce). Both $M_c$ and $M_{ab}$ are measured with an increasing and decreasing field, but no observable hysteresis is detected. The field dependence of $M_{ab}$ measured at $T = 2, 3, 4,$ and $10$ K are presented in figure 3.6 (b). As the temperature is increased to $T = 3$ K, the metamagnetic transitions visible at $T = 2$ K becomes less pronounced. Changes in the slope are seen at $H = 10$ and $21$ kOe in the $T = 3$ K data, albeit subtle in comparison to the $T = 2$ K data. At $T = 4$ K, the step-like behaviour is even further broadened, with a change
in $dM/dH$ observed at $H = 9$ and 19 kOe. At $T = 10$ K, the metamagnetic transitions are no longer observed.

### 3.1.3 Ce$_3$ZrSb$_5$

The temperature dependence of $\chi^{-1}_c$ and $\chi^{-1}_{ab}$ for Ce$_3$ZrSb$_5$ is presented in figure 3.7. A linear fit is performed on the inverse magnetic susceptibility data above 175 K for $\chi_c$ and above 150 K for $\chi_{ab}$. The values $\mu_{eff} = 2.85 \mu_B$/Ce and $\theta_p = -172$ K for $H||c$ and $\mu_{eff} = 2.58 \mu_B$/Ce and $\theta_p = -5$ K for $H||ab$ are obtained from the linear fits to the Curie-Weiss law. Similar to the Ce$_3$TiSb$_5$, Ce$_3$ZrSb$_5$ displays a significant difference between the obtained $\theta_p$ for $H||c$ and $H||ab$. The obtained value of $\mu_{eff} = 2.60 \mu_B$ for $\chi_{poly}$ is close to the theoretical value for the free Ce$^{3+}$ ion. For $\chi_{poly}$, the Weiss temperature is found to be a negative value of $\theta_p = -32$ K, indicating antiferromagnetic exchange interactions between the Ce$^{3+}$ ions in Ce$_3$ZrSb$_5$, which is also seen in Ce$_3$TiSb$_5$.

Figure 3.8 shows the magnetic susceptibility curves along the $c$-axis and in the $ab$-plane. $\chi_{ab}$ indicates a peak at $T = 5.1$ K, whereas $\chi_c$ shows a kink at the same temperature. The peak in $\chi_{ab}$ suggests that there is an antiferromagnetic ordering below 5.1 K. In the inset of figure 3.8, the temperature dependence of $\chi_{ab}$ for $H = 1, 2.5, 5, 10, 15,$ and $20$ kOe are shown. The peak observed at $H = 1$ kOe shifts to a lower temperature with increasing field, and is eventually suppressed below $T = 2$ K for $H > 20$ kOe.
Figure 3.8: The temperature dependence of the magnetic susceptibility $\chi$ for Ce$_3$ZrSb$_5$. In the inset, the temperature dependence of $\chi_{ab}$ is presented for applied magnetic fields of $H = 1, 2.5, 5, 10, 15, \text{ and } 20 \text{ kOe}$.

Figure 3.9: (a) The field dependence of the magnetization $M$ of Ce$_3$ZrSb$_5$. The data displayed with open symbols and solid lines represents measurements conducted under an increasing magnetic field and a decreasing magnetic field, respectively. (b) The $M_{ab}$ data for Ce$_3$ZrSb$_5$ is presented for temperatures $T = 2, 3, 4, \text{ and } 10 \text{ K}$.
Figure 3.10: The temperature dependence of the inverse magnetic susceptibility $\chi^{-1}$ for Ce$_3$HfSb$_5$. The solid lines represents fits to the Curie-Weiss law. The open circular, square, and triangular symbols represent $\chi_c$, $\chi_{ab}$, and the polycrystalline average, respectively.

The field dependence of magnetization for Ce$_3$ZrSb$_5$ are presented in figure 3.9 (a). $M_c$ increases linearly, up to 0.35 $\mu_B$/Ce at $H = 70$ kOe, whereas $M_{ab}$ shows a jump at $H = 12$ kOe. In Ce$_3$TiSb$_5$, multiple steps representing metamagnetic transitions are observed in $M(H)$, but only one step is observed in Ce$_3$ZrSb$_5$. $M_{ab}$ approaches a value around 0.75 $\mu_B$/Ce at $H = 70$ kOe, which is lower than the free ion saturation moment of Ce$^{3+}$. Figure 3.9 (b) presents the field dependence of $M_{ab}$ measured at $T = 2$, 3, 4, and 10 K. As the temperature is increased to 4 K, the steps become less pronounced, similar to what is seen in the Ce$_3$TiSb$_5$ data. The step is no longer observed at 10 K, and the field dependence becomes linear.

3.1.4 Ce$_3$HfSb$_5$

Figure 3.10 shows the temperature dependence of the inverse magnetic susceptibility for Ce$_3$HfSb$_5$. From the fit to the Curie-Weiss law, the values $\mu_{eff} = 2.79$ $\mu_B$/Ce and $\theta_p = -169$ K for $H||c$ and $\mu_{eff} = 2.60$ $\mu_B$/Ce and $\theta_p = -3$ K for $H||ab$ are found. The significant difference between the obtained $\theta_p$ for $H||c$ and $H||ab$ is clearly visible in Ce$_3$TiSb$_5$ and Ce$_3$ZrSb$_5$ data as well, and is most likely attributed to the crystalline electric field effect. For $\chi_{poly}$, the values $\mu_{eff} = 2.59$ $\mu_B$ and $\theta_p = -30$ K are obtained. For all three of the Ce-containing compounds, the $\mu_{eff}$ is close to the the theoretical value 2.54 $\mu_B$, indicating that the Ce atoms in the Ce$_3$TMSb$_5$ compounds are in the Ce$^{3+}$ state.
Figure 3.11: The temperature dependence of the magnetic susceptibility $\chi$ for Ce$_3$HfSb$_5$. In the inset, the temperature dependence of $\chi_{ab}$ is presented for applied magnetic fields of $H = 1, 5, 10, 15, 20, 25, 30, 35,$ and $40$ kOe.
Figure 3.12: (a) The field dependence of the magnetization $M$ of Ce$_3$HfSb$_5$. The data displayed with open symbols and solid lines represents measurements conducted under an increasing magnetic field and a decreasing magnetic field, respectively. (b) The $M_{ab}$ data for Ce$_3$HfSb$_5$ is presented for temperatures $T = 2$ and 10 K.

$\chi_c$ and $\chi_{ab}$ for Ce$_3$HfSb$_5$ are shown in figure 3.11. Below 100 K, a large anisotropy is observed between $\chi_c$ and $\chi_{ab}$, which is also demonstrated by Ce$_3$TiSb$_5$ and Ce$_3$ZrSb$_5$. $\chi_{ab}$ shows a peak at $T = 5.2$ K, whereas $\chi_c$ shows a kink at the same temperature. The peak in $\chi_{ab}$ is evidence that antiferromagnetic ordering occurs below 5.2 K. The temperature dependence of $\chi_{ab}$ for $H = 1$, 5, 10, 15, 20, 25, 30, 35, and 40 kOe is shown in figure 3.11. As the applied magnetic field is increased, the peak observed at $H = 1$ kOe moves towards a lower temperature. The $\chi_{ab}(T)$ behaviour changes above $H = 15$ kOe, as no peak is detected, but a broad hump is seen instead. As the applied field is further increased, the hump becomes less pronounced, and finally no longer observable at $H = 40$ kOe. The suppression of the peak below $T = 2$ K with an increasing field is also observed in the Ce$_3$TiSb$_5$ and Ce$_3$ZrSb$_5$ samples.

$M_c(T)$ and $M_{ab}(T)$ for Ce$_3$HfSb$_5$ are shown in figure 3.12 (a). $M_c$ increases linearly, up to 0.22 $\mu_B$/Ce at $H = 70$ kOe, whereas $M_{ab}$ shows slope changes at $H = 12$ and 28 kOe. It is noted that $M_{ab}$ approaches a value around 0.95 $\mu_B$/Ce at $H = 70$ kOe, which is significantly lower than the free ion saturation moment of Ce$^{3+}$. Both $M_c$ and $M_{ab}$ is measured with an increasing and decreasing field, but no hysteresis is observed. The field dependence of $M_{ab}$ measured at $T = 2$ and 10 K are presented in figure 3.12 (b). As the temperature is increased to $T = 10$ K, the slope changes detected at $T = 2$ K disappears, and the field dependence becomes smooth.
Figure 3.13: (a), (b), and (c) shows the temperature dependence of the electrical resistivity $\rho$ for $\text{La}_3\text{TiSb}_5$, $\text{La}_3\text{ZrSb}_5$, and $\text{La}_3\text{HfSb}_5$, respectively, with the current directed along the $c$-axis.
Figure 3.14: (a), (b), and (c) shows the temperature dependence of the electrical resistivity \( \rho \) for Ce₃TiSb₅, Ce₃ZrSb₅, and Ce₃HfSb₅, respectively, with the current directed along the \( c \)-axis. The insets show the low temperature region of \( \rho \), \( T \leq 10 \) K for Ce₃TiSb₅ and Ce₃ZrSb₅ and \( T \leq 35 \) K for Ce₃HfSb₅.

3.2 Resistivity

3.2.1 La₃TMSb₅ (TM = Ti, Zr, Hf)

Figure 3.13 (a), (b), and (c) shows the temperature dependence of electrical resistivity \( \rho(T) \) for La₃TMSb₅ (TM = Ti, Zr, and Hf). In zero field, the \( \rho(T) \) for all three compounds follows a metallic behavior, but with a broad peak structure at high temperatures around \( \sim 75 \) K for TM = Ti, \( \sim 220 \) K for Zr, and \( \sim 210 \) K for Hf. At low temperatures, \( \rho(T) \) for TM = Ti and Hf shows a saturation behavior, whereas \( \rho(T) \) for TM = Zr indicates an upturn below 10 K. The \( \rho(T) \) at \( H = 90 \) kOe for all three compounds shows a small, positive magnetoresistance at low temperatures.

3.2.2 Ce₃TMSb₅ (TM = Ti, Zr, Hf)

The temperature dependence of the electrical resistivity, \( \rho(T) \), for Ce₃TiSb₅ is shown in figure 3.14 (a). In zero field, the \( \rho(T) \) curve above \( T = 10 \) K displays a gradual increase, all
Figure 3.15: (a) The temperature dependence of specific heat $C_P(T)$ for La$_3$TiSb$_5$ and Ce$_3$TiSb$_5$. The solid line represents the calculated Dulong-Petit limit value, $C_P = 224.3$ J/mol-K. The inset shows the temperature dependence of $C_P$ for La$_3$TiSb$_5$ and Ce$_3$TiSb$_5$ in the low temperature region. (b) $C_P/T$ for La$_3$TiSb$_5$ and Ce$_3$TiSb$_5$ are shown. The solid lines represent the linear fit used to obtain the $\gamma$ and $\beta$ values.

the way up to $T = 300$ K, with a broad hump centred around $T = 100$ K. This temperature dependence is typical for the Kondo lattice compounds. The $\rho(T)$ below $T = 10$ K is shown in the inset of figure 3.14 (a). A minimum in the resistivity is seen around $\sim 5$ K, followed by a broad maximum around $\sim 4$ K. The derivative of the electrical resistivity with respect to the temperature, $d\rho(T)/dT$, in the low temperature region clearly shows a pronounced minimum at $T = 5.2$ K (see discussion), which corresponds to the peak position in the magnetic susceptibility. The low temperature broad feature observed in the resistivity is completely suppressed by external magnetic field of $H = 90$ kOe.

Figure 3.14 (b) and (c) presents the $\rho(T)$ for Ce$_3$ZrSb$_5$ and Ce$_3$HfSb$_5$, respectively. The $\rho(T)$ curves for both compounds follow typical Kondo lattice behavior. Unlike the Ce$_3$TiSb$_5$, a shallow minimum in the resistivity curve is clearly visible at $T = 37$ K for Ce$_3$ZrSb$_5$ and $T = 25$ K for Ce$_3$HfSb$_5$. At low temperatures, $\rho(T)$ for Ce$_3$ZrSb$_5$ demonstrates a kink as a signature of phase transition as shown in the inset of figure 3.14 (b). The resistivity curve for Ce$_3$HfSb$_5$ displays a sharp increase up to $T = 4.4$ K, where a peak is attained, with a dip at $T = 5.1$ K. From there, $\rho$ increases again to reach another peak at $T = 7.5$ K (inset (c)). The curve decreases until a shallow minima is approached around $T = 25$ K. The phase transition temperature is determined from the $d\rho/dT$ analysis (see discussion). In the $H = 90$ kOe data, the anomalies displayed by the $H = 0$ data is suppressed.
3.3 Specific Heat

3.3.1 La$_3$TiSb$_5$ and Ce$_3$TiSb$_5$

The temperature dependence of specific heat, $C_P(T)$, for La$_3$TiSb$_5$ and Ce$_3$TiSb$_5$ are shown in figure 3.15 (a). The $C_P(T)$ curves for both compounds reaches $\sim 224$ J/mol-K at 300 K, which is close to the Dulong-Petit limit [27]. It is noted that the $C_P(T)$ for Ce$_3$TiSb$_5$ is greater than La$_3$TiSb$_5$ below 300 K, where the difference can be attributed to the electronic Schottky contributions. The inset of figure 3.15 (a) shows $C_P(T)$ in the low temperature region, where the two compounds behave differently. The $C_P(T)$ for La$_3$TiSb$_5$ smoothly decreases to zero as the temperature is decreased, whereas Ce$_3$TiSb$_5$ has a pronounced peak at $T = 5.3$ K, indicating an antiferromagnetic transition. The difference in $C_P(T)$ between the two compounds is most likely associated with the magnetic Ce$^{3+}$ moments, as the two compounds are isostructural. Figure 3.15 (b) shows the $C_P(T)/T$ plotted against $T^2$ for each of the RE$_3$TMSb$_5$ compounds. It is noted that the $\gamma$ values for the Ce-based compounds are overestimated, as the fits are conducted over a much wider temperature range in comparison to the La-based compounds. The specific heat measurements for both La$_3$TiSb$_5$ and Ce$_3$TiSb$_5$ compounds are consistent with the earlier report [30].

3.3.2 La$_3$ZrSb$_5$ and Ce$_3$ZrSb$_5$

$C_P(T)$ for La$_3$ZrSb$_5$ and Ce$_3$ZrSb$_5$ are shown in figure 3.16 (a). Similarly to the Ti-based compounds, the obtained specific heat curves for both compounds approach a value close to the Dulong-Petit limit at 300 K and the $C_P$ of Ce$_3$ZrSb$_5$ is slightly greater than that of La$_3$ZrSb$_5$ below 300 K. At low temperatures, the $C_P(T)$ of La$_3$ZrSb$_5$ demonstrates a smooth decrease to zero as the temperature is decreased, whereas a peak is seen in Ce$_3$ZrSb$_5$ at $T = 4.7$ K with a kink at $T = 4.3$ K as shown in the inset of figure 3.16 (a). The $\gamma$ values are extracted from a linear fit on $C_P/T$ vs $T^2$, as shown in the figure 3.16 (b), where $\gamma = 235$ mJ/mol-K$^2$ and $\gamma = 10.84$ J/mol-K$^2$ for Ce$_3$ZrSb$_5$ and La$_3$ZrSb$_5$, respectively. The obtained Debye temperatures $\theta_D = 233$ K for La$_3$ZrSb$_5$ and $\theta_D = 213$ K for Ce$_3$ZrSb$_5$ are similar to the values obtained for the Ti-based compounds.

3.3.3 La$_3$HfSb$_5$ and Ce$_3$HfSb$_5$

Figure 3.17 (a) presents the specific heat for La$_3$HfSb$_5$ and Ce$_3$HfSb$_5$. Both compounds are in good agreement with the Dulong-Petit law, as they approach the expected value at $T =
Figure 3.16: (a) The temperature dependence of specific heat $C_P(T)$ for $\text{La}_3\text{ZrSb}_5$ and $\text{Ce}_3\text{ZrSb}_5$. The solid line represents the calculated Dulong-Petit limit value, $C_P = 224.3$ J/mol-K. The inset shows the temperature dependence of $C_P$ for $\text{La}_3\text{ZrSb}_5$ and $\text{Ce}_3\text{ZrSb}_5$ in the low temperature region. (b) $C_P/T$ for $\text{La}_3\text{ZrSb}_5$ and $\text{Ce}_3\text{ZrSb}_5$ are shown. The solid lines represent the linear fit used to obtain the $\gamma$ and $\beta$ values.

Figure 3.17: (a) The temperature dependence of specific heat $C_P(T)$ for $\text{La}_3\text{HfSb}_5$ and $\text{Ce}_3\text{HfSb}_5$. The solid line represents the calculated Dulong-Petit limit value, $C_P = 224.3$ J/mol-K. The inset shows the temperature dependence of $C_P/T$ for $\text{La}_3\text{HfSb}_5$ and $\text{Ce}_3\text{HfSb}_5$ in the low temperature region. (b) $C_P/T$ for $\text{La}_3\text{HfSb}_5$ and $\text{Ce}_3\text{HfSb}_5$ are shown. The solid lines represent the linear fit used to obtain the $\gamma$ and $\beta$ values.
Table 3.2: $\gamma$ and $\theta_D$ values and ordering temperature $T_N$ for the grown $\text{RE}_3\text{TMSb}_5$ compounds.

300 K. The inset of figure 3.17 (a) shows the low temperature region of $C_P$ to inspect the peak displayed by $\text{Ce}_3\text{HfSb}_5$. The peak occurs at $T = 4.6$ K, whereas no peak is seen in $\text{La}_3\text{HfSb}_5$. Figure 3.17 (b) shows the $C_P/T$ to show the linear fits conducted to obtain the $\gamma$ values and Debye temperatures. The obtained values are $\gamma = 298$ mJ/mol-K$^2$ for $\text{Ce}_3\text{HfSb}_5$ and $\gamma = 9.45$ mJ/mol-K$^2$ for $\text{La}_3\text{HfSb}_5$. Debye temperatures of $\theta_D = 218$ and 232 K were obtained for $\text{Ce}_3\text{HfSb}_5$ and $\text{La}_3\text{HfSb}_5$, respectively. The estimated Debye temperatures for the Hf-based compounds are close to those obtained from Ti- and Zr-based compounds.
Chapter 4

Discussion

At low temperatures, all three Ce-based compounds show signatures of antiferromagnetic (AFM) ordering. The AFM ordering temperature can be determined from different measurements. The feature in magnetic specific heat with simple AFM order is similar to \( d\rho/dT \) and \( d(\chi T)/dT \) at the ordering temperature [32–35].

Figure 4.1 summarizes the location of the peaks observed in both the magnetic specific heat \( C_m(T) \) and the temperature derivative of magnetic susceptibility \( d\chi_{ab}(T)/dT \) curves for the Ce\(_3\)TMSb\(_5\) compounds, as well as the sharp slope change seen in the temperature derivative of the electrical resistivity \( d\rho(T)/dT \). Here, the \( C_m \) for the Ce\(_3\)TMSb\(_5\) group of compounds is defined as the \( C_P \) for Ce\(_3\)TMSb\(_5\) subtracted by the \( C_P \) for La\(_3\)TMSb\(_5\). Ce\(_3\)TiSb\(_5\) indicates a peak at \( T \sim 5.3 \) K in \( C_m(T) \), while a minimum at slightly lower temperature \( T \sim 5.2 \) K in \( d\rho(T)/dT \) and a maximum at \( T \sim 5 \) K in the \( d\chi_{ab}(T)/dT \). For the Ce\(_3\)HfSb\(_5\) compound, the general trend is very similar to that of Ce\(_3\)TiSb\(_5\), with a peak in both \( C_m(T) \) and \( d\chi_{ab}(T)/dT \) at \( \sim 4.6 \) K and a minimum in \( d\rho(T)/dT \) at \( \sim 4.6 \) K. Since the resistivity of Ce\(_3\)TiSb\(_5\) and Ce\(_3\)HfSb\(_5\) shows an enhancement below the magnetic ordering temperature due probably to the formation of magnetic superzone gap, the derivative curve doesn’t follow well the magnetic part of the specific heat. Ce\(_3\)ZrSb\(_5\) behaves differently from the Ti- and Hf-containing samples, where the specific heat displays two visible structures. The location of the slope changes are at \( T \sim 4.3 \) and 4.7 K, which we define as our \( T_N \) values for \( C_m(T) \). Similarly to \( C_m(T) \), the \( d\chi_{ab}(T)/dT \) displays two peaks at \( T \sim = 4.1 \) and 4.8 K. In contrast to the Ce\(_3\)TiSb\(_5\) and Ce\(_3\)HfSb\(_5\), the \( d\rho(T)/dT \) for Ce\(_3\)ZrSb\(_5\) displays a peak at \( T = 4.3 \) K and a sharp kink at \( T = 5 \) K. We define the peak position and the location between the peak and sharp kink to be the phase transition temperatures. The determined \( T_N \) values for all three of the Ce\(_3\)TMSb\(_5\) compounds are summarized in table 3.2.

The determined \( T_N \) is lower for both Ce\(_3\)ZrSb\(_5\) and Ce\(_3\)HfSb\(_5\), in comparison to Ce\(_3\)TiSb\(_5\). Referring back to the lattice parameters summarized in figure 2.2, it is noted that the Ce\(_3\)TiSb\(_5\), which has the smallest lattice parameters across the Ce\(_3\)TMSb\(_5\) samples, re-
Figure 4.1: The location of anomalies observed in the $d\rho(T)/dT$, $d\chi_{ab}(T)/dT$, and $C_m(T)$ for the Ce$_3$TMSb$_5$ compounds. The y-axis is chosen to be arbitrary values. The vertical lines are guided to the eye.
Figure 4.2: The linear fit in $T^2$ conducted on $C_m(T)/T$ for all three of the $\text{Ce}_3\text{TMSb}_5$ ($\text{TM} = \text{Ti, Zr, Hf}$) compounds in the low temperature region.

sulted in the highest ordering temperature $T_N$. When replacing the Ti with Zr, the lattice parameters showed an increase, while replacing the Zr with Hf showed a subtle decrease. In a local moment metallic systems with a simple approximation, the strength of the RKKY interaction is dependent on the distance between magnetic ions within the crystal lattice, which explains the lower $T_N$ values for the $\text{Ce}_3\text{ZrSb}_5$ and $\text{Ce}_3\text{HfSb}_5$ samples. However, according to the measured lattice parameters (distance between Ce-ions), the $T_N$ for $\text{Ce}_3\text{ZrSb}_5$ is expected to be lower than the $T_N$ for $\text{Ce}_3\text{HfSb}_5$, but this is not the case. Thus, it has to be considered additional contributions such as Kondo effect.

As seen in the figures 3.14 (a), (b), and (c), each of the $\text{Ce}_3\text{TMSb}_5$ compounds display a minimum in the resistivity $\rho(T)$ plots, which is a characteristic observed across Kondo lattice systems [5]. As summarized in table 3.1, the Curie-Weiss temperature $\theta_p$ for the $\text{Ce}_3\text{TMSb}_5$ are all negative values, indicating that the AFM exchange interaction is dominant. The $\theta_p$ value for the polycrystalline average (order of $-30$ K) is much bigger than the magnetic ordering temperature, which is typical for the Kondo lattice systems. Further, the Kondo effect is evidenced from the specific heat measurement.

The Ce-based compounds all have a high $\gamma$ value around $\gamma \sim 300$ mJ/mol-K$^2$, estimated from the high temperature $C/T$ vs $T^2$ plots (figures 3.15 (b), 3.16 (b), and 3.17 (b)), which is a property of compounds exhibiting the Kondo effect. Since the high temperature specific heat can be affected by the Schottky contribution (discussed below), the $\gamma$ values are also estimated from the magnetic part of specific heat at low temperatures.
Figure 4.3: The temperature dependence of the magnetic contributions to specific $C_m(T)$ for all three Ce$_3$TMSb$_5$ (TM = Ti, Zr, Hf) compounds. The temperature axis is plotted on a logarithmic scale.

Figure 4.2 shows the linear fits conducted on the $C_m(T)/T$ in $T^2$ below $T_N$ for Ce$_3$TiSb$_5$, Ce$_3$ZrSb$_5$, and Ce$_3$HfSb$_5$. All three of the obtained $\gamma$ values are $\gamma \sim 1.5$ J/mol-K$^2$ for Ce$_3$TiSb$_5$, $\gamma \sim 0.7$ J/mol-K$^2$ for Ce$_3$ZrSb$_5$, and $\gamma \sim 1.7$ J/mol-K$^2$ for Ce$_3$HfSb$_5$. The $\gamma$ values extracted from the low temperature specific heat are significantly larger than the high temperature $\gamma$ values, which can be due to the magnetic contribution below $T_N$ and probably due to the Schottky contribution above $T_N$. For Ce$_3$TiSb$_5$, the $C_p/T$ vs $T^2$ is linear over the temperature range 0.1 K to 0.4 K, resulting $\gamma \sim 598$ mJ/mol-K$^2$ [30]. Note that the current specific heat measurement down to 1.8 K for Ce$_3$TiSb$_5$ is consistent with earlier report [30]. Thus, it is necessary to perform specific heat measurement below 1.8 K to properly extract the $\gamma$ value.

Figure 4.3 shows $C_m$ for Ce$_3$TiSb$_5$, Ce$_3$ZrSb$_5$, and Ce$_3$HfSb$_5$ with the temperature axis plotted on a logarithmic scale. The sharp peaks seen in the $C_P$ for the Ce$_3$TMSb$_5$ compounds at around $T = 5.3$ K are visible in $C_m$, with another broad peak centred at $T \sim 100$ K. The sharp peaks at low temperatures are associated with the antiferromagnetic
Figure 4.4: The entropy calculated from the magnetic part of specific heat for the Ce$_3$TMSb$_5$ compound.

ordering. The high temperature broad peak is a result of the electronic Schottky contributions. By using the equation 1.13, the energy level splitting of the $J = 5/2$ Hund’s rule ground state of Ce$^{3+}$ ion is estimated. The solid line in figure 4.3 is a fit curve for Ce$_3$TiSb$_5$ with three doublets, where the energy level splittings are $E_1 = 165$ K and $E_2 = 380$ K. We note that the fit was focused on the low-temperature range of the peak, as the high-temperature region is not as reliable, due to amplified subtraction errors. The obtained energy level splittings is in relatively good agreement with the values $E_1 = 178$ K and $E_2 = 336$ K estimated from $\chi(T)$ data in the previous study [30]. The Schottky peak for Ce$_3$ZrSb$_5$ and Ce$_3$HfSb$_5$ are very close in magnitude and location to the peak observed in Ce$_3$TiSb$_5$, indicating that all three compounds present a similar CEF effect.

Figure 4.4 shows the magnetic entropy $S_m(T)$, which is the integral of the $C_m/T$ with respect to $T$, for the three Ce$_3$TMSb$_5$ compounds. The $S_m(T)$ reaches a value of $\sim 0.6R \ln(2)$ at $T_N$, which is smaller than $R \ln(2)$ expected for a doublet ground state. This lower $S_m$ value at $T_N$ is a clear indication of the Kondo effect. The estimated entropy for all three compounds approaches or slightly exceeds the $R \ln(4)$ around $T = 165$ K, which clearly
indicates the energy level splitting of $J = 5/2$ state due to the CEF effect. The magnetic susceptibility curves for three compounds shows a deviation from the Curie-Weiss law below 150 K, which reflects the contribution from the CEF effect and Kondo interaction.
Chapter 5

Summary

We have grown single crystals of $\text{RE}_3\text{TMSb}_5$ ($\text{RE} = \text{La}$ and Ce, $\text{TM} = \text{Ti}$, Zr, and Hf), which crystallize in the hexagonal $\text{Hf}_3\text{Sn}_3\text{Cu}$-type structure ($\text{P6}_3/\text{mcm}$). The obtained thermodynamic and transport data show that $\text{Ce}_3\text{TMSb}_5$ compounds are antiferromagnetic Kondo lattices with a strong crystalline electric field effect. The magnetic susceptibility measurements indicate that the $\text{Ce}^{3+}$ ions are well localized at high temperatures. The specific heat, resistivity, and magnetic susceptibility measurements confirm that all three Ce-based compounds undergo antiferromagnetic transitions below $\sim5.3$ K. All three compounds reveal similar phase transition temperature, implying similar RKKY interaction among the Ce-ions. The Kondo interaction is evident from the $-\log(T)$ dependence in the resistivity and the large negative Curie-Weiss temperature in the magnetic susceptibility. The large $\gamma$ value in the specific heat suggests that $\text{Ce}_3\text{TMSb}_5$ compounds are new heavy fermion compounds. The analysis of the magnetic part of the specific heat confirms that the ground state of title compounds is doublet and well separated from the first and second excited states. We also confirm that the superconducting phase transition in these family arises from the residual Sn flux. For the $\text{La}_3\text{TMSb}_5$ compounds, the electrical resistivity shows a broad anomaly at high temperatures. Further measurements are desirable in order to understand the origin of the anomaly.
Bibliography


