Searching for heavy fermion materials in Ce intermetallic compounds

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Searching for heavy fermion materials in Ce intermetallic compounds

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in Ce intermetallic compounds

by

Jinke Tang

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I. INTRODUCTION

A. Heavy Fermions

It is well known that the low temperature heat capacity, $C$, of an ordinary metallic material as a function of temperature, $T$, can be written as

$$C = \gamma T + \beta T^3.$$  \hspace{1cm} (1)

The linear term in Equation (1) is the electronic contribution to the heat capacity, and $\gamma$ is the temperature independent linear coefficient known as the electronic specific heat coefficient. The cubic term is lattice heat capacity with

$$\beta = \frac{1944}{\Theta_D^3} \text{ J/gram atom K}^4,$$  \hspace{1cm} (2)

where $\Theta_D$ is the Debye temperature of the lattice [1]. When $C/T$ is plotted against $T^2$ a straight line is obtained. The intercept of this straight line with $C/T$ axis is $\gamma$, and $\gamma$ is of the order of a few mJ/gram atom K$^2$ in an ordinary metal. $\beta$ is the slope of this line.

In some intermetallic compounds where one of the constituents is a rare earth or actinide atom with a partially filled $4f$ or $5f$ electron shell, it is found that the straight line behavior in the $C/T$ versus $T^2$ plot no longer holds. In contrast to common metallic materials, the $\gamma$ is temperature
dependent and the resulting value for $\gamma$ when $T$ approaches 0K is extraordinarily large, about two orders of magnitude larger than in ordinary metals. Figure 1 shows the low temperature heat capacities as $C/T$ versus $T^2$ of CeAl$_3$, UPt$_3$ and UCd$_{11}$, which are typical heavy fermion materials [2]. As can be seen, the $\gamma(T)$ values start to increase with decreasing temperature at ~10K for CeAl$_3$ and UPt$_3$. This increase continues until $T$ approaches 0K, with $\gamma(0) = 1620$ mJ/mole K$^2$ for CeAl$_3$ [3] and $\gamma(0) = 450$ mJ/mole K$^2$ for UPt$_3$ [4]. These huge $\gamma$ values are one of the most important characteristics of this type of material. The $\lambda$-peak in UCd$_{11}$ is due to an antiferromagnetic ordering at $T_N = 5.0K$ [5]. Above the ordering temperature, $\gamma$ is almost temperature independent and has a large value of 840 mJ/mole K$^2$ [5]. About 30% of this large value remains even after the system orders antiferromagnetically. Data below 1K give $\gamma(0) = 250$ mJ/mole K$^2$ for UCd$_{11}$. It is another interesting fact that a large $\gamma$ is also found for magnetically ordered state. Actually a large $\gamma (> 250$ mJ/mole K$^2$) was also found in a magnetically ordered material UCu$_5$ by Ott et al. [6].

As the first step towards the understanding of the origin of these large $\gamma(T)$ values at low temperature, we adopt the free electron form for the electronic specific heat coefficient [7]

$$\gamma = \left(\frac{k_B^2 \pi^2}{3}\right) N(E_F) \frac{m^*}{k_F^2},$$

(3)
Fig. 1. C/T versus $T^2$ plot of CeAl$_3$, UPt$_3$ and UCd$_{11}$ [2]
where $k_B$ is the Boltzmann's constant, $N(\varepsilon_F)$ is the density of electronic states at the Fermi level $\varepsilon_F$, $k_F$ is the wave vector at Fermi surface, $h$ is the Planck's constant, and $m^*$ is the effective mass of electrons. We can see that a large value of $\gamma$ must be interpreted as evidence for enormous density of states at $\varepsilon_F$. This in turn implies a large effective mass, $m^*$, for the electrons involved (Equation 3). Hence the name "heavy fermion" or "heavy electron" are used for these systems.

This large effective mass is also evident in low temperature magnetic susceptibility. At high temperature, the magnetic susceptibilities of the heavy fermion materials behave just like ordinary metals, following the Curie-Weiss law,

$$\chi(T) = C/(T-\theta_p),$$

(4)

where $C$ is the Curie constant, and $\theta_p$ is the paramagnetic Curie temperature. $\theta_p$ is found to be negative for all the heavy fermion materials. The effective moments, $P_{eff}$, deduced from Curie constant, $C$, are usually close to those expected for the free-ion moments of respective 4f or 5f electron carrying ions. This indicates the localized and independent nature of the 4f or 5f electrons in heavy fermion materials. As temperature decreases, deviations from Curie-Weiss behavior are observed. The magnetic susceptibility, $\chi(T)$, becomes almost temperature independent, a behavior which is characteristic of Pauli
paramagnetism. And $\chi$ values are quite enhanced, two or more orders of magnitude larger than Pauli paramagnetic susceptibility in ordinary metals. Again, if we adopt free electron form for the Pauli susceptibility of electrons \[8\],

$$\chi = \mu_B^2 N(\epsilon_F) = \left(\frac{\mu_B^2 k_F}{\hbar^2 \pi^2}\right) m^*,$$

where $\mu_B$ is the Bohr magneton, it is obvious that the large $\chi$ comes from the large density of state at $\epsilon_F$, or large effective mass, $m^*$, of the electrons involved. This means that both the huge electronic specific heat coefficient and the enhanced Pauli-type susceptibility at low temperature are essentially from the same origin. As a matter of fact, the ratio $\chi(0)/\gamma(0)$ obtained from experiments for these heavy fermion materials \[9\] falls indeed in the vicinity of that expected for an ordinary metal.

Electrical resistivity, $\rho(T)$, is another physical property in which heavy fermion materials show distinguishing features. In ordinary metals, $\rho(T)$ decreases rapidly from room temperature values, (1-10 $\mu\Omega cm$), with decreasing temperature below 300K. While in heavy fermions, the $\rho(T)$ has little temperature dependence at room temperature and is usually rather high, of the order of 100 $\mu\Omega cm$ \[10\]. Instead of dropping to lower values upon cooling, the resistivity is found to increase with decreasing temperature before it reaches a maximum at a temperature $T_{\text{max}}$ ($T_{\text{max}}$ is normally less than ~50K). After passing over the
maximum, \( p \) drops significantly to a residual value of resistivity determined by impurities and crystal lattice imperfections. At very low temperature, \( p \) often can be cast in the form [3,11]

\[
\rho(T) = \rho_o + AT^2,
\]

where \( \rho_o \) is the residual resistivity, and \( A \) is a numerical factor. One of the most characteristic and common features for heavy fermions is this rapid drop in \( \rho(T) \) below \( T_{\text{max}} \). To explain this phenomenon, it is proposed that the 4f or 5f electrons, which act as local individual scattering centers for conduction electrons at high temperature, somehow form a coherent state at low temperature so that conduction electrons can coherently propagate through the periodic f electron set in the same way that a wave propagates through a perfect lattice. This explains the drop in resistivity mentioned earlier. How and when this coherent state develops is an open question that needs to be answered.

There are many other important experimental aspects about heavy fermions, e.g., some heavy fermions go to superconducting at low temperature, and the mechanism for the superconductivity is believed to be nonconventional. Due to our primary interest, only the normal state properties were discussed above.

The essential physical picture of heavy fermions can be described as follows. At high temperature, these rare earth or
actinide intermetallic compounds act no differently than ordinary compounds with local moments arising from the partially filled 4f or 5f shell. At low temperature, instead of going to magnetically ordered state, the local f electrons and conduction electrons become more and more strongly coupled, and at the same time a coherent state is developed among the f electrons. The effective mass, $m^*$, describing this highly correlated electron system becomes strongly enhanced over ordinary metals. The theoretical understanding of the heavy fermion system is just at its beginning. A variety of models has been proposed. Several approaches have given some hope to finally open the door to the physics of heavy fermions.

Anderson lattice model is now under a concentrated study. Although a detailed and satisfactory result is lacking, some features are understood. In this approach [2,12], f electrons are treated as localized with energy level $-1eV$ below $\varepsilon_F$. The coupling between the local f electron and conduction electrons through their spins is of the antiferromagnetic type. This coupling induces a cloud of conduction electrons with antiparallel spin about f electron, which screens out the local moment of the f electron. This accounts for the disappearance of the local moment at low temperature in heavy fermion materials. The electron cloud shows up as a resonance state at Fermi level
$\varepsilon_F$ and plays an important role in determining the large effective mass, $m^*$. This is the so called Kondo effect. Furthermore, the RKKY interaction between local $f$ electrons mediated by the conduction electrons, which is the result of the coupling just mentioned, gives rise to an antiferromagnetic correlation among $f$ electrons. Some believe that the fluctuation of this correlation provides a base for the interaction between the conduction electrons, and it is this interaction between conduction electrons that induces a large density of state of conduction electrons at $\varepsilon_F$, thus explaining the enormous electronic specific heat coefficient. According to this model, the large effective mass is not due to large density of state of $f$ band at $\varepsilon_F$, rather it is from the conduction electrons themselves. This seems quite attractive because we can possibly separate the magnetic behavior of local $f$ electrons from the itinerant heavy fermion behavior of conduction electrons. Therefore one can easily explain the coexistence of heavy fermion behavior and magnetic ordering discussed earlier.

Band structure calculations give a totally different approach. Calculations have been carried out for many heavy fermion systems. Examples are CeSn$_3$ [13,14], CeCu$_2$Si$_2$ [15], UA1$_2$ [16], UBe$_{13}$ [17,18] and UPt$_3$ [18-21]. All the band structure calculations assume the narrow $f$ band pinned at $\varepsilon_F$. Since the
spacings between f electrons in these heavy fermion compounds are relatively large, direct f-f overlap is absent, and the hybridization with non-f electrons of neighboring atoms dominates the f band width [22]. Although these calculations result in a relatively narrow f band width (~1eV), i.e., a relatively large density of state at $\varepsilon_F$, it is still much smaller than the experimental value. The inclusion of the interaction between f electrons by calculation of renormalized band structure of quasiparticles [9] seems to be necessary. In fact the view that the correlation between f electrons is responsible for the very narrow f band in heavy fermions offers the only possible solution. Here we mention the work of F. Marabelli and P. Wachter [23]. In their low energy far-infrared (FIR) and point contact spectroscopy (PCS) experiments, they find that two narrow quasiparticle bands (in meV range) with f characteristics exist at and near $\varepsilon_F$ for various heavy fermion materials. They also demonstrated that the extraordinary heat capacities, magnetic susceptibilities and resistivities can be explained by the electronic structures consisting of two quasiparticle bands.

Fermi liquid theory is another approach that has been extensively investigated. The Pauli-type low temperature magnetic susceptibility and the $T^2$ behavior of resistivity both suggest the Fermi liquid behavior. The Fermi liquid theory also
predicts the $T^3 \ln T$ term in the heat capacities of some heavy fermion materials like UPt$_3$ [24,25]. According to this theory, spin fluctuations play an important role in determining the large effective mass, $m^*$. Fermi liquid theory was developed by Landau in describing liquid $^3$He system [26]. The similarity between liquid $^3$He and heavy fermion is that both systems consist of localized interacting Fermi particles ($^3$He atom in liquid $^3$He and the $f$ electron in heavy fermion). But they are different in that liquid $^3$He is a isotropic system while the $f$ electrons are influenced by crystalline anisotropy and the spin-orbit effect. So far this theory can only handle the isotropic case with no spin-orbit coupling as in $^3$He. Therefore the important crystalline anisotropy and spin-orbit effects in heavy fermions have not been included in the theory. In addition, this theory provides little detail about the electronic structure of heavy fermion system compared with the other two models discussed above.

Although there are several theoretical models, we still have a long way to go to reach the complete understanding of the heavy fermion systems. First, it is obvious that three approaches gave three different physical pictures of the heavy fermion. For example, in the Anderson lattice model, the $f$ electron level is below $\varepsilon_F$ with a localized character, while the $f$ electrons in
band structure calculations are assumed to be itinerant forming a narrow band at $\varepsilon_F$. The answers to the origin of the large effective mass, $m^*$, are different: in the Anderson lattice model it is from highly correlated conduction electrons; in the band structure model it is from the narrow $f$ electron band; and in the Fermi liquid model it is from spin fluctuations. These three different pictures are surely, in some way, related, but we do not know how at the present time.

Second, no theory has given a satisfactory explanation of the transition from a independent local $f$ electron state at high temperature to a correlated coherent state at low temperature. Little is known about how and when this coherent state develops as temperature is lowered.

Third, the competition between RKKY interaction, which favors magnetic ordering, and the $f$-conduction electron coupling, which favors demagnetization of local $f$ moment, is a puzzling question. On one hand, RKKY interaction seems to be important to bring about the magnetic ordering; on the other hand, strong $f$-conduction electron coupling is necessary to explain the large density of state. This coexistence of the two opposite tendencies is clearly seen in the cases where heavy fermion behaviors are found in magnetic ordered materials. Although Anderson lattice model, which separates the magnetic behavior of
f electron from heavy fermion behavior of conduction electron, gives us some hope. But it only provides some expectations, and an extensive study of this model is needed.

One important reason that we do not understand so much about heavy fermion behavior is that we still do not know all the experimental aspects of this group of materials. Searching for new heavy fermion systems is an excellent way to enrich our knowledge. We can learn new experimental facts as well as testing the existing theories. Even if we do not find new heavy fermions, the comparison of the physical properties of the already known heavy fermions and those of the non-heavy fermions can provides some useful information. The primary purpose of this research is to search for heavy fermion materials in Ce intermetallic compounds.

B. Occurrence of Heavy Fermion Materials

The number of reported heavy fermion compounds has increased rapidly during the last several years. Conditions under which the formation of heavy fermion state occurs has been studied by many authors.

It was suggested by Hill [27] that the occurrence of superconductivity and magnetic ordering in rare earth or actinide
compounds depends upon the spacing between the f electron atom in
the lattice. For a sufficiently short f-f spacing (less than
Hill limit = 3.4Å), the overlap of neighboring f wavefunctions
leads to the formation of broad f band which favors a
superconducting or non-magnetic ground state. For large f-f
spacing, the f electrons are essentially localized, hence
magnetically ordered state occurs. All the heavy fermion
materials are found to lie within the magnetic regime with f-f
spacings larger than Hill limit or at least close to it. Figure
2 shows the electronic specific heat coefficient γ of some
typical heavy fermion materials and related compounds versus
their f-f spacings [22]. The fact that no heavy fermion was
found in cases where f-f spacings are less than Hill limit
suggests that the formation of broad f band by overlapping of
neighboring f wavefunction prohibits heavy fermion behavior. The
Hill limit provides a necessary condition, but not a sufficient
one, for the occurrence of heavy fermions. Our study of some Ce
intermetallic compounds confirmed this point.

The local environment about the f electron is important.
Many heavy fermion materials with large f-f spacing show no sign
of magnetic ordering down to the lowest temperature possible.
This is because the local moment of f electron is believed to be
Fig. 2. The electronic specific heat coefficient versus \( f-f \) spacing of some typical heavy fermion materials and related compounds [22]
smeared out either by a cloud of conduction electrons of antiparallel spin around it as discussed in Anderson model, or by hybridization with the conduction electrons of neighboring non-f-atom [22]. Both indicate the importance of local environment about the f electron. So far, all the heavy fermion materials are found where one of the constituents is at the end of d-block such as Pt or the beginning of sp-blocks such as Al in the periodic table. The role played by these "d" or "sp" electrons of neighboring non-f-atom is still not well understood. Our interest is to investigate the low temperature properties of some Ce-Cd, Ce-Zn, Ce-Hg, Ce-Ir, Ce-Pt and Ce-Ga binary compounds and some related Ce ternary compounds.

Certain crystal structures seem to favor heavy fermion behavior. Since the local environment of f electron is important, the crystal structure, which determines this environment by changing the nearest neighbors, the symmetries and lattice parameters, is surely a big factor in the formation of the heavy fermion state. Both heavy fermions CeAl₃ [3] and UPt₃ [4] crystallize in hexagonal Ni₃Sn-type structure. It is of interest to study the behavior of isostructural compound CeHg₃. The result of our study is given in this thesis.

Another crystal structure worth mentioning is cubic AuCu₃-type structure. Several this type of compounds show heavy
fermion or spin fluctuation behaviors. Examples are USn$_3$ with $\gamma \sim 170$ mJ/mole $K^2$ [28], CeSn$_3$ with $\gamma \sim 53$ mJ/mole $K^2$ [29] and CePb$_3$ with $\gamma \sim 200-1400$ mJ/mole $K^2$ (depending on sample preparation) [30,31]. On the other hand, several of them form antiferromagnetically ordered states, e.g., CeIn$_3$, UPb$_3$ and UIn$_3$ order at 10K, 31.8K and 108K, respectively [28]. The Ce and U based AuCu$_3$-type intermetallic compounds has provided an excellent area to explore the nature of heavy fermion, spin fluctuations, magnetism and their interrelationships.

The cubic AuBe$_5$ structure also seems to favor heavy fermion behavior. UCu$_5$, which crystallizes in this type of structure, shows a heavy fermion behavior within the magnetically ordered state. The coexistence of the heavy fermion state and the magnetic state in UCu$_5$ is an important experimental fact. UPt$_5$ also shows a intermediate heavy fermion behavior with $\gamma \sim 92$ mJ/mole $K^2$ [32]. By replacing one Pt atom with an Au atom, UAuPt$_4$ shows a significant enhancement, $\gamma \sim 725$ mJ/mole $K^2$ [33]. The isostructural CeIr$_5$ is a superconductor with $T_c \sim 1.8K$ [34], and its heat capacity is one of the compounds studied in this thesis.
II. EXPERIMENTAL DETAILS

A. Sample Preparation and Characterization

Samples of CePt$_5$, CeIr$_5$, CeGa$_2$, LaGa$_2$, CePtGa$_3$, LaPtGa$_3$, CeNi$_{12}$B$_6$, LaNi$_{12}$B$_6$, CeRh$_3$Si$_2$, Ce$_5$Ni$_6$In$_{11}$, CeNiAl and CeNi(Al$_{0.5}$Ga$_{0.5}$) were prepared from high purity elements (at least 99.9 at.% pure) by arc-melting in a Zr-gettered argon atmosphere on a water-cooled Cu hearth. The weight losses during the arc-melting were determined for each case.

Samples of CeCd$_2$, CeCd$_3$, Ce$_{13}$Cd$_{58}$, CeCd$_6$, CeCd$_{11}$, LaCd$_{11}$ and Ce$_2$Zn$_{17}$ were prepared by melting stoichiometric amounts of the constituents in sealed tantalum crucibles under helium atmosphere using a resistance furnace due to the high vapor pressures of Cd and Zn. In the cases of incongruent melting, samples were then annealed in a sealed quartz tube under helium atmosphere to obtain homogeneous single-phase compounds. The time periods and temperatures at which the samples were annealed depend on samples' melting temperatures.

CeHg$_3$ was prepared in a different way. Small pieces of Ce metal and corresponding amount of Hg were sealed under helium in a quartz tube, which was heated to ~650°C. At this temperature, which is below the melting temperature of CeHg$_3$, the Hg slowly
vaporizes and reacts with Ce to form CeHg\(_x\). Heating for about two months allows the reaction between Ce and Hg to occur through diffusion and to finally form the uniform compound, CeHg\(_3\).

Sample characterizations were done by both optical metallography and X-ray diffraction. Metallography is generally a better approach to determine the amount of second phase in a sample than X-ray diffraction. All of our samples except for CeHg\(_3\) which is too reactive with air were examined by metallography. The magnification used is typically around 100-500X. All of the samples were essentially single phase. If in the initial preparation, the samples contained more than 1 to 2% second phase, they were heat treated, or re-heat treated, or remade by slightly changing the Ce to M (+N) ratio to obtain a single phase material.

X-ray diffraction was done on a SCINTAG rotating diffractometer using Cu-K\(\alpha\) radiation. The diffractometer was controlled by a microcomputer. A small portion of sample was ground into powders before being mounted onto the sample holder. No annealing was done prior to X-ray diffraction, which might account for the poor quality in some of the diffraction patterns. X-ray diffraction patterns were taken of most of our samples. These patterns confirmed the previously reported crystal
structures. The crystal structures and lattice parameters of the compounds studied are listed in Appendix.

In case of CePtGa$_3$, a transmission electron microscope (TEM) was used to exam a tiny impurity phase, which apparently precipitated out.

B. Heat Capacity

Low temperature (1.3K to 70K) heat capacity measurements were carried out on these compounds using adiabatic heat pulse type calorimeter (Fig. 3). Samples, typically ~1 gram, were cooled down to liquid helium temperature by condensing helium in helium pot. Subsequent pumping on helium pot can cool the sample down to ~1.3K. Then sample with addenda was thermally isolated from the helium pot by a mechanical heat switch. A vacuum of ~1x10$^{-6}$ torr was maintained in sample chamber. A timed heat pulse is given, and the temperature rise is measured. The heat capacity of the sample C is calculated by

$$C = \frac{IVt}{\Delta T} - C_{\text{add}}/\text{mole}, \quad \text{(7)}$$

where $I$ is the heater current, $V$ the heater voltage, $t$ the heating time, $\Delta T$ the temperature change during the heating, $C_{\text{add}}$ the heat capacity of addenda, and mole is the number of moles of the sample. The measuring process was controlled by a computer,
Fig. 3. Low temperature adiabatic heat pulse type calorimeter
which also collected all of the raw data and calculated the heat capacities. The details of calibration of thermometer and calorimeter are given in ref. [35].

C. Magnetic Susceptibility

Most magnetic susceptibility measurements were made from 1.3K to ~298K using a Faraday magnetometer. Figure 4 is a schematic diagram which shows the principle involved. A sample is suspended from an electromagnetic balance in a magnetic field whose field strength and field gradient are known. As the field is turned on and off, the weight of sample changes. This change is due to the force exerted on the sample by magnetic field gradient. Since this magnetic force is proportional to the susceptibility of the sample (Fig. 4), the susceptibility is calculated from the weight change. A detailed description can be found in ref. [36]. A helium atmosphere at 1-10 torr was maintained in the sample chamber. The temperatures were controlled by a resistance heater. Field strength used varied from 0.5T to 2T.

An ac susceptibility apparatus in Dr. Finnemore's group and a SQUID magnetometer in Dr. Johnston's group were also used to measure the magnetic susceptibility of some of the samples.
Balance

Magnetic Force $= 1/2 \ m \times dH^2/\text{dz}$

$m = \text{mass}$

$X = \text{gram susceptibility}$

$H = \text{magnetic field}$

Fig. 4. Principal diagram of Faraday magnetometer
D. Electrical Resistivity

A conventional four probe technique was used for both ac and dc resistivity measurements. Samples were cut into 1x1x5 mm$^3$ blocks. Four Pt wires were spot-welded onto the sample, the two at the ends served as current leads and the two near the ends as voltage leads. In some cases when the material was extremely brittle, e.g., CePtGa$_3$, silver print was used to connect Pt wires to the sample. A lock-in amplifier was used in ac resistivity measurements. In dc resistivity measurement, current was applied in both directions to eliminate thermal voltages.
III. RESULTS AND DISCUSSIONS

A. Spin Glass Behavior in CePtGa_3

1. Introduction to spin glasses

"Classical" spin glass behavior is found in dilute metallic alloys AuFe or CuMn containing ~1 at.% of magnetic impurities Fe or Mn [37,38]. In these systems, a rather sharp cusp is observed in low field magnetic susceptibility at the freezing temperature T_f. Below T_f the spins of magnetic impurities are believed to be "frozen" in various directions that are randomly oriented.

Unlike the ferromagnetic or antiferromagnetic system, in which the RKKY interaction between the nearest neighboring spins are either positive or negative, the RKKY interaction between the impurity spins in a spin glass system is random. Figure 5 shows the sketch of spins randomly diluted in a metallic matrix together with the RKKY interaction constant J(R) as a function of the distance between two spins R [39]. Since the RKKY interaction is a strong function of distance R, the random distribution of spins can cause some spins to align parallel and some spins to align antiparallel. It is because of this competition between ferromagnetic and antiferromagnetic exchange interactions that the spins can be frustrated in trying to choose
Fig. 5. The sketch of spins randomly diluted in a metallic matrix together with the RKKY interaction constant $J(R)$ as a function of the distance between two spins $R$ [39]
one state over another, and the resulting state is that spins are locked together in a configuration where they are oriented in random directions. The difference between a spin glass state and a paramagnetic state is that at long times there is a probability that a given spin will be in the same orientation where it is first observed in a spin glass state, while in a paramagnetic state, the direction of a spin changes all the time. This difference can be expressed by a local autocorrelation function in time [40],

\[ q = \lim_{t \to \infty} < S_i(0) S_i(t) > \]  

where \( S_i(t) \) is the spin of site \( i \) at time \( t \), and the brackets represent the thermal average over all spins. \( q \) is finite for \( T < T_g \) and is zero for \( T > T_g \) when the system is in the paramagnetic state.

The spin glass behavior was also observed in concentrated metallic alloys, such as \( \text{Fe}_x\text{Al}_{1-x} \) [41], and insulators such as \( \text{Eu}_x\text{Sr}_{1-x}\text{S} \) [42]. In both cases, the random distribution of magnetic ions in the lattice is responsible for the spin glass behavior. Apart from crystalline alloys, the randomness, which causes spin glass behavior, can come from the non-crystallinity, i.e., amorphous solids [43,44]. Recently Rauchschwalbe et al. [45] found spin glass behavior in \( \text{CeCu}_{6.5}\text{Al}_{6.5} \), which is different from the previously known spin glasses. In this case
the Ce$^{3+}$ moments form a periodic array, and the randomness in the system is introduced by the statistical occupation of non-magnetic sites in the cage surrounding each Ce$^{3+}$ ion. A similar situation was also found in CePd$_3$B$_{0.3}$ [46] where Ce$^{3+}$ ions and Pd atoms occupy regular periodic sites in the lattice, the corners and faces, respectively, but the B atom only partially (~1/3) occupies the body-centered site. In this compound the random distribution of boron atoms and vacancies which changes the electronic environment around Ce$^{3+}$ ions and, thus, the varying RKKY interaction between the Ce$^{3+}$ ions is responsible for the spin glass behavior in CePd$_3$B$_{0.3}$.

Some of the typical spin glass behaviors can be briefly described as follows.

A sharp peak in low field ac magnetic susceptibility is found at $T_f$ which can be smeared and transformed into a broadened peak by an applied dc magnetic field [47].

The static susceptibility $\chi$ reveals a cusp at $T_f$ only when the sample is cooled in zero field. If the sample is cooled through $T_f$ with the field applied, a plateau in $\chi$ will be found due to the alignment of spins by the field which are frozen in as $T$ passes through $T_f$ [40].
Near and below $T_f$, irreversible behavior including remanence and coercivity appears, and the remanent magnetization decays slowly with time in a logarithmic way [48].

A broad peak in heat capacity appears at a temperature about 20% above $T_f$, which is progressively rounded and pushed to a higher temperature by an applied magnetic field [49]. The interesting fact is that no singularity in heat capacity is found at $T_f$.

In many cases, the entropy associated with the peak is about 70% of the expected value, e.g., 70% of $R \ln 2$ for a doublet ground state such as is normally found in Ce systems [50,51]. This indicates the presence of correlated spins at temperature high above $T_f$.

At high temperature the magnetic susceptibility obeys the Curie-Weiss law with a relatively small Curie temperature $\theta_p$ [38].

The theoretical understanding of spin glass behavior is still underway. Many models have been proposed. It is one of the most active areas in solid state physics.

2. Sample characterization

Samples CePt$_{1.1}$Ga$_{2.9}$, CePtGa$_3$ and CePt$_{0.9}$Ga$_{3.1}$ together with their corresponding La partners were prepared by arc-melting.
The samples were then heat treated at 600°C for about 2 weeks. While samples CePt$_{1.1}$Ga$_{2.9}$ and CePt$_{0.9}$Ga$_{3.1}$ were clean single phase alloys (Fig. 6), metallographic examination of CePtGa$_3$ showed many parallel black strips distributed in the grains which at one time were thought to be twins (Fig. 7). To verify this a portion of the CePtGa$_3$ sample was examined by transmission electron microscope (TEM) in Ames Laboratory. Careful analysis shows that these black strips are an impurity phase. In addition an electron diffraction pattern showed that some of the diffracted beams are due to a second phase. The magnetization measurements also revealed the existence of the second phase (see below).

The crystal structures of these Ce-Pt gallides were first reported by Grin et al. [52]. They found that CePt$_x$Ga$_{4-x}$ (0.2 < x < 1.15) crystallizes in body-centered tetragonal BaAl$_4$-type structure. In this structure the Ce atoms occupy 2(a) positions (0,0,0); (1/2,1/2,1/2). The Pt and Ga atoms randomly occupy the 4(e) [(0,0,z); (0,0,z); (1/2,1/2,1/2+z); (1/2,1/2,1/2+z)] and the 4(d) positions [(0,1/2,1/4); (1/2,0,1/4); (1/2,0,3/4); (0,1/2,3/4)]. It is this random distribution of Pt and Ga atoms that provides a random environment around Ce which may cause spin glass behavior in these systems as will be discussed below. Grin et al. [52] also observed, within the homogeneous range of the
Fig. 6. Metallography of CePt$_{0.9}$Ga$_{3.1}$ (upper) and CePt$_{1.1}$Ga$_{2.9}$ (lower). Magnification: 250X
Fig. 7. Metallography of CePtGa₃. Magnification: 500X
BaAl₄-type structure, the existence of a phase with a small orthorhombic deviation from BaAl₄ structure at the composition CePtGa₃.

X-ray diffraction experiments were performed on our samples. The CePt₁.₁Ga₂.₉ sample crystallizes in BaAl₄-type structure in agreement with the report of Grin et al. CePtGa₃ also has the BaAl₄ structure in contrast to the report of Grin et al. which stated that CePtGa₃ has a face-centered orthorhombic structure. We believe that the reason for this difference is as follows. Since our sample contains some second phase, which might be Ga rich (see below), the real composition of our sample can be slightly different from the nominal composition, i.e., CePt₁⁺δGa₃−δ (where δ is a small positive value). Therefore, its crystal structure is the BaAl₄-type. CePt₀.₉Ga₃.₁ had a face-centered orthorhombic structure as indicated by the double peaks in X-ray pattern associated with planes like (h,k,1) and (k,h,1). It also indicates that the face-centered orthorhombic structure exists at least over the composition range between CePt₀.₉Ga₃.₁ and CePtGa₃. The crystal structures and lattice parameters of these compounds are listed in the Appendix.
3. Heat capacity

The heat capacity of CePtGa$_3$ as a function of temperature at three different magnetic fields is shown in Fig. 8. The heat capacity at zero field starts to increase with decreasing temperature when temperature passes through 7K, and then it reaches a maximum at ~1.7K. The maximum shifts to a higher temperature if a magnetic field is applied. This suggests that the maximum is due to a magnetic phase change and not heavy fermion behavior, such as has been observed in CeCu$_2$Si$_2$. The significant feature for this compound is that this maximum in zero field heat capacity is not a sharp but a broad one. While for an ordinary ferromagnetic or antiferromagnetic phase transition, a sharp \(\lambda\)-type peak is normally found. One possible explanation is that the system undergoes a spin glass type transition since a rounded peak is one of the characteristics of spin glass system [49]. The heat capacity under magnetic field also suggests the spin glass behavior. As just mentioned, the peak is shifted to a higher temperature and becomes even more rounded in an applied field. This shift of the peak is typical of spin glass behavior [49], although a shift to higher temperature also occurs in ferromagnetic materials (e.g., see below CeGa$_2$ - Fig. 28). As will be seen in magnetic susceptibility, the peak is not due to a ferromagnetic ordering.
Fig. 8. Heat capacity of CePtGa$_3$ under fields of $H = 0$, 5.3T and 9.8T
The heat capacity of LaPtGa$_3$ which also crystallizes in BaAl$_4$-type structure was measured in order to estimate the lattice and nuclear contributions to the heat capacity of CePtGa$_3$. The heat capacity of LaPtGa$_3$ and CePtGa$_3$ and the difference (C$_{\text{CePtGa}_3}$ - C$_{\text{LaPtGa}_3}$) for temperature T < 10K are shown in Fig. 9. As seen, the rounded peak is obvious. The entropy associated with the peak in (C$_{\text{CePtGa}_3}$ - C$_{\text{LaPtGa}_3}$) was estimated to be ~4.7 J/mole K, which is ~80% of the expected value Rln2 = 5.76 J/mole K, and is what is typically found in other spin glass systems [50,51]. It is believed that at temperatures above T$_f$, the spins in the system are already somewhat correlated with each other, and accounts for the 20% loss of the entropy. This is the so called "frozen-in entropy".

Figure 10 shows the heat capacity of CePt$_{1.1}$Ga$_{2.9}$, CePtGa$_3$ and CePt$_{0.9}$Ga$_{3.1}$. The peak in CePtGa$_3$ is shifted to a lower temperature by replacing some Ga atoms with Pt atoms as in the case of CePt$_{1.1}$Ga$_{2.9}$, while the opposite is true when replacing some Pt atoms with Ga atoms. Although the crystal structure of CePt$_{0.9}$Ga$_{3.1}$ is different from the other two (see Sec. 2), the magnetic properties are practically unchanged as indicated by the similar peak at ~2K in the heat capacity. This conclusion has also been stated by Grin et al. as based on their susceptibility data. It is not surprising that the change of crystal structure
Fig. 9. Heat capacity of CePtGa$_3$ and LaPtGa$_3$ and their difference

$C_{\text{CePtGa}_3} - C_{\text{LaPtGa}_3}$
Fig. 10. Heat capacity of CePt$_{1.1}$Ga$_{2.9}$, CePtGa$_3$ and CePt$_{0.9}$Ga$_{3.1}$
has little influence on the magnetic behavior if we notice that
the face-centered orthorhombic structure is only a slight
distortion from the BaAl\textsubscript{4}-type structure [52].

Shown in Fig. 11 is the C/T versus T\textsuperscript{2} plot for CePtGa\textsubscript{3} and
LaPtGa\textsubscript{3} and their difference over temperature range 10K < T < 20K
(100K\textsuperscript{2} < T\textsuperscript{2} < 400K\textsuperscript{2}). This difference is the electronic specific
heat coefficient of CePtGa\textsubscript{3} in excess of that of LaPtGa\textsubscript{3} since it
is assumed that CePtGa\textsubscript{3} and LaPtGa\textsubscript{3} have the same lattice and
nuclear contributions to the heat capacity and thus these two
contributions to the heat capacity of CePtGa\textsubscript{3} have been
subtracted off. The specific heat coefficient of CePtGa\textsubscript{3}, \( \gamma = \sim 71 \text{ mJ/mole K}^2 \), was determined by adding the average value of
this difference to the \( \gamma \) of LaPtGa\textsubscript{3}, which was determined in the
usual way (C/T versus T\textsuperscript{2}) at much lower temperatures (1.3K to
4.5K). The Debye temperature was estimated from that of LaPtGa\textsubscript{3},
see the Appendix.

The electronic specific heat coefficients of CePt\textsubscript{1.1}Ga\textsubscript{2.9}
and CePt\textsubscript{0.9}Ga\textsubscript{3.1} were determined in the same way by assuming that
their Debye temperatures are the same as that of LaPtGa\textsubscript{3}.

A portion of our sample was sent to Prof. F. Steglich and
his student R. Caspary (Inst. Festkörperphysik, Darmstadt, FRG)
to study the heat capacity and susceptibility at extremely low
temperature (down to \sim 60mK) using dilution refrigerator. Their
Fig. 11. $C/T$ versus $T^2$ plot of CePtGa$_3$ and LaPtGa$_3$ and their difference (100K$^2$ to 400K$^2$)
heat capacity results agree with ours, where the data overlap, and clearly show the rounded peak which was just evident in our zero field data (compare Fig. 9 and Fig. 12). At temperatures below 1K, the $\Delta C/T = (C - C_{\text{nuc}})/T$ versus $T$ plot of heat capacity after the nuclear hyperfine contribution (a $T^{-2}$ term) has been subtracted out is shown in Fig. 13. In the case of $H = 8T$, the electronic specific heat coefficient can be obtained from the $\Delta C/T$ value at ~0.2K where $\Delta C/T$ becomes temperature independent. Unfortunately, $\gamma$ can not be extracted for the low-field and zero-field cases. If we assume that $\gamma$ is field independent, $\gamma$ at $H = 8T$ can be taken as $\gamma$ at $H = 0T$, which is $-120$ mJ/mole K$^2$. This value is substantially larger than the value obtained from above the peak temperature.

The entropy associated with the peak for zero field data seems to saturate at 90% of Rln2 above ~6K. Although it is slightly larger than our entropy value (80% of Rln2 at ~8K), still, 10% of the total entropy is frozen in. The smaller entropy value from our measurements are probably due to the lack of data points below the peak temperature. The shape of the $C/T$ versus $T$ curve used to calculate the entropy was estimated for temperatures below the peak in our case, because the Steglich Caspary results were not available at the time.
Fig. 12. Heat capacity of CePtGa$_3$ in fields of $H = 0T$, $H = 2T$ and $H = 8T$ at lower temperatures.
Fig. 13. \((C - C_{\text{nucl}})/T\) versus \(T\) in fields of \(H = 0\, \text{T}, H = 2\, \text{T}\) and \(H = 8\, \text{T}\), see text.
4. Magnetic susceptibility

The ac magnetic susceptibility $\chi_{ac}$ of CePtGa$_3$ from ~0.4K to 3K is shown in Fig. 14. The absence of a peak around 1.7K in $\chi_{ac}$ suggests that the peak in heat capacity at the same temperature is not due to an ordinary magnetic phase transition, e.g., ferromagnetic phase transition, since the peaks in $\chi_{ac}$ and heat capacity occur at about the same temperature for an ordinary magnetic phase transition. On the other hand, we did not find the spin glass derived peak below 1.7K which is supposed to be broadened and wiped out by a static magnetic field. Instead, an apparent plateau in $\chi_{ac}$ is found at ~0.5K, which may actually be the top of a broad peak (Fig. 15). Measurements to lower temperatures in this regard would be useful. The behavior of this plateau under applied magnetic field is at least partially consistent with spin glass behavior, however the existence of some antiferromagnetic ordering at $T_N = ~0.5K$ in the sample could account for the unusual temperature and field dependences.

Combining the data on ac susceptibility and heat capacity, the following conclusion can be made. Most of the Ce spins freeze into a "glassy state", but a small part of the sample forms an antiferromagnetic cluster which is evident in the $\chi_{ac}$ data. The possibility that this antiferromagnetic behavior is from the second phase black strips present in the sample is quite
Fig. 14. The ac magnetic susceptibility $\chi_{ac}$ of CePtGa$_3$
Fig. 15. The ac magnetic susceptibility $\chi_{ac}$ in different applied fields.
strong. Additional measurements on the other two CePtGa$_{3}$ samples, which are free of this second phase, would be helpful.

Surprisingly, a peak was found in ac susceptibility ~8K (Fig. 16), which was also confirmed in the Faraday magnetic susceptibility measurement (see below). In a previous report [53] we were unable to explain the origin of this peak. But it is now believed that this peak is due to a magnetic impurity. As we mentioned, many black strips were found in CePtGa$_{3}$ sample which turned out to be impurity phase. Since CePt$_{1.1}$Ga$_{2.9}$ and CePt$_{0.9}$Ga$_{3.1}$ are clean single phase samples, we conducted the ac susceptibility measurements on both of them from 1.4K to 20K. As shown in Fig. 17, no peak can be seen in $\chi_{ac}$ around 8K in either samples. This comparison suggests that the impurity in CePtGa$_{3}$ is responsible for the peak at ~8K. One curious fact is that there is no indication of a peak ~8K in heat capacity of CePtGa$_{3}$. Normally the heat capacity is more sensitive to a magnetic impurity than the magnetic susceptibility.

The data of CePt$_{1.1}$Ga$_{2.9}$ and CePt$_{0.9}$Ga$_{3.1}$ are less scattered than that of CePtGa$_{3}$. It is much more obvious that there is no peak around 2K in $\chi_{ac}$ (Fig. 17).

The dc susceptibility of CePtGa$_{3}$ is shown in Fig. 18 as $\chi^{-1}$ versus T for temperature range 1.3K $< T < 300K$. Above 70K, it follows Curie-Weiss law. The effective moment and Curie
Fig. 16. The ac magnetic susceptibility $\chi_{ac}$ in zero field at higher temperatures (measuring field $H = 1$ Oe, frequency $f = 100$ Hz)
Fig. 17. $\chi_{ac}$ of CePt$_{1.1}$Ga$_{2.9}$ and CePt$_{0.9}$Ga$_{3.1}$
Fig. 18. The inverse dc magnetic susceptibility $1/\chi$ as a function of temperature.
temperature were found to be $\mu_{\text{eff}} = 2.89\mu_B$ and $\Theta_p = -14K$, respectively. The negative $\Theta_p$ value for a spin glass system does not mean that the interaction between the spins is antiferromagnetic. In fact, the $\Theta_p$ value can be either positive or negative depending on the deviation from random mixing [49].

$\chi^{-1}$ shows a drop above 8K which is believed to be related to the peak in ac susceptibility at ~8K.

The linear response of magnetization $M$ to the applied magnetic field $H$ of CePtGa$_3$ at different temperatures (Fig. 19) implies the paramagnetic behavior of CePtGa$_3$ above ~9K. At high temperature the extrapolations of the straight lines to zero field have zero intercept with $M$ axis. As temperature is lowered below ~8.6K, non-zero intercept appears. This is an indication of the presence of magnetic impurity phase in the sample.

Compared with the ac susceptibility data, there seems to be no doubt that this non-zero intercept and the peak in $\chi_{\text{ac}}$ at ~8K are from the same magnetic impurity. In order to find out what the impurity phase could be, we went through the literature to see if there is a CePt$_x$ or CeGa$_x$ or another CePt$_x$Ga$_y$ which orders magnetically at ~8K. It was found that CeGa$_2$ (also see Sec. B) is a ferromagnet with $T_C = 8.4K$. Assuming that the impurity compound is CeGa$_2$, the amount of impurity can be estimated from the non-zero intercept $M_0$ at $H = 0$. Since the saturation moment
Fig. 19. Magnetization $M$ versus applied field at different temperatures
of CeGa$_2$ is $\sim$1.3 $\mu_B$/Ce (Sec. B), the $M_Q$ value at 1.5K, $\sim$250 emu/mole.Ce, infers that $\sim$3.4% of the total Ce atoms are in CeGa$_2$, i.e., the amount of CeGa$_2$ impurity present is $\sim$3.4%, which is consistent with the metallographic results, see Fig. 7.

5. Summary

The rounded peak in heat capacity, which was once considered as a heavy fermion behavior, is due to spin glass type transition. Unlike the ordinary spin glasses, the spin-carrying Ce$^{3+}$ ions in CePtGa$_3$ occupy the periodic lattice sites. The random RKKY interaction between the spins which provides the basis for spin glass behavior is induced by the random distribution of Pt and Ga atoms around Ce$^{3+}$ ions. The heat capacity and susceptibility data support this conclusion.

B. Crystalline Electric Field (CEF) Effect in CeCd$_{11}$ and CeGa$_2$

1. CeCd$_{11}$

   a. Crystal structure and CEF

CeCd$_{11}$ crystallizes in cubic BaHg$_{11}$-type structure, with lattice constant $a = 9.319A$ [54]. Detailed examination of the structure reveals that a Ce atom is surrounded by 12 nearest neighboring Cd atoms and 8 second nearest neighboring Cd atoms. Figure 20 shows the atomic
Fig. 20. A projection along the $c$-axis of the atomic arrangement of CeCd$_{11}$. The solid circles show the arrangement of Cd atoms about a Ce atom. The big circles represent the Ce atoms and the small ones the Cd atoms.
arrangement in CeCd_{11}. The neighboring Cd form a polyhedron of tetragonal symmetry about the Ce atom. Under the crystalline electric field (CEF), the 6-fold degenerate ground state of Ce^{3+} ion, \( ^{2}F_{5/2} \), will be split into three doublets. According to the CEF Hamiltonian for Ce^{3+} ion \((J = 5/2)\) with tetragonal symmetry \([55]\),

\[
H_{CEF} = B_{2}^{0}O_{2}^{0} + B_{4}^{0}O_{4}^{0} + B_{4}^{6}O_{4}^{6} \tag{9}
\]

where coefficients \(B_{n}^{m}\) and operators \(O_{n}^{m}\) were defined in Hutchings \([56]\). The final eigenstates consist of three doublets \(|_{1/2}^{+1/2}\), \(a|_{5/2}^{+5/2} + b|_{3/2}^{+3/2}\) and \(b|_{5/2}^{+5/2} - a|_{3/2}^{+3/2}\). The actual energy levels of these doublets and the values of \(a\) and \(b\) depend upon the coefficients \(B_{n}^{m}\). This CEF splitting will influence the behaviors of heat capacity, magnetic susceptibility and electrical resistivity of CeCd_{11} over the temperature range comparable to the energies of splitting. Low temperature property measurements, especially the heat capacity, allowed us to determine the energies of this 3-level CEF in CeCd_{11}.

b. Heat capacity

The heat capacity of CeCd_{11} was measured over the temperature range \(1.5K < T < 70K\), and it is shown in Fig. 21. Also shown in Fig. 21 is the heat capacity of LaCd_{11}, which is isostructural with CeCd_{11}. The more typical \(C/T\) vs. \(T^2\) is shown in Fig. 22. The temperature dependence is quite unusual and the magnitude above 6K (36K^2) is quite large (-800
Fig. 21. Heat capacities of CeCd$_{11}$ and LaCd$_{11}$ from 1.5K to 70K. The inset shows an expanded version of the data below 20K.
Fig. 22. C/T versus T² plot for CeCd₁₁. The crosses are for a sample weighing 1.58 g and the dots are for a sample weighing 14.27 g.
mJ/mole \( K^2 \)). Below 2K, it appears that CeCd\(_{11}\) may be tending towards ordering magnetically. In order to understand this behavior we have assumed that the electronic and lattice heat capacities of CeCd\(_{11}\) are the same as that of LaCd\(_{11}\). This is quite reasonable because of the similar lattice constants \( a = 9.339\text{Å} \) for LaCd\(_{11}\) [54] and 9.313Å for CeCd\(_{11}\) and the same outer electronic configurations of the two compounds (Ce is trivalent, see 1.4. Magnetic susceptibility, below). Therefore, the difference between the two heat capacities \( (C_{\text{CeCd}_{11}} - C_{\text{LaCd}_{11}}) \) should represent the contributions essentially due to the 4f electrons in Ce\(^{3+}\) ion. The shape of curve \( (C_{\text{CeCd}_{11}} - C_{\text{LaCd}_{11}}) \) versus temperature (see Fig. 23) shows a fairly sharp bump at ~7K and a broader bump at ~25K, suggesting the existence of 3-level CEF effect. The main peak near \( T = 7\text{K} \) is due to the excitation of 4f electron from ground state level to the 1st excited level and the 25K shoulder could be due to the excitation from the 1st excited level to the 2nd excited level. To make sure this interpretation is correct we calculated the magnetic heat capacity of a 3-level CEF system, which takes the form

\[
C_{\text{CEF}} = \frac{R[E_1^2 \exp(-E_1/T) + E_2^2 \exp(-E_2/T) + (E_2-E_1)^2 \exp(-(E_1+E_2)/T)]}{T^2 [1 + \exp(-E_1/T) + \exp(-E_2/T)]^2} \tag{10}
\]

where \( R \) is the universal gas constant, \( E_1 \) and \( E_2 \) are the energies
Fig. 23. The difference of the two heat capacities

\[(C_{\text{CeCd11}} - C_{\text{LaCd11}}) \text{ (+) and } C_{\text{CEF}} + \gamma'T \text{ (line).}\]

Inset: energy levels of the CEF
(in K) of the 1st and 2nd excited levels, respectively. After several trials of fitting, $C_{\text{CEF}}$ to $C_{\text{CeCd11}} - C_{\text{LaCd11}}$, good agreement between the two was obtained when we added a small linear term $\gamma'T$ to the calculated $C_{\text{CEF}}$. Shown in Fig. 23 (solid line) is the function $C_{\text{CEF}} + \gamma'T$. The agreement between this function and the experiment is obvious. Energy levels and the constant $\gamma'$ obtained in this manner are:

\begin{align*}
E_0 &= 0, \quad (11) \\
E_1 &= 17.5 \text{K}, \quad (12) \\
E_2 &= 80.2 \text{K}, \quad (13) \\
\gamma' &= 9.0 \text{ mJ/mole K}^2. \quad (14)
\end{align*}

$E_1 = 17.5 \text{K}$ is one of the lowest CEF splittings found in Ce compounds. The only Ce compound having a lower CEF splitting, that we know of, is cerium ethylsulphate with $E_1 = 6.6 \text{K}$ [57]. Usually CEF splittings occur at temperatures 5 times to an order of magnitude higher.

$\gamma'T$ is the electronic contribution to heat capacity of CeCd$_{11}$ in excess of that of LaCd$_{11}$. The electronic specific heat constant, $\gamma$, and the Debye temperature $\Theta_D$ of LaCd$_{11}$ are 17 mJ/mole K$^2$ and 280K, respectively, and were obtained from a least squares fit of the data to a C/T versus $T^2$ plot between 1.3K and 2.5K. Adding $\gamma'$ to the $\gamma$ of LaCd$_{11}$, the electric specific heat
constant is estimated to be 26 mJ/mole K^2 for CeCd_{11}. The Debye temperature of CeCd_{11} is assumed to be 280K.

The magnetic entropy, $S_m$, associated with our heat capacity data was also calculated. Near $T = 70K$, $S_m$ reaches a value close to 9.13 J/mole K (Fig. 24), which is the expected value for a 3-level CEF system

$$S_{CEF} = R \ln (m) = R \ln 3 = 9.13 \text{ J/mole K.}$$

In the above expression, $m$ is the number of doublets in a CEF system [58], where $m = 3$ in our case. The agreement between the experimental entropy and the theoretical value confirms the splitting of a 3-level CEF. Since $J = 5/2$ for Ce^{3+}, we expect the total magnetic entropy $S_t^{tot} = R \ln (2J + 1) = R \ln 6$. Knowing the entropy associated with CEF is $R \ln 3$, we believe that the difference ($R \ln 6 - R \ln 3 = R \ln 2$) is associated with magnetic ordering below $T = 1.3K$. Because of the low temperature limit of our apparatus we were unable to make measurements below 1.3K, but the tendency toward magnetic ordering at a lower temperature can be clearly seen from the upturn in heat capacity at $T \approx 2K$ (and is also evident in the magnetic susceptibility, see 1.4.). Also it is not difficult to understand that the offset between the experiment and $C_{CEF} + \gamma' T$ (Fig. 23) below $\approx 10K$ is due to the non-zero tail of the magnetic ordering peak.
Fig. 24. Entropy associated with the CEF
The ac resistivity of our CeCd$_{11}$ sample is shown in Fig. 25. The resistivity data over a wider temperature range is also shown in the Fig. 25 inset. We can see that there is a resistivity drop near $T = 7K$ as temperature decreases. We believe this is associated with the spin-disorder resistivity of a CEF system. Since the 2nd excited level lies high above both the ground and the 1st excited levels, we assume that the 2nd excited level remains unoccupied over the temperature of concern and treat resistivity as a 2-level system.

According to V. Rao and W. Wallace [59], the spin-disorder resistivity of a 2-level CEF system can be derived from the first Born approximation. It follows below:

$$\rho_s = \frac{A + B \exp(-E_1/T)}{1 + \exp(-E_1/T)} + \frac{C}{(1 + \exp(-E_1/T))(1 + \exp(E_1/T))}$$  

(16)

where $A$, $B$ and $C$ can be determined from fitting the experimental data to this equation. The total resistivity is composed of three parts. One is the spin-disorder resistivity $\rho_s$ as discussed above, another comes from the phonon scattering of conduction electrons $\rho_{ph}$, and the third part is the temperature independent residual resistivity due to impurities $\rho_o$. Since the phonon scattering resistivity near liquid helium temperature is about two orders of magnitude smaller than experimental
Fig. 25. Experimental resistivity of CeCd$_{11}$ (circles) and $\rho_{\text{tot}} = \rho_0 + \rho_s$ (line), with $A = 0.394$, $B = 4.04$, $C = 2.20$ and $\rho_0 = 0.655$ $\mu\Omega\text{cm}$.

Inset: experimental data over a wider temperature range.
resistivity (estimated from Debye temperature) [60], we neglected phonon scattering resistivity $\rho_{ph}$. Therefore, the total resistivity is the sum of two parts

$$\rho_{tot} = \rho_0 + \rho_s$$

(17)

This equation was taken to fit the experimental data for temperature $1.5K < T < 20K$, and the constants $A$, $B$, $C$ and $\rho_0$ were determined. Such a determined equation is shown in Fig. 25 together with the experimental data. The values of $A$, $B$, $C$ and $\rho_0$ are given in the caption of Fig. 25. We see that, in spite of a slight difference between experiment and Equation (17), the drop of resistivity near $T = 7K$ can be explained with spin-disorder resistivity as expressed by Equation (17).

d. Magnetic susceptibility

The magnetic susceptibility measurement was carried out at a field $H = 0.96T$ over the temperature range $1.5 < T < 250K$. The experimental data can be expressed by the following equation for $T > 4K$

$$\chi = \frac{C}{(T-\theta)} f + \alpha$$

(18)

where $C = 0.830$ emu K/mole,

(19)

$\theta = -5.5K$,

(20)

$\alpha = -5.7 \times 10^{-4}$ emu/mole,

(21)
Fig. 26. Magnetic susceptibility times the temperature versus temperature for CeCd\textsubscript{11} - a comparison of experiment with theory. The inset shows the low temperature region on an expanded scale.
and \( f \) is the modification factor due to CEF (see below). The experimental susceptibility (in the form as \( \chi T \)) and the fit of the data to Equation (18) are shown in Fig. 26. The term \( C/(T-\Theta) \) in Equation (18) is the Curie-Weiss paramagnetic contribution from 4f electrons of \( \text{Ce}^{3+} \) ions. The value of \( C = 0.830 \) corresponds to an effective moment \( p_{\text{eff}} = 2.57\mu_B \), which is close to the expected theoretical value of a free \( \text{Ce}^{3+} \) ion \( p_{\text{eff}} = 2.54\mu_B \) [61]. This indicates that the 4f electrons in \( \text{CeCd}_{11} \) are well localized in agreement with a large \( \text{Ce-Ce} \) distance \( d = 6.59\text{Å} \). The negative paramagnetic Curie temperature \( \Theta = -5.5\text{K} \) infers that the system will order antiferromagnetically at low temperature. Actually, the tendency toward magnetic ordering was seen from heat capacity data at \( T < 2\text{K} \), as mentioned earlier (1.2.), and is seen in the inset of Fig. 26.

The 2nd term in Equation (18), \( \alpha \) comes from the orbital motion of core electrons. Since the diamagnetic susceptibility of \( \text{Cd} \) metal is about \(-20\times10^{-6} \text{ emu-per-gram-atom} \) [62], we expect that the Larmor diamagnetic susceptibility of \( \text{CeCd}_{11} \) would have a value of the same magnitude. The experimental value \( \alpha = 5.7\times10^{-4} \text{ emu-per-mole} \), which is \(-52\times10^{-6} \text{ emu-per-gram-atom of Cd}, \) is in fair agreement with the value for pure \( \text{Cd} \) metal.

Under the influence of CEF, the magnetic susceptibility of a 3-level system will be modified by multiplying a factor.


\[
f = \frac{p_1^2 + p_2^2 \exp(-E_1/T) + p_3^2 \exp(-E_2/T)}{1 + \exp(-E_1/T) + \exp(-E_2/T)}
\]  \hspace{1cm} (22)

to Curie-Weiss term (see Equation 18) [63], where constants \( p_1 \), \( p_2 \) and \( p_3 \) depend on the values of coefficients \( B_n^{\text{m}} \) in Equation (9). These constants have been determined from our experiment, \( p_1 = 0.97, p_2 = 0.99 \) and \( p_3 = 1.05 \). Since all of them are in the vicinity of unity, the factor \( f \) has a weak temperature dependence, which explains why the influence of CEF is hardly observed in magnetic susceptibility. Note, the large temperature dependence shown in Fig. 26 is due to the Curie-Weiss portion of Equation (18) \([C/(T-\Theta)]\) and not \( f \).

**Summary** The existence of CEF effect in CeCd\(_{11}\) was established. The heat capacity data and associated magnetic entropy confirmed the splitting of a 6-fold degenerate ground state into three doublets. AC resistivity showed a drop near \( T = 7\text{K} \) which can be explained by spin-disorder resistivity in presence of CEF. Both the heat capacity and magnetic susceptibility indicate that CeCd\(_{11}\) orders slightly below 2K.

2. CeGa\(_2\)

a. Some background CeGa\(_2\) has been studied by several research groups [64-69]. It crystallizes in hexagonal AlB\(_2\)-type
structure with Ce at (0,0,0) and Ga at \( \pm (1/3, 2/3, 1/2) \). Tsai et al. [65] and Tsai and Sellmeyer [66] described CeGa\(_2\) as an antiferromagnetic compound with \( T_N = 9.5\text{K} \) in which long-range ferromagnetic interaction also exists. No Kondo-like behavior was observed. Dijkman [67] reported a peak at \(-9.9\text{K}\) in heat capacity which was broadened and shifted to a higher temperature by an applied magnetic field. The possibility of the existence of short range order above \( 9.9\text{K} \) was suggested by Dijkman from the fact that entropy associated with the peak in heat capacity is considerably smaller than \( R\ln 2 \). He also excluded the occurrence of intermediate valence of Ce. Burlet et al. [68] reported the neutron study of single crystal CeGa\(_2\). One sample showed antiferromagnetic ordering at \( 9.5\text{K} \) with a sine wave modulated incommensurate structure. Another sample showed the incommensurate structure below \( 9.5\text{K} \) followed by a ferromagnetic ordering at \( 8.5\text{K} \). It seems that the behavior of CeGa\(_2\) is very sensitive to sample preparation and the presence of impurities. In contrast to the previous reports, they concluded that CeGa\(_2\) is a Kondo lattice in which anisotropic exchange interactions are important. The CEF splitting was also determined from their inelastic neutron scattering spectra. Lately Takahashi et al. [69] studied a single crystal prepared by floating-zone technique. The resistivity data show no Kondo-like behavior,
which agrees with the reports of Tsai et al. and Dijkman. The heat capacity and magnetic measurement indicate that CeGa$_2$ undergoes a series of antiferromagnetic phase transitions between 8.4K and 11.4K before it finally orders ferromagnetically below 8.4K. Total entropy associated with these multiple phase transitions is estimated to be about Rln2.

b. Our results As a part of an effort to clarify the inconsistency of the previous reports, our experimental data on a polycrystalline sample are given here. Metallography of the sample prepared by arc-melting is shown in Fig. 27. As seen, it is a fairly clean single phase sample (The black spots are cracks on surface of the sample).

The heat capacities of CeGa$_2$ were measured from 1.3K to 20K under different magnetic fields (1.5T < H < 10T), and the data are shown in Fig. 28. One large combined peak at ~10K in zero field, which might be the result of the conjunctive magnetic phase transitions between 8.4K and 11.4K mentioned earlier [69], is obvious, and the peak is broadened and shifted to higher temperatures by the applied fields. This behavior seems to support the result of Takahashi et al. that CeGa$_2$ undergoes several conjunctive antiferromagnetic states of low spin-flip field (< 0.1T) between 8.4K and 11.4K before it reaches a ferromagnetic ground state at 8.4K. Actually, the broadening and
Fig. 27. Metallography of CeGa\textsubscript{2}. Magnification: 100X.

*(see text for explanation)*
Fig. 28. Heat capacity of CeGa$_2$ in different magnetic fields
the shift of the combined peak implies that the antiferromagnetic states between 8.4K and 11.4K are unstable and destroyed by the large applied fields. It also implies that the ground state of the system is ferromagnetic in nature. This shift was seen in Dijkman's data also, but no conclusion about the nature of the ordering was given at the time.

Magnetic susceptibility measured from 1.3K to 280K under field $H = 0.5T$ is shown in Fig. 29 as $\chi^{-1}$ versus $T$. It has a Curie-Weiss behavior with effective moment $\mu_{\text{eff}} = 2.85\mu_B$ and Curie temperature $\theta_p = +1.8K$. Compared with other reported $\theta_p$ values, $\theta_p = -18K$ [64], +12.5K [65] and -5K [67], it can be seen that $\theta_p$ depends very much on each individual sample.

Understanding of these differences in $\theta_p$ is important because the sign of $\theta_p$ (+ or -) usually predicts the type of magnetic interaction (ferromagnetic or antiferromagnetic),

$$\theta_p = \frac{S(S+1) J_o}{3 k_B},$$

where $S$ is the spin quantum number, and $J_o$ is the coupling constant [70]. A positive $J_o$ corresponds to a ferromagnetic coupling, and a negative $J_o$ corresponds to an antiferromagnetic coupling. We believe that the differences in the measured $\theta_p$ are due to the different grain orientations in the samples. As a matter of fact, susceptibility measurement on a single crystal
Fig. 29. The inverse magnetic susceptibility as a function of temperature
sample in both parallel to c axis and perpendicular to c axis gave $\theta_p^{(\text{para})} = -107K$ and $\theta_p^{(\text{perp})} = 22K$ [68, 69]. It is not difficult to understand that, depending on the orientations of each individual grain, theoretically we can have any value of $\theta_p$ between -107K and 22K for a polycrystalline sample. Clear indication of ferromagnetic ground state can be seen from the saturation behavior in low temperature magnetic moment $M$ versus $T$ plot (Fig. 30).

c. CEF in CeGa$_2$ Shown in Fig. 31 is the heat capacities of CeGa$_2$ and isostructural LaGa$_2$ as C/T versus $T^2$ in zero field. Data are taken from another independent experiment, in which temperature range is expanded to (1.3-70K). Above the peak temperature, the C/T versus $T^2$ curve of CeGa$_2$ follows nearly a straight line. The extrapolation of the straight line to 0K gives a moderately large C/T value (~340 mJ/mole K$^2$), which might suggest heavy fermion (Kondo lattice) behavior. The origin of this moderately large heat capacity is now believed to be due to CEF effect in CeGa$_2$ rather than a Kondo lattice effect. The CEF in a hexagonal structure of CeGa$_2$ will split the 6-fold degenerate ground state of Ce$^{3+}$ ion, $^2F_{5/2}$ into three doublets $<\pm 1/2|$, $<\pm 3/2|$ and $<\pm 5/2|$ [71]. According to the inelastic neutron scattering experiment on CeGa$_2$ by Burlet et al. [68], the CEF energy levels of the three doublets are 0, 62.5K and 310K,
Fig. 30. Low temperature magnetic moment of CeGa$_2$
Fig. 31. $C/T$ versus $T^2$ of $C_{\text{CeGa}_2}$, $C_{\text{CEF}}$, $C_{\text{LaGa}_2}$ and 

$C_{\text{CeGa}_2} - C_{\text{CEF}} - C_{\text{LaGa}_2}$
respectively. The contribution to the heat capacity from this 3-level CEF system, which takes exactly the same form as that used for CeCd$_{11}$ (Equation 10), is significant and is shown in Fig. 31. As seen, after subtraction of the heat capacity of CEF and that of isostructural LaGa$_2$ from the heat capacity of CeGa$_2$ the difference is only a magnetic peak, in C/T values, from 0K to -20K (i.e., -400K$^2$). The entropy associated with the peak reaches Rln2 at ~25K. This suggests that the moderately large heat capacity in CeGa$_2$ is due to the CEF effect.

The electronic specific heat coefficient of CeGa$_2$ is 32.6 mJ/mole K$^2$, which was estimated by adding C/T value of (C$_{CeGa2}$ CCEF - C$_{LaGa2}$), which is a constant from 25K to 40K (500K$^2$ to 1600K$^2$, only part of this region is shown in Fig. 31), to the electronic specific heat coefficient of LaGa$_2$. The low temperature part of the C/T versus T$^2$ plot for LaGa$_2$ is shown in Fig. 32. It follows a straight line. The electronic specific heat coefficient and Debye temperature of LaGa$_2$ are determined from the straight line, and they are listed in the Appendix. The Debye temperature $\Theta_D$ of CeGa$_2$ is assumed to be the same as that of LaGa$_2$.

In summary, our heat capacity data show no sign of heavy fermion behavior in CeGa$_2$. Magnetic behavior of the compound supports the conclusion that the ground state of the system is a
Fig. 32. C/T versus $T^2$ plot for LaGa$_2$
ferromagnetic one. A interesting point is that CEF effect, which plays an important role in the heat capacity of both CeGa$_2$ and CeCd$_{11}$, sometime can show up as a false signal of heavy fermion behavior when the CEF splittings are small. Precaution is recommended.

C. Some Other Ce Binary Compounds

1. CeHg$_3$

CeHg$_3$ has a hexagonal Ni$_3$Sn-type structure with lattice parameters $a = 6.760 \text{Å}$ and $c = 4.941 \text{Å}$ [72]. The Ce-Ce spacing in CeHg$_3$ $d_{\text{CeHg}_3} = 4.62\text{Å}$ is just slightly larger than Ce-Ce spacing in the isostructural CeAl$_3$ $d_{\text{CeAl}_3} = 4.43\text{Å}$ [10]. Since CeAl$_3$ is a typical heavy fermion, it would be interesting to study the low temperature behavior of CeHg$_3$.

CeHg$_3$ is a very unstable compound and reacts readily with air. In order to avoid its reaction with the air, the heat capacity was measured by sealing a CeHg$_3$ sample in a small brass container under helium atmosphere, then the heat capacity of the sample together with the container were measured and finally the heat capacity of the container was subtracted off. Figure 33 shows the low temperature portion of the heat capacity of CeHg$_3$ as $C/T$ versus $T^2$. The magnetic peak at $\sim 1.6\text{K}$ is obvious in the C
Fig. 33. C/T versus $T^2$ plot for CeHg$_3$. The inset shows the heat capacity as a function of $T$ for lower temperatures.
versus T plot (Fig. 33, inset). The entropy associated with this peak was estimated to be ~2.4 J/mole K, which is ~40% of the expected value $R \ln 2 = 5.76$ J/mole K. This tells us that the magnetic peak is an intrinsic property but not an impurity effect. The reason that the experimental entropy is so far off the expected value is perhaps due to the lack of experimental data below the ordering temperature. Actually we were only able to reach a temperature just below the peak (~1.5K). Therefore, the extrapolated values of the heat capacity used to calculate the entropy below the peak temperature can be significantly different from the real situation. The nature of the peak will be discussed later. Above the peak temperature, the $C/T$ versus $T^2$ plot shows a straight line. The Debye temperature $\Theta_D$ and electronic specific heat coefficient $\gamma$ were determined and are listed in the Appendix. The $\gamma$ value of 52 mJ/mole K$^2$ indicates that CeHg$_3$ is not a heavy fermion material. Compared with CeAl$_3$, we may conclude that by increasing the Ce-Ce spacing from 4.43Å for CeAl$_3$ to 4.62Å for CeHg$_3$ the non-magnetic heavy fermion behavior is destroyed and a magnetically ordered state is created. Although a large Ce-Ce spacing is necessary for the formation of heavy fermion state, it is not, as noted in the Introduction, a sufficient condition. Probably the 4f-p state
Fig. 34. The inverse magnetic susceptibility of CeHg₃
interaction (hybridization) changes sufficiently between Al and Hg in these CeMg compounds to give these different behaviors.

The inverse of magnetic susceptibility of CeHg₃ is shown in Fig. 34 for temperature range 2K < T < 300K. The Curie-Weiss behavior is indicated by the straight line in this plot. The effective moment and Curie temperature were found to be $\mu_{\text{eff}} = 2.32\mu_B$ and $\theta_p = -10K$, respectively. These values are quite different from the ones of Olcese [72], who reported $\mu_{\text{eff}} = 2.93\mu_B$ and $\theta_p = -53K$. One point that both experiments agree on is the negative Curie temperature $\theta_p$, which implies that the peak in heat capacity at ~1.6K is due to an antiferromagnetic phase transition.

2. CeIr₅ and CePt₅

a. CeIr₅ The superconductivity in CeIr₅ was first reported by Geballe et al. in 1965 [34]. Our heat capacity data confirmed this transition at $T_C \sim 1.8K$. Shown in Fig. 35 are the heat capacities of CeIr₅ under zero field and under field $H = 1.46T$. The zero-field heat capacity clearly indicates the superconducting transition at $T_C \sim 1.8K$. This critical temperature is suppressed to below 1.5K under the applied field. The value of $(C_S - C_n)/C_n$ at $T_C$ is ~1.3, which is close to the predicted value of 1.43 from BCS theory [73].
Fig. 35. Heat capacity of CeIr$_5$ in zero field and in field $H = 1.46T$
Fig. 36. $C/T$ versus $T^2$ plot for CeIr$_5$ in zero field
The C/T versus T² plot for CeIr₅ (Fig. 36) follows a straight line from ~4K to ~10K (i.e., ~15K² to ~100K², only part of this region is shown). The Debye temperature θD and electronic specific heat coefficient γ were determined from this linear region. γ is found to be 19 mJ/mole K², which means that CeIr₅ is another ordinary non-heavy fermion compound.

The crystal structure of CeIr₅ is cubic AuBe₅-type with Ce-Ce spacing dCe-Ce = 5.31Å [74]. Although it lies high beyond the Hill limit [27], CeIr₅ is a superconductor. This was explained by Huber [75] who suggested that it is the transition metal (Ir), not Ce, which carries the superconductivity. Therefore Hill's criterion does not apply to this system.

It is interesting to compare CeIr₅ with UNi₅ and UCu₅, which also have cubic AuBe₅-type structures [76]. While UNi₅, with a U-U spacing of dU-U = 4.796Å, has an essentially temperature independent magnetic susceptibility below room temperature and stays paramagnetic, UCu₅, with dU-U = 4.973Å, orders antiferromagnetically below 15K and has a C/T value of 86 mJ/mole K² below 0.5K. On one hand, the magnetic ordering in UCu₅ is due to the presence of f electron carrying U atoms. On the other hand, the non-magnetic behavior of UNi₅ is determined by an almost filled Ni 3d band [76]. The transition from magnetic UCu₅ to non-magnetic UNi₅ arises from the disappearance
of U^{3+} ions in the compound. The behavior of superconductor CeIr\textsubscript{5} seems to be similar to that of UNi\textsubscript{5} in the sense that both of them are non-magnetic and have the characteristics of transition metal. Since Ni and Cu are immediate neighbors in periodic table, it would be interesting to replace Ir in CeIr\textsubscript{5} by its immediate neighbor Pt in order to see if the UCu\textsubscript{5}-like behaviors, i.e., the appearance of Ce\textsuperscript{3+} ions, magnetic ordering and the relatively large C/T value can be found in CePt\textsubscript{5}. Unfortunately, CePt\textsubscript{5}, which is supposed to have a slightly larger \(d_{\text{Ce-Ce}}\) than CeIr\textsubscript{5}, crystallizes in a different structure (see below). Therefore we were unable to study this trend.

Our sample contained some second phase. X-ray diffraction pattern showed that the second phase could be Ce\textsubscript{2}Ir\textsubscript{7}. However, the fact that \((C_{S} - C_{n})/C_{n}\) at \(T_{C}\) is so close to the BCS theoretical value indicates that the influence of the second phase on heat capacity can be ignored.

\textbf{b. CePt}\textsubscript{5} \(\quad\) CePt\textsubscript{5} has been studied by Schroder et al. [77]. It crystallizes in hexagonal CaCu\textsubscript{5}-type structure. Although CePt\textsubscript{5} has a much smaller Ce-Ce spacing (\(d_{\text{Ce-Ce}} = 4.38\text{Å}\)) than CeIr\textsubscript{5} (\(d_{\text{Ce-Ce}} = 5.31\text{Å}\), cubic AuBe\textsubscript{5} structure), it undergoes a magnetic transition at \(T_{N} = 1.0\text{K}\) into an antiferromagnetic structure [77]. The tendency toward magnetic ordering is clearly
Fig. 37. \( C/T \) versus \( T^2 \) of CePt\(_5\). Inset: heat capacity as a function of temperature \( T \).
seen from the upturn in our heat capacity data at ~3K (Fig. 37, inset). Because of the low temperature limit of our apparatus we were unable to make measurements below 1.3K. The electronic specific heat coefficient γ determined from the linear region of C/T versus T^2 plot (20K^2 < T^2 < 100K^2) (Fig. 37) is ~15 mJ/mole K^2.

3. Ce_2Zn_{17}

Ce_2Zn_{17} has been extensively studied by both Olivier et al. [78] and Sato et al. [79]. The former concluded that Ce_2Zn_{17} is a Kondo lattice (or 4f instability) from the resistivity and magnetic susceptibility behaviors. While the latter suggested that there was no evidence of dense Kondo effect for resistivity and Ce_2Zn_{17} is a stable trivalent cerium compound. They also suggested that some short range ordering occurred before the system undergoes an antiferromagnetic ordering at T_N ~1.6K from the entropy calculation.

The experiments conducted on a polycrystalline sample in our laboratory revealed that the compound showed no sign of Kondo lattice behavior and no short range ordering above T_N was evident in our sample. Figure 38 shows the heat capacity of Ce_2Zn_{17} as C/T versus T^2. The peak at ~1.7K (Fig. 38, inset) is due to the antiferromagnetic ordering just mentioned. The entropy
Fig. 38. C/T versus $T^2$ of Ce$_2$Zn$_{17}$. Inset: heat capacity as a function of temperature $T$. 

Ce$_2$Zn$_{17}$
associated with this peak was calculated, and it reached Rln2 per mole-Ce at ~5K. No large tail was found above the ordering temperature in heat capacity. All these suggest that there is no short range order above T_N. The conclusion made by Sato et al. that short range ordering exists was based on the fact that entropy up to T_N is less than half of the total entropy Rln2 per mole-Ce [79], which is not quite convincing because the rest of the entropy might be recovered above T_N. Above ~7K, (~50K^2), C/T versus T^2 follows a straight line, and the electronic specific heat coefficient γ and Debye temperature θ_D were determined. The small value of γ = 15 mJ/mole Ce K^2 is typical of an ordinary metallic compound. No sign of heavy fermion behavior was seen.

The inverse of magnetic susceptibility is plotted against temperature in Fig. 39. The susceptibility χ can be expressed as

\[ \chi = \frac{C}{T - \Theta_p} + \alpha \]  

where

\[ C = 1.06 \text{ emu K/mole Ce} \]  

\[ \Theta_p = -1.7K \]  

\[ \alpha = -1.8 \times 10^{-3} \text{ emu/mole}. \]

The effective moment derived from Curie constant C is 2.91μ_B, which is somehow larger than the expected value 2.54μ_B. The small Curie temperature Θ_p = -1.7K is consistent with the Θ_p values of the other rare earth R_2Zn_{17} compounds according to
Fig. 39. The inverse susceptibility as a function of temperature
DeGennes' scaling [78]. While in Olivier's report, $\theta_p = -25K$ for $\text{Ce}_2\text{Zn}_{17}$, which is inconsistent the $\theta_p$ values of other $R_2\text{Zn}_{17}$ compounds, was attributed to either a 4f instability or Kondo effect [78]. Our results support the conclusion that $\text{Ce}_2\text{Zn}_{17}$ is an ordinary stable trivalent compound. The relatively large Larmor diamagnetism as indicated by $\alpha$ value explains the obvious deviation from the Curie-Weiss law.

4. Ce-Cd compounds

As mentioned in the introduction of this thesis, the interaction between f electron and conduction electrons of the neighboring non-f atoms is important in determining the behaviors of a system. It seems to be necessary that one of these neighboring elements is from the end of d-block or the beginning of the sp-block in the periodic table for a heavy fermion system. Since Cd is an early sp-block member, we studied the low temperature properties of some Ce-Cd binary intermetallic compounds. Among them, $\text{CeCd}_{11}$ has been discussed earlier in Section B.

a. CeCd$_2$ The crystal structure and low temperature susceptibility data above ~80K have been reported [80,72]. Other information is lacking. In studying the low temperature properties of this compound, two samples had been prepared. The
first one has a small amount of impurity phase in it, while the other is a clean single phase sample. The original measurements were conducted on the first sample before the second one was made.

The heat capacity of the first sample showed some interesting features. As shown in Fig. 40, two conjunctive peaks were found at ~18.5K and ~22K, respectively. To find out the origin of the two peaks, we measured the dc magnetic susceptibility $\chi$ using a field of $H = 0.5T$. Figure 41 shows the $\chi$ as a function of temperature from 1.3K to 50K. One local maximum was found at ~23K. This maximum suggests that the transition associated with the peak(s) in heat capacity is an antiferromagnetic one.

The question is why there is only one peak in $\chi$ while there are two peaks in heat capacity. There are two possible answers to this question. One possibility is that the system undergoes two conjunctive antiferromagnetic phase transitions. Since the measuring field ($H=0.5T$) is large, one of the transitions is smeared out due to a small spin-flip field. Therefore, we see only one peak in susceptibility. Another possibility is that one of the peak in heat capacity is from the impurity present in the sample and actually there is only one magnetic phase transition at ~22K. This latter suggestion is supported by the
Fig. 40. Heat capacity of CeCd$_2$ over temperature range 8K < T < 50K
Fig. 41. Magnetic susceptibility versus temperature. (measuring field H = 0.5T)
Fig. 42. Magnetic susceptibility versus temperature. (measuring field $H = 10$ Gauss)
susceptibility measurement on the second sample, which was free of the impurity phase. Shown in Fig. 42 is the dc susceptibility of CeCd$_2$ (clean sample) for an extended temperature scale. The measurement was done using a SQUID magnetometer with a measuring field $H = 10$ Gauss. Such a small field will assure that the antiferromagnetic phase transition would not be smeared out. As seen, within the experiment error, there is only one peak at \(~23K\). This indicates that the antiferromagnetic phase transition shows no sign of a "two-step" character. In another words, only one peak in heat capacity is associated with the phase transition, while the other is from the impurity phase.

Also can be seen in Fig. 41, below the maximum $\chi$ starts to increase with decreasing temperature at \(~8K\), which implies that the antiferromagnetic state below \(~22K\) is only a metastable one. The system might go to a stable magnetically ordered ground state at a temperature below 1.3K. A further investigation below 1.3K is needed.

Above \(~30K\) the susceptibility follows Curie-Weiss law (Fig. 43). The Curie temperature and effective moment determined from the linear region in Fig. 43 is listed in the Appendix.

The electronic specific heat coefficient and Debye temperature are difficult to determine in this case. Figure 44
Fig. 43. The inverse susceptibility as a function of temperature
Fig. 44. $C/T$ versus $T^2$ of CeCd$_2$ for $T < 10K$ ($T^2 < 100K^2$)
shows the C/T versus T^2 plot for T < 10K. The non-linear behavior, which is part of the reason that makes it difficult to determine γ and θ_p, is due to the magnetic contribution to the heat capacity. The situation is complicated by the fact that there might be another magnetic phase transition below 1.3K whose contribution to the heat capacity is hard to estimate.

b. CeCd_3 The only information available about CeCd_3, as we know of, were its crystal structure, effective moment and Curie temperature [72,81]. Therefore, the low temperature heat capacity and magnetic susceptibility of this compound were studied. Shown in Fig. 45 is the susceptibility γ as a function of temperature for temperature range 1.3K < T < 30K. The cusp at 2.0K is a clear indication that the system undergoes a transition into an antiferromagnetic state. The effective moment and Curie temperature determined from the Curie-Weiss type susceptibility (30K < T < 200K) are μ_eff = 2.60μ_B and θ_p = -52K, respectively. The negative θ_p value, which is twice as large, in amplitude, as the previously reported value (θ_p = -29K) [72], agrees with the fact that CeCd_3 is an antiferromagnet at the lowest temperature. The heat capacity of CeCd_3 up to 30K is shown in Fig. 46. The Néel temperature T_N was determined from the location of the peak, which turned out to be 2.0K. The C/T versus T^2 plot (Fig. 47) showed a perfect straight line between ~7K and ~16K.
Fig. 45. Magnetic susceptibility $\chi$ of CeCd$_3$ for temperature range $1.3K < T < 30K$
Fig. 46. Heat capacity of CeCd₃ for temperature $1.3K < T < 30K$
Fig. 47. C/T versus $T^2$ plot for CeCd$_3$
(−50K² and −260K²), and the electronic specific heat coefficient and Debye temperature were determined from these data (Appendix).

c. Ce₁₃Cd₅₈ Ce₁₃Cd₅₈ crystallizes in hexagonal Pu₁₃Zn₅₈-type structure [81]. The Ce-Ce spacing determined from the lattice parameters is d_Ce-Ce = 4.37Å (Appendix). Since it is larger than the Hill limit, the system is expected to order magnetically [27]. Thus the tendency towards the magnetic ordering at a temperature lower than 1.3K as indicated by the upturn in C/T versus T² plot at ~3K (10K², Fig. 48) is not surprising.

The inverse of magnetic susceptibility χ⁻¹ is plotted as a function of temperature in Fig. 49. The Curie temperature determined from the straight line (a Curie-Weiss behavior) at high temperature is −12K, which implies that the possible magnetic phase transition below 1.3K is of antiferromagnetic type.

d. CeCd₆ Similar to Ce₁₃Cd₅₈, CeCd₆ also showed a tendency towards magnetic ordering at temperature below 1.3K. As shown in Fig. 50, the upturn in C/T versus T² plot at ~3K (10K²) is obvious. The inverse susceptibility of CeCd₆ is shown in Fig. 51, and the Curie temperature and effective moment were
Fig. 48. C/T versus $T^2$ of Ce$_{13}$Cd$_{58}$
Fig. 49. The inverse susceptibility as a function of temperature.
Fig. 50. C/T versus \( T^2 \) of CeCd₆
Fig. 51. The inverse susceptibility of CeCd$_6$
determined. Again, a negative Curie temperature was found which infers antiferromagnetic ordering.

Both the electronic specific heat coefficients and Debye temperatures of CeCd₆ and Ce₁₃Cd₅₈ are listed in the Appendix.

5. Summary

In spite of the fact that the Ce binary system studied satisfy most of the conditions for the formation of heavy fermion state, e.g., the relatively large Ce-Ce spacings and the favorable electronic structures of non-f electron ligand atoms, no heavy fermion behavior was found (the γ values are listed in the Appendix). All compounds, except for superconductor CeIr₅, show magnetic ordering or the tendency towards the magnetic ordering. It is demonstrated that a large Ce-Ce spacing is a necessary condition but not a sufficient one for the formation of heavy fermion state.

D. Studies on Some Ce Ternary Compounds

1. CeNiAl and CeNiAl₁₀₅Ga₀₅

Both CeNiAl and CeNiAl₁₀₅Ga₀₅ have a hexagonal Fe₂P-type structure [82]. In this structure Ce atoms occupy 3g positions (x,0,1/2), Al (and Ga) atoms occupy 3f positions (x,0,0), and Ni
Fig. 52. The inverse susceptibility for CeNiGa$_{1-x}$Al$_x$ alloys and calculated least squares fit [82]
atoms occupy 1b position (0,0,1/2) and 2c positions (1/3,2/3,0) [83]. The magnetic properties of isostructural CeNiAl\(_x\)Ga\(_{1-x}\) (0 ≤ x ≤ 1) alloys have been studied by Grin et al. [82]. They found a remarkable deviation from the simple Curie-Weiss law in all cases of the CeNiAl\(_x\)Ga\(_{1-x}\) alloys (Fig. 52). With increasing Al content the magnetic properties are characterized by a pronounced minimum in the inverse susceptibility, which is satisfactorily explained with Ce valence fluctuation.

It is certainly of interest to study the calorimetric behavior of this system. Samples CeNiAl, CeNiAl\(_{0.5}\)Ga\(_{0.5}\) and CeNiGa were prepared by arc-melting. CeNiAl was a single phase compound, while the other two had some second phase in the samples. Therefore, a heat treatment was conducted on these two samples. X-ray diffraction patterns showed that CeNiAl\(_{0.5}\)Ga\(_{0.5}\) sample after the heat treatment is essentially single phase with the expected crystal structure and that CeNiGa sample still had a significant amount of second phase in it. The heat capacities of the single phase samples CeNiAl and CeNiAl\(_{0.5}\)Ga\(_{0.5}\) were measured and are shown in Fig. 53 for temperature range 1.3K < T < 20K. As seen, there is no apparent difference between the two in this temperature range.

The C/T versus T\(^2\) plot is shown in Fig. 54 for a narrower temperature range. Both alloys have a simple straight line
Fig. 53. Heat capacities of CeNiAl and CeNiAl$_{0.5}$Ga$_{0.5}$
Fig. 54. C/T versus $T^2$ for CeNiAl and CeNiAl$_{0.5}$Ga$_{0.5}$
behavior. The Debye temperatures are about the same, $\Theta_D = 290K$ for CeNiAl and $\Theta_D = 283K$ for CeNiAl$_{0.5}$Ga$_{0.5}$. The electronic specific heat coefficient is slightly higher for the latter, but neither one is large ($\gamma = 7.2$ mJ/mole K$^2$ for CeNiAl and $\gamma = 8.7$ mJ/mole K$^2$). As a matter of fact the $\gamma$ values are smallest of all the Ce samples studied. It is not unusual that a valence fluctuation system has such a $\gamma$ value, e.g., the valence fluctuator $\alpha$-Ce has a $\gamma$ of $\sim 12.8$ mJ/mole K$^2$ [84].

According to Sales and Wohlleben [85], the magnetic susceptibility of a valence fluctuation system involving Ce can be expressed phenomenologically as

$$\chi = N(2.54\mu_B)^2\nu(T)/3k_B(T+T_{sf})$$

and

$$\nu(T) = 6/[6+\exp[-E_{ex}/k_B(T+T_{sf})]]$$

where $E_{ex} = E_1 - E_0$ is the energy difference between the supposed $f^1$ state and $f^0$ state, and $T_{sf}$ is the measurement of transition rate between the two states. Grin et al. have used above equations to fit the experimental data, and they obtained an acceptable agreement between the calculation and experiment. The fitting gave $E_{ex} = 1400$ cm$^{-1}$, i.e., $\sim 2000K$ and $T_{sf} = -380K$ [82]. Such a large $E_{ex}$ explains the normal behavior of heat capacity at low temperature (Fig. 54) since the anomalous behavior is expected to occur at $-E_{ex}$ [86,87]. The difference in $\gamma$'s
indicates that, by replacing half Al with Ga, the density of state at Fermi level $\varepsilon_F$ is increased from CeNiAl to CeNiAl$_{0.5}$Ga$_{0.5}$ by 20%.

2. CeNi$_{12}$B$_6$

The crystal structures of CeNi$_{12}$B$_6$ and LaNi$_{12}$B$_6$ were reported in ref. [88,89]. The lattice parameters of the orthorhombic unit cell are listed in the Appendix. The closest Ce-Ce spacing in CeNi$_{12}$B$_6$ is found to be 6.06Å, which is a relatively large separation.

Shown in Fig. 55 is the heat capacity of CeNi$_{12}$B$_6$ for temperature range 1.3K < T < 55K. The magnetic ordering at 1.7K is clearly indicated by a sharp peak (see Fig. 55 inset for an expanded view). The entropy calculated from the heat capacity data is $S = 4.88$ J/mole K at ~8K, which is ~85% of the expected value Rln2. In the calculation the contributions to the heat capacity from lattice and conduction electrons have been removed by subtracting the heat capacity of LaNi$_{12}$B$_6$ from that of CeNi$_{12}$B$_6$. In another words, the entropy is calculated from the area between the two curves in Fig. 56, inset. As seen, the lattice and conduction electron heat capacities are, in fact, negligible over the temperature range shown.
Fig. 55. Heat capacity of CeNi$_{12}$B$_6$ for temperature $1.3\text{K} < T < 55\text{K}$.

Inset: an expanded plot at low temperatures
Fig. 56. $C/T$ versus $T^2$ plot for CeNi$_{12}$B$_6$. Inset: $C/T$ versus temperature at lower temperatures.
The $C/T$ versus $T^2$ plot (Fig. 56) above the ordering temperature reveals that there is no sign of heavy fermion behavior. The electronic specific heat coefficient $\gamma$ was determined in the same way as was done in the case of CePtGa$_3$. The difference in $C/T$ between CeNi$_{12}$B$_6$ and LaNi$_{12}$B$_6$ in temperature region $10\text{K} < T < 20\text{K}$ was considered as the $\gamma$ of the former in excess of that of the latter. The average value of this difference ($33 \text{ mJ/mole K}^2$) was added to the $\gamma$ of LaNi$_{12}$B$_6$ ($32.3 \text{ mJ/mole K}^2$) to give the $\gamma$ value of CeNi$_{12}$B$_6$ ($\sim 65 \text{ mJ/mole K}^2$). Also shown in Fig. 56 is the same plot for LaNi$_{12}$B$_6$. Its linear behavior at low temperature ($T < 10\text{K}$) allowed us to determine the $\gamma$ and $\Theta_p$ for LaNi$_{12}$B$_6$. At the same time the Debye temperature of LaNi$_{12}$B$_6$ serves as a good estimation to that of CeNi$_{12}$B$_6$.

A broad maximum at $\sim 3\text{K}$ in dc magnetic susceptibility (Fig. 57) is associated with the peak in heat capacity at $1.7\text{K}$, and it indicates that the magnetic ordering is antiferromagnetic. The inverse susceptibility $\chi^{-1}$ as a function of temperature is shown in Fig. 58. The positive Curie temperature determined from the data above $80\text{K}$, $\Theta_p = +9.3\text{K}$, is contradictory to the antiferromagnetic ordering at $1.7\text{K}$. A detailed examination of the $\chi^{-1}$ versus $T$ curve reveals that it is not a perfect straight line. While the $\Theta_p$ obtained from low temperature region is
Fig. 57. Magnetic susceptibility of CeNi$_{12}$B$_6$ for temperature $2K < T < 20K$
Fig. 58. The inverse susceptibility of CeNi$_{12}$B$_6$ over a wider temperature range 2K < T < 300K
negative, $\theta_p$ obtained from high temperature region is positive. If the temperature is raised near room temperature, the $\theta_p$ seems to become negative again. The cause of this deviation from the Curie-Weiss behavior might be the presence of crystalline electric field effect.

3. Ce$_5$Ni$_6$In$_{11}$

This sample was prepared by arc-melting. During this process a weight loss of 0.244 gram occurred for the sample of total mass = 22.96 gram. If we assume that only In was lost, which is reasonable because In has a higher vapor pressure than Ce and Ni [90,91], the actual composition should be Ce$_5$Ni$_6$In$_{10.8}$.

The crystal structure of this compound was reported by Kalychak et al. [92]. The Ce-Ce spacing in Ce$_5$Ni$_6$In$_{11}$ is ~3.99Å.

The heat capacity of Ce$_5$Ni$_6$In$_{11}$ measured from 1.5K to 20K is shown in Fig. 59 together with that of La$_5$Ni$_6$In$_{11}$. The upturn at ~5K is an indication that Ce$_5$Ni$_6$In$_{11}$ will become magnetically ordered below 1.5K. Figure 59 inset is the C/T versus $T^2$ plot for the same temperature range. Also shown in the inset is the difference $\delta = (C/T_{Ce5Ni6In11} - C/T_{La5Ni6In11})$ as a function of $T^2$. The electronic specific heat coefficient $\gamma$ of Ce$_5$Ni$_6$In$_{11}$ was determined in the same way as were done in the case of CePtGa$_3$ and CeNi$_{12}$B$_6$. By adding the average value of the difference $\delta$ in
Fig. 59. Heat capacities of $\text{Ce}_5\text{Ni}_6\text{In}_{11}$ and $\text{La}_5\text{Ni}_6\text{In}_{11}$. Inset: $C/T$ versus $T^2$ plot for both compounds and their difference (see text).
Fig. 60. The inverse susceptibility as a function of temperature.

Temperature range: $2K < T < 160K$
temperature region $10K < T < 20K$ to the $\gamma$ of La$_5$Ni$_6$In$_{11}$, which was determined at lower temperatures ($T < 3K$), the $\gamma$ value of Ce$_5$Ni$_6$In$_{11}$ was found to be $\approx 160$ mJ/mole Ce K$^2$. This relatively large $\gamma$ places Ce$_5$Ni$_6$In$_{11}$ into an intermediate heavy fermion category.

Figure 60 shows the inverse susceptibility of Ce$_5$Ni$_6$In$_{11}$. The effective moment $\mu_{\text{eff}} = 2.62\mu_B$ is close to the theoretical value $2.54\mu_B$ for Ce$^{3+}$ ion. The Curie temperature is found to be $\theta_p = -8.0K$, which implies that the ground state of this compound is antiferromagnetic in nature.
IV. CONCLUSION AND SUMMARY

In search of heavy fermion materials, the low temperature properties of a series of cerium intermetallic binary and ternary compounds were studied.

Although the spin-carrying Ce atoms in CePtGa$_3$ form a periodic array, the compound shows a spin glass behavior in its low temperature susceptibility and heat capacity. This spin glass behavior is believed to be due to the random distribution of Pt and Ga atoms around the Ce atoms which induces a random RKKY interaction between the spins. This finding places CePtGa$_3$ as the third known NMAD (non-magnetic atomic disorder) spin glass material after CeCu$_{6.5}$Al$_{6.5}$ and CePd$_3$B$_{0.3}$.

Crystalline electric field (CEF) effect plays an important role in both CeCd$_{11}$ and CeGa$_2$. The CEF splittings were determined in the case of CeCd$_{11}$ from the Schottky anomaly in heat capacity. The splitting between the first excited doublet and the ground state $E_1 = 17.5$K is one of the lowest CEF splittings found in Ce compounds. The Schottky anomaly of this kind of low energy level sometime can show up as a false signal of heavy fermion behavior. An immediate example is found in CeGa$_2$ where the Schottky heat capacity from the relatively small CEF splitting $E_1 = \sim 62$K in CeGa$_2$ accounts for $\sim 40\%$ of the large
C/T value (~400mJ/mole Ce K²) obtained above the ordering temperature.

The antiferromagnetic phase transitions in CeHg₃, CeCd₂, CeCd₃ and CeNi₁₂B₆ are reported for the first time, and strong evidence for antiferromagnetic ordering below ~1.4K is presented for Ce₁₃Cd₅₈, CeCd₆, CeCd₁₁ and Ce₅Ni₆In₁₁.

It seems that the experimental parameters such as Ce-Ce spacing, crystal structure and the type of non-f ligand atoms which determine the heavy fermion behavior is still unknown. This study shows that a large Ce-Ce spacing might be a necessary condition for heavy fermion but it is surely not a sufficient one.
V. REFERENCES


[31] C. L. Lin, J. Teter, J. E. Crow, T. Michalisin, J. Brooks,


Japan, 57, 1069 (1988).


## VI. APPENDIX

Table A.1. Crystal structures and lattice parameters of the Ce compounds studied

<table>
<thead>
<tr>
<th>compound</th>
<th>structure</th>
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<th>b</th>
<th>c</th>
<th>d\textsubscript{Ce-Ce}</th>
</tr>
</thead>
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<tr>
<td>CePt\textsubscript{Ga\textsubscript{3}}</td>
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<td>10.513</td>
<td>4.307</td>
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Table A.2. Selected properties of the Ce compounds studied

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<th>$\theta_D$</th>
<th>$P_{\text{eff}}$</th>
<th>$\theta_P$</th>
<th>$T_s, T_C, T_N, T_{SG}$</th>
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<td>&lt;1.5 (SG)$^d$</td>
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<td>~2.0 (SG)$^d$</td>
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<td>CeCd$_{11}$</td>
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<td>&lt;1.3 (N)</td>
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<td>T$_{SG}$ (K)</td>
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*In units of mJ/mole Ce(La) K$^2$.*

*71, obtained above the spin glass transition; 120, below the transition.*

*Data estimated from LaPtGa$_3$, LaCd$_{11}$, LaGa$_2$, LaNi$_{12}$B$_6$ and La$_5$Ni$_6$In$_{11}$.*

*T$_{SG}$ refers to the peak temperature in heat capacity.*

*After [93].*

*Data not reliable.*

*V = valence fluctuation.*
VII. ACKNOWLEDGEMENTS

This is a great opportunity to express my sincere thanks to Karl Gschneidner, my major professor, who directed me through this study. His enormously rich knowledge and great sense of understanding has made the last three years rewarding and pleasant.

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THIS THESIS IS DEDICATED TO MY PARENTS

WHO HAVE DEVOTED MOST OF THEIR LIVES TO THE SCIENCE.