Electron Paramagnetic Resonance and High Temperature Susceptibility Measurements in Cesium Hexabromide.

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ELECTRON PARAMAGNETIC RESONANCE AND HIGH TEMPERATURE SUSCEPTIBILITY MEASUREMENTS IN CeB₆

A Dissertation

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

in

The Department of Physics and Astronomy

by

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Dedicated
To
My Father
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ABSTRACT

To our knowledge the research reported here represents the first attempt to understand the 4f electronic structure in CeB₆ using EPR. We report extensive temperature and angular dependent EPR measurements on a single crystal of CeB₆ in the paramagnetic phase from 4 to 300 K at 35, 95, and a few measurements at 220 GHz. The 35 GHz measurements were performed at LSU and the 95 and 220 GHz measurements were performed at the National High Magnetic Field Laboratory, Tallahassee, FL. These experiments were made using a standard microwave frequency-locked spectrometer and magnetic field modulation. The measurements are supplemented by temperature and field dependent DC measurements of the sample magnetization. From the EPR line shapes, g-value and spin-lattice relaxation time (T₁) were extracted. The EPR results for CeB₆ showed one absorption peak at the magnetic field corresponding to temperature independent g-value of g = 1.98 and T₁ = 6.35*10¹¹ seconds at room temperature. The g factor for this transition is independent of temperature between 4 and 300 K, depends on magnetic field (measurement frequency) in a non-monotonic manner, and depends slightly on crystal orientation with respect to the applied field direction in the [100] plane. The line width of the EPR spectra decreased and the relaxation time increased with increasing temperature because of exchange narrowing.

Similar measurements were performed on ferromagnetic EuB₆ and g values and spin-lattice relaxation times were extracted.
CHAPTER 1

INTRODUCTION

Localized f-electrons are found in lanthanide and actinide rare-earth (RE) atoms. The largest Hund’s rules atomic moments are found in the REs due to the potentially large total electronic angular momentum J of the f-electron orbitals. In contrast to s and d-electrons, the f-electrons are very tightly bound (localized) to the atomic cores. Because they are so tightly bound, f-electrons often retain their atomic magnetic moments in solids. This is why commercial permanent magnets often contain RE elements.

In f-electron lattice materials with conduction electrons and local f-moments, something very different can happen as the temperature decreases. The local f-moments are coupled antiferromagnetically to the conduction electron moments with a coupling strength J. The interaction between the f and conduction electron moments results in an indirect coupling of the local f-moments to one another. The indirect interaction between local f-moments is called the Ruderman-Kittel-Kasuya-Yosida (RKKY) interaction and can be either ferromagnetic or antiferromagnetic. For example, Kasuya [1] used the RKKY interaction to described the presence of ferromagnetism and antiferromagnetism in RE metals. The characteristic energy scale for the indirect f-f coupling is the Curie temperature T_C (ferromagnetic ordering) or Néel temperature T_N (antiferromagnetic ordering). The dependence of T_C and T_N on J is given by [2]

\[ T_{C,N} \propto J^2. \]  

(1.1)
However, there is an alternative to f-moment magnetic ordering when J is large. In the case of large J, the antiferromagnetic f and conduction electrons (f-c) coupling causes the conduction electron moments to screen the f-electron moments. This effect is called the Kondo effect. The characteristic energy scale for the f-c coupling is called the Kondo temperature $T_K$ and its dependence on J is given by [3]

$$T_K \propto \exp \left( -\frac{1}{J} \right).$$

(1.2)

The net magnetic moment at each lattice site is the sum of the local f-moment and the conduction electron moment coupled to it. Because the two types of moments form a spin zero singlet state the net moment at each lattice site is reduced. In other words, the local f-electron moment is screened by the conduction electrons moments. If the f-moment is completely screened (zero net moment per site) the result is a nonmagnetic ground state. Depending on the value of J there is a competition between the indirect f-f coupling and the f-c coupling. Comparison of the J dependence of $T_K$ with the J dependence of $T_{C,N}$ shows that, in the limit of small J, $T_{C,N}$ will be largest while in the limit of large J, $T_K$ will be largest. In either case, the f and conduction electron moments are still randomized by thermal vibrations at temperatures greater than $T_{C,N}$ and $T_K$. If we assume that $T_K >> T_{C,N}$ then at very low temperatures $T << T_{C,N} << T_K$ the conduction electron moments will align antiferromagnetically with the f-moments. At $T = 0$ the energy that would be required to align the f and conduction...
moments is $k_B T_K$. On the other hand, if $T_{C,N} \gg T_K$ then at temperatures below $T_{C,N}$ the $f$-electron moments will order.

In the above paragraph we did not discuss whether the low temperature ground states of the Kondo lattice systems, $T_K \gg T_{C,N}$, were metals or insulator. If the Fermi level falls in a band the material is metallic. If there are no partially filled bands the Fermi level falls in the energy gap between the filled and empty bands and the material is an insulator.

The electronic structures of cerium compounds have been investigated extensively because they exhibit a number of properties such as the Kondo effect (CeAl$_2$) [4], heavy Fermion (HF) behavior (CeCu$_6$) [5], anti-ferromagnetism (CeB$_6$) [6], and superconductivity (CeCu$_2$Si$_2$) [7]. This unusual variety of properties is due to the behavior of the 4f electron in Ce and has its basis in the competition between a localized character due to strong intra-atomic coulomb interactions within the atoms and an itinerant nature due to hybridization with the valence electrons. A complete picture of the combined itinerate-localized electronic system requires understanding the conduction electron electronic structure, as well as the more localized structure of the 4f electron in these systems. Electron Paramagnetic Resonance (EPR) and temperature dependent magnetic susceptibility are useful methods for determining the low-lying energy levels of localized electronic states in crystals and can give detailed information about the local symmetry of a magnetic ion situated in a crystalline potential [8].

In Ce the degeneracy of the single 4f orbital is lifted by spin-orbit coupling into two energy separated multiplets with $J = 5/2$ and $J = 7/2$. The $J = 5/2$ multiplet is
lowest in energy with the separation, $\delta$, between them being of order 270 meV (3100 K) [9]. In CeB$_6$ the cubic crystalline electric field (CEF) further splits the six-fold degenerate $J = 5/2$ level into a quartet, $\Gamma_8$, and a doublet, $\Gamma_7$. The ordering of these levels has been a subject of controversy [10,11,12], but it is now generally conceded that the $\Gamma_8$ is lowest in energy. The energy separation, $W$, between the $\Gamma_8$ and $\Gamma_7$ has been measured to be near 46 meV (530 K) by means of polarized Raman scattering [13], inelastic neutron scattering [14], and specific heat measurements [15].

At high temperatures ($T > 4$ K) and low magnetic fields CeB$_6$ is paramagnetic (Phase I) [10,11,16]. At temperatures below 4 K in zero magnetic field CeB$_6$ undergoes two magnetic ordering transitions, $T_Q = 3.2$ K (Phase II) and $T_N = 2.3$ K (Phase III) [17]. Each phase shows unusual properties. The high temperature paramagnetic phase exhibits the Kondo effect in that the electrical resistivity increases logarithmically with decreasing temperature [18]. This observation implies the existence of localized moments at high temperatures in CeB$_6$.

The ordering in Phase II has been studied by neutron diffraction and proposed to be an ordering of orbital quadrupole moments [19]. As can be seen from the published phase diagram [20], the state is not destroyed by the application of a magnetic field up to 32 T. In this model it is the coupling between the orbital quadrupole and spin dipole moments that allows the phase transition to be observed with magnetic measurements. Because of the measured diffraction peaks corresponding to a wave vector $k_0 = [\frac{1}{2}, \frac{1}{2}, \frac{1}{2}]$ observed in neutron diffraction [19] the ordering in Phase II was proposed to be that of electric quadrupole moments, requiring a
splitting of the four-fold degenerate $\Gamma_8$ ground state into two doublets. Several models have been given for this splitting. Various models include a dynamic Jahn-Teller effect involving acoustic phonons, a hybridization-mediated anisotropic coupling of the 4$f$ wave functions to the p-like boron or 5d-type cerium wave functions have been suggested as possibilities [13]. In an early paper, Ohkawa [21] proposed that indirect exchange interactions between pairs of cerium atoms would produce a splitting of the four-fold level (4 x 4) into sixteen levels split into a group of two triplets and a group consisting of a singlet plus a nine-fold degenerate level with Phase II representing an ordering of the orbital moments. Most recently, an alternate interpretation of the neutron scattering results was given by Uimin [22] in which he interprets the low temperature frequency shift of the $\Gamma_7 - \Gamma_8$ splitting to arise from collective modes caused by the orbital degrees of freedom. It should be noted that muon spin rotation measurements in zero applied magnetic field yield a different magnetic structure for CeB$_6$ for both Phase II and Phase III [23,24].

In the lowest temperature Phase III the dipole moments of the Ce atoms become anti-ferromagnetically ordered. The long-range magnetic order has several sub-structures that have been observed by neutron diffraction [25] and nuclear magnetic resonance (NMR) [26,27]. We will not be concerned with the structure of Phase III other than to point out that at all applied magnetic fields above about 2.2 T and temperatures above 2.1 K where the measurements reported here are made it does not exist.
Like other rare-earth hexaborides EuB$_6$ crystallizes in a CsCl structure, with both Eu ions and boron octahedra located on single cubic lattice sites. In this material the Eu ions are embedded in a very rigid boron frame so that the Eu-Eu spacing is approximately the same (about 4.15 Å) between every Eu ion. This structural simplicity makes EuB$_6$ an important model for fundamental studies of magnetic interactions in solids. EuB$_6$ is unique among the rare-earth hexaborides in that it is a semiconductor at high temperatures with a semiconductor to metal transition at the ferromagnetic Curie temperature of 15 K [28,29]. Of fundamental importance in EuB$_6$ is the mechanism of the exchange interaction between the Eu $^{2+}$ moments. Four possible exchange mechanisms have been suggested for EuB$_6$ in the literature: 1.) direct or superexchange [30,31], 2.) the RKKY interaction [29,32], 3.) Bloembergen-Rowland (BR) interaction [33-36], and 4.) magnetic polaron formation [37]. At high temperatures, the susceptibility $\chi$ of EuB$_6$ follows a Curie-Weiss behavior for fields applied along the main cubic unit cell directions. Fitting $\chi$ above 50 K to Curie-Weiss functions yields the effective high temperature moments $\mu_{\text{eff}}$, 7.9 $\mu_B\parallel[100]$, 8.0 $\mu_B\parallel[110]$, 8.2 $\mu_B\parallel[111]$ and Curie temperatures $\theta_c$, 14 K $\parallel[100]$, 15 K $\parallel[110]$, 14 K $\parallel[111]$ [38]. The values of $\mu_{\text{eff}}$ are in good agreement with the magnetic moment of Eu$^{2+}$ ion calculated from Hund’s rule, 7.94$\mu_B$.

In EuB$_6$ the 4$f^7$ level is estimated to be about 1 eV below the Fermi level [39]. The 4$f^7$ levels should actually form extremely narrow bands. However, according to Kasuya et al. [40], there is mixing between these 4f states and the 2p boron states. In
the paramagnetic region this mixing pushes the top of the valence band up to above 0.1 eV, and makes the band gap narrower. Magnetization and de Haas van Alphalen experiments were carried out on EuB₆ early by an LSU group [41]. Since EuB₆ has highly localized moments with spin S = 7/2, the shape of the magnetization vs. temperature curve in the magnetization experiments is expected to follow a Brillouin function. However, they found that this was not the case. An excellent fit is obtained from zero to 5.5 T if what is expected from a two level spin ½ system having Langevin paramagnetism, M = Nμtanh(μ₅B/k₅T) is added to the Brillouin function. In addition, from pulsed field magnetization and low field torque dHvA measurements it is concluded that the Fermi Surface (FS) of EuB₆ consist of two pockets per Brillouin zone. These results were interpreted to be an electron and a hole ellipsoid both centered at the X point of the Brillouin zone as predicted by energy band calculations.

EPR experiments using 9 and 35 GHz in the temperature range of 1.4 to 300 K on single crystal EuB₆ were made by Oseroff et al [42]. A value of g = 1.995 ± 0.010 was measured at both frequencies. Then, EPR in ferromagnetic EuB₆ single crystals was observed and compared with the results of EPR in EuB₆ ferromagnetic bulk polycrystals [43]. Here EPR measurements were made using the X, K, and Q band spectrometers in the temperature range from 1.5 to 300 K.

One single line is observed and g = 2.0 and no anisotropy is observed in EuB₆ single crystals at all temperatures and all frequency bands.

The EuB₆₋ₓCx compounds also have been studied by EPR in the X band at temperatures above the magnetic ordering temperature [44]. At first sight they
expected that $\text{EuB}_{6-x}\text{C}_x$, in which every carbon atom donates an extra electron to the material, would have a behavior similar to that of $\text{Eu}_{1-y}\text{Gd}_y\text{B}_6$, in which each substituting gadolinium cation leads to the addition of an electron into the conduction band. Since in both $\text{EuB}_{6-x}\text{C}_x$ and $\text{Eu}_{1-y}\text{Gd}_y\text{B}_6$ alloys the density of the $4f^7$ ions in the cationic sub-lattice to remain constant, one might expect that the dependence of the peak-to-peak linewidth $\Delta H_{p-p} = f(x \text{ or } y)$ in the two compounds would coincide. However, this was not the case. For the same linewidths, the value of $x$ is observed to be twice as large for $\text{EuB}_{6-x}\text{C}_x$ as $y$ is for $\text{Eu}_{1-y}\text{Gd}_y\text{B}_6$ [45].

Section II gives general information about the rare earth hexaborides, a full description of $\text{CeB}_6$, and the relevant theory for heavy Fermion $\text{CeB}_6$. Section III gives general information about EPR and its relationship to the other experiments. In section IV the experimental procedure and data analysis used in this experiment are described. Section V and VI give a discussion of the results. The last section gives the conclusions of the work in this dissertation.
2.1 Introduction

Rare-earth hexaboride (REB₆) materials have attracted considerable attention for over 30 years, due to their anomalous transport and magnetic properties [45, 46]. Interest in these materials arises from the fact that although the hexaborides show the same crystal structure similar to CsCl, they exhibit a number of attractive properties such as a Kondo insulator (SmB₆) [47], a semiconductor (SrB₆), a normal metal not having an f electron (LaB₆) [48], heavy Fermion (HF) behavior (CeB₆) [40, 49]. The electronic and magnetic properties of the REB₆ are strongly influenced by the filling of the 4f shell of the RE atoms and a wide variety of behaviors are observed. The next two sections will be devoted to rare-earth hexaborides and heavy Fermions because CeB₆ is a heavy Fermion material.

2.2 Crystal Structure of Rare-earth Hexaborides

The crystal structure of REB₆ hexaborides was determined in the early 1930s [50]. They belong to the CaB₆ structure type in which rare-earth atoms and regular octahedra of boron atoms are arranged in the manner of Cs and Cl ions in the CsCl structure type (see Figure 2.1) [51]. The band structure calculations [52, 53] show that the boron octahedron requires two extra electrons for its stability, which are donated by the rare-earth metal atoms. Therefore, it is possible that the hexaborides of trivalent
Figure 2.1: Crystal structure of CeB₆.
rare-earth metals have, in principle, up to a third of their metal sites vacant, according to the observed compositional changes within the homogeneity regions.

This situation called for high-precision X-ray and neutron diffraction studies of the crystal structure of the REB$_6$. Many the results of X-ray single-crystal diffractometry studies have been reported for LaB$_6$ [54-56], CeB$_6$ [56,57], and SmB$_6$ [56]. They showed the complete occupancy of the metal site and indicated the occurrence of vacancies at the boron site for LaB$_6$ and CeB$_6$. For SmB$_6$, the occurrence of about 20% of vacancies at the metal site was reported [56].

2.3 Electronic Structure

A very simple description of the electronic structure of the REB$_6$ is produced if the valence electrons of the elements are taken into account. Some of these electrons fill the bonding orbitals, and the others are in a conduction band. Thus, according to the theoretical model of Languet-Higgins [58], the stabilization of the boron framework of REB$_6$ requires the addition of two electrons from each metal atom.

It is clear that borides with RE$^{3+}$ trivalent rare-earths are metallic with one electron per RE atom in the conduction band, while borides with divalent cations are either narrow gap semiconductors or insulators [48,58-61]. Quantitative band calculations have been carried out for the hexaborides YB$_6$ and LaB$_6$ [48,52,62,63], EuB$_6$ [64] and CaB$_6$ [53]. These calculations show that the valence bands are formed by the bonding and the non-bonding orbitals of the B$_6$ octahedra, and that they require two electrons for each octahedron.
2.4 Electrical Properties

Most of the RE hexaborides are metallic conductors except EuB₆, SmB₆ and YbB₆ which are semiconducting [65,66]. In the general case, one electron per RE atom is delocalized in the conduction band, which supposes the formation of RE³⁺ cations. With an empty 4f shell, LaB₆ is one of the most typical monovalent metals and detailed information on the Fermi surface obtained from dHvA experiments [61] is in good agreement with the band structure calculation [62]. LaB₆ has a high electrical conductivity mainly due to the light effective mass of the conduction electrons [40]. Actual materials such as SmB₆ and YbB₆ seem to be narrow gap semiconductors with gap of the order of 1000 K [59,67]. YbB₆ is the only compound among the RE hexaborides which has been found to be superconducting at a relatively high temperature (Tc = 7.1 K) [30]. In EuB₆, the 4f levels are situated about 1 eV below the gap [39].

2.5 Magnetic Properties

The RE’s are generally in a 3+ oxidation state except, Eu and Yb, which are typically divalent in their hexaborides, and Sm and Yb, which are in a mixed-valence (non-integral) state in their hexaborides.

The hexaborides with RE = Pr, Nd, Gd, Tb, and Dy order ferromagnetically [30,68-70], while EuB₆ is only ferromagnetic at low temperatures [30,71]. According to the neutron scattering measurement [72], the multiplet J = 4 in PrB₆ splits into Γ₃(0 K)-Γ₃(314 K)-Γ₄(377 K)-Γ₁(464 K) by the CEF, and this compound shows antiferromagnetic orderings at T_{N₁} = 7 K and T_{N₂} = 4.3 K [73,74]. The multiplet J =
9/2 in Nd$_6$ splits into $\Gamma_8^{(2)}$ (0 K)-$\Gamma_8^{(1)}$ (135 K)-$\Gamma_6$ (278 K) [72] and it has an antiferromagnetic ordering at $T_N = 8$ K [70,75]. Gd$_6$ is antiferromagnetic below $T_{N1} = 15.5$ K and $T_{N2} = 10$ K [76]. Sm$_6$ [77,78] is a semiconducting mixed valence compound, having a gap in the narrow $f$ band at the Fermi energy.

The magnetic susceptibilities of the hexaborides of La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy have been measured [79] in the temperature range between 80 and 300 K. The results indicate that the rare-earth hexaborides can be divided into three groups, according to their magnetic behavior: Group I include La$_6$ and Yb$_6$, which show weak paramagnetism with a slightly temperature-dependent magnetic susceptibility. Group II includes Pr$_6$, Nd$_6$, Eu$_6$, Gd$_6$, Tb$_6$ and Dy$_6$. All these compounds are strongly paramagnetic with the magnetic susceptibilities obeying the Curie-Weiss law in the temperature range in question. Ce$_6$ shows similar behavior at temperatures above 150 K. The paramagnetic Curie points, $\theta_p$, except for Eu$_6$ are negative. Group III contains Sm$_6$ only. The magnetic susceptibility of this paramagnetic compound shows anomalous temperature dependence in comparison with those of other RE$_6$ compounds.

It is well known that Ce$_6$ is a typical Kondo material and shows heavy Fermion behavior [40]. For this purpose, we are going to review heavy Fermions in the next section.

2.6 Heavy Fermions

In general heavy Fermion (HF) materials can be described at high temperatures as metals with well localized $f$ electrons, whereas at low temperatures hybridization
effects take over generating a strongly correlated electron system of the conduction and $f$ electrons. Below a characteristic temperature, Kondo temperature, this leads to Kondo-like anomalies in the physical properties, including a strongly enhanced electronic specific heat and correspondingly large cyclotron mass.

It has been suggested that $f$ electrons in these compounds may have inertial masses as high as 1000$m_e$, where $m_e$ is the electron rest mass, because of the weak overlap of wave functions of $f$ electrons on neighboring ions. The main characteristic, the large low-temperature specific heat (LTSCH), indicates an exceptionally high electronic density of states at the Fermi energy. A high density of states results when the conduction electrons are very heavy or, in other words, very slow.

These compounds usually contain rare earth or actinide ions with unfilled $4f$ and $5f$ shells respectively. The heavy Fermion systems have almost localized electronic states at the Fermi surface that are primarily $f$ in character. The electrons in these states interact strongly and give rise to an unusual transformation evident at low temperatures. At high temperatures the sub-lattice of rare earth (e.g. Ce) or actinide (e.g. U) atoms has properties resembling those of weakly interacting magnetic moments immersed in a sea of conduction electrons with normal masses [80]. The temperature at which the $f$ electrons begin to interact with sufficient strength to induce changes in the specific heat coefficients and the susceptibility is called the coherence temperature, which varies from material to material.

Table 2.1 shows some of the heavy Fermion systems with their ground states and ordering temperatures. As can be seen from the table heavy Fermion systems exhibit a variety of ground states: superconducting, antiferromagnetic, paramagnetic,
Table 2.1 Ordering temperature of some heavy Fermion systems.

<table>
<thead>
<tr>
<th>Principal Order</th>
<th>Compound</th>
<th>Ordering Temperature</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>( T_c(K) )</td>
<td>( T_N(K) )</td>
</tr>
<tr>
<td><strong>Superconductors</strong></td>
<td>( \text{CeCu}_2\text{Si}_2 )</td>
<td>0.65</td>
<td></td>
</tr>
<tr>
<td></td>
<td>( \text{UBi}_3 )</td>
<td>0.90</td>
<td></td>
</tr>
<tr>
<td></td>
<td>( \text{UPt}_3 )</td>
<td>0.50</td>
<td></td>
</tr>
<tr>
<td></td>
<td>( \text{UPd}_2\text{Al}_3 )</td>
<td>2.00</td>
<td></td>
</tr>
<tr>
<td><strong>Antiferromagnets</strong></td>
<td>( \text{CeB}_6 )</td>
<td>2.3</td>
<td></td>
</tr>
<tr>
<td></td>
<td>( \text{NpB}_3 )</td>
<td>9.7</td>
<td></td>
</tr>
<tr>
<td></td>
<td>( \text{U}<em>2\text{Zn}</em>{17} )</td>
<td>5.0</td>
<td></td>
</tr>
<tr>
<td></td>
<td>( \text{UCd}_{11} )</td>
<td>0.88</td>
<td></td>
</tr>
<tr>
<td></td>
<td>( \text{CePt}_2\text{Sn}_2 )</td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>No long Range Ordering to 0.02 K</strong></td>
<td>( \text{CeAl}_3 )</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>( \text{CeCu}_6 )</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>( \text{YbAgCu}_4 )</td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>Semiconductors</strong></td>
<td>( \text{CeNiSn} )</td>
<td>Gap(K)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>( \text{Ce}_3\text{Bi}_4\text{Pt}_3 )</td>
<td>6.0</td>
<td></td>
</tr>
<tr>
<td></td>
<td>( \text{Ce}_3\text{Bi}_4\text{Pt}_3 )</td>
<td>35.0</td>
<td></td>
</tr>
</tbody>
</table>

no ordering down to 0.050 K and semiconducting. Attempts to develop a microscopic theory of heavy Fermions began with Kondo theory [81] a description of the low temperature effects of a single magnetic impurity in a sea of conduction electrons. The Kondo model is analogous to heavy Fermions if the f electron states, each possessing a magnetic moments, are viewed as magnetic impurities. The generalization of the Kondo theory to heavy Fermions is found in the Anderson Lattice Model or the single impurity model. It is worth noting that a non-Kondo theory has been put forward by Sheng and Cooper [89]. They treat the f electron behavior as a mixture of two types of liquid, a non-magnetic and magnetic liquid. Thus the f
electrons retain both their itinerant and local nature. All local degrees of freedom are retained; whereas, in the Kondo picture, these local degrees of freedom are destroyed.

The common feature between Kondo-lattice, heavy Fermion, and intermediate-valence compounds is the hybridization of the normally local f electrons with the conduction band of s, p, and d electrons. If the hybridization is strong the f electrons form a narrow band which is situated at the Fermi energy as in CeSn$_3$ [90]. On the other hand, if the hybridization is very weak the f electrons will be local as CeSb, which behaves as an ordinary local-moment rare-earth system [91,92]. Heavy Fermion materials are found for hybridization strength in between these two extremes. CeB$_6$ has a local electron which sits below the Fermi energy. Nevertheless, there is a significant hybridization as shown by the Kondo-type behavior of the resistivity and the large electron mass. Thus CeB$_6$ represents a different limit of heavy Fermion behavior from UPt$_3$. In UPt$_3$ no local-moment order is observed at low temperature, suggesting the formation of a hybridized f conduction band which quenches the local moments. In CeB$_6$ hybridization is not strong enough to destroy the local moment behavior but is strong enough to allow many-body effects which raise the electron mass by nearly 2 orders of magnitude.

Due to a regular arrangement of localized f electrons, magnetic exchange competes with the Kondo effect. In the simplest picture the competition can be described by only one parameter, the exchange coupling J between conduction and f electrons. J itself is dependent on the interatomic distances between localized electrons and increases with decreasing interatomic distances. Therefore, by applying high pressure an increase of the coupling J will be achieved.
Table 2.2: Low temperature properties of some heavy Fermion systems.

<table>
<thead>
<tr>
<th>Compound</th>
<th>$\rho_0$ ($\mu\Omega$ cm)</th>
<th>$\gamma(0 , T)$ (mJ/mol-K$^2$)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>CeCu$_2$Si$_2$</td>
<td>4.8</td>
<td>1000</td>
<td>[7]</td>
</tr>
<tr>
<td>UB$_{13}$</td>
<td>18.0</td>
<td>1100</td>
<td>[82]</td>
</tr>
<tr>
<td>UPt$_3$</td>
<td>0.5</td>
<td>450</td>
<td>[93]</td>
</tr>
<tr>
<td>UPd$_2$Al$_3$</td>
<td>3.5</td>
<td>150</td>
<td>[80]</td>
</tr>
<tr>
<td>CeB$_6$</td>
<td></td>
<td>260</td>
<td>[94]</td>
</tr>
<tr>
<td>U$<em>2$Zn$</em>{17}$</td>
<td></td>
<td>500</td>
<td>[84]</td>
</tr>
<tr>
<td>UCd$_{11}$</td>
<td></td>
<td>840</td>
<td>[85]</td>
</tr>
<tr>
<td>CeAl$_3$</td>
<td>0.77</td>
<td>1620</td>
<td>[87]</td>
</tr>
</tbody>
</table>

In the case of a magnetically ordered heavy Fermion system this increase of exchange coupling $J$ can be examined by means of specific heat measurement under pressure. The shift of the magnetic transition temperature $T_N$ and of the Kondo temperature $T_K$, determined by $\gamma$, give insight into their interplay and role of $J$.

In ordinary metals the electrical resistivity $\rho$ decreases rapidly with decreasing temperature below 300 K. In heavy Fermion systems, $\rho$ often increases with decreasing temperature and only after passing over a maximum at $T \leq 50$ K does $\rho$ decrease to low values as $T \to 0$ K. Examples of this behavior are shown in Figure 2.2 [95].

The LTSH of the metallic heavy Fermion systems differs dramatically from that of an ordinary metal. Table 2.2 lists some of the heavy Fermion systems with $\rho$ and $\gamma$. 

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Figure 2.2: The electrical resistivity as a function of temperature for the heavy Fermion systems [95].
at zero magnetic field. In a usual metal the specific heat consists of an electronic contribution linear in temperature and a contribution from phonons,

\[ C_p = \gamma T + \beta T^3. \]  

(2.1)

Therefore, a \( C/T \) vs. \( T^2 \) plot of a normal metal at sufficiently low temperatures has an intercept of \( \gamma \) and a positive slope of \( \beta \) which are temperature independent constants. In addition there is a \( T^3 \ln T \) term in the specific heat in some of the heavy Fermion materials (for example UPt\(_3\) [80]), which is predicted by Landau Fermi liquid theory for a system of interacting quasiparticles.

Specifically, the electronic specific heat coefficient \( \gamma \) (see Eq. 2.1), which is a direct probe of the effective mass and the density of states at the Fermi level \( n(E_F) \), is enhanced by 1 to 3 orders of magnitude over that of sodium [80].

\[ \gamma = \frac{\pi}{3} k_B^2 n(E_F). \]  

(2.2)

Early theories of the properties of metals always assumed that, whereas the conduction electrons interact with the ionic lattice forming the solid, they do not interact at all among themselves. Quantum statistics then determine the low-temperature properties of this electron gas. The specific heat of this electron gas \( C_p \) varies linearly with
temperature as \( T \to 0 \). The low temperature magnetic susceptibility, \( \chi \), is independent of temperature. In this simple theory the ratio

\[
\frac{\chi}{\gamma} = \frac{3\mu_B^2}{\pi^2 k_B^2}
\]

is obviously a universal number. \( \mu_B \) is the Bohr magneton and \( k_B \) is the Boltzmann constant. The factor which determines the magnitude of both \( \chi \) and \( \gamma \) is the density of electronic states per unit energy, \( n(E_f) \), at the Fermi energy \( E_f \). Hence \( n(E_f) \) varies inversely with the characteristic energy of the electrons, leading \( n(E_f) \) to be proportional to effective mass.

2.7 Cerium Hexaboride

Cerium hexaboride, \( \text{CeB}_6 \), is one of the \( \text{REB}_6 \) compounds and exhibits anomalous transport and magnetic properties [17]. \( \text{CeB}_6 \) has a cubic structure similar to \( \text{LaB}_6 \) of the \( \text{CaB}_6 \)-type with Ce-atoms at the cubic corner sites and the boron octahedron at the body center sites or vice versa. The crystal structure of \( \text{CeB}_6 \) is shown in Figure 2.1. There are no indications of a structural phase transition of \( \text{CeB}_6 \) at low temperature [96].

From de Has van Alphen effect (dHvA) measurements it has been found that the effective mass of the conduction electrons in \( \text{CeB}_6 \) is strongly suppressed at high magnetic fields [6,97-100]. The results of the effective mass measurements in several experiments are shown in Figure 2.3 [100]. A theory for the dHvA effect in heavy
Figure 2.3: The $m^*/m_0$ data is taken from Joss et al. [97]; Onuki et al. [6]; Haannappel [98], and van Deursan [99]. The lowest field point, 7.1 T, is from measurements made by Hall [100] at LSU ($m^* = 26.4 \pm 1$). This figure is reproduced from Ref. [100].

Fermion systems, based on the Anderson lattice model [101], links the quenching of heavy mass in high magnetic fields with Zeeman splitting of the many-body band at the Fermi energy, which arises from the combined effects of hybridization and Coulomb interaction between the conduction and f electrons. The strong suppression of the electron mass as observed in CeB$_6$ in higher fields is exactly what one would expect in a Kondo system when the Kondo temperature is smaller than the Zeeman energy $\mu_0 H$. The effect is so clearly observed in CeB$_6$ because the Kondo temperature of CeB$_6$ is very low, only a few degrees Kelvin [102]. van Deursen et al. [99,103] first studied the $d$HvA effect in CeB$_6$ by using a high field pulse magnet and confirmed that the Fermi
surface of CeB₆ is roughly similar (10% larger) to that of LaB₆ as shown in Figure 2.4, indicating that the 4f-electron is almost localized. If 4f electron was completely localized there would be no hybridization between the 4f electron and conduction electrons, and the Fermi surface and cyclotron mass would be expected to be similar to those in the La compounds.

Two subsequent studies by Bredl [94] and Muller et al. [104] focused on measurements of the LTSH below 1 K to determine the electronic specific coefficient γ. Recently, G. Stewart made LTSH measurements on one sample of CeB₆ at the University of Florida. The measurements were made at temperatures from 0.4 to 1.3 K in fields 0, 2, 7, 8.5, 10, 12, and 14 T. The data is shown in Figure 2.5 [100]. The low temperature specific heat coefficient γ of CeB₆ is very large, 260 mJ/mol.K² at zero tesla [94], nearly one hundred times larger than the value 2.6 mJ/mol.K² in LaB₆ [94]. The Ce Kondo-lattice compound displays a large electronic specific heat typically f electron hybridization, but still retains a large enough moments to order magnetically at low temperature in CeB₆.

2.7.1 Ground State and Crystalline Electric Field Splitting

Since the Ce³⁺ 4f-orbitals are shielded by fully occupied 5-s and 5-p orbitals, the CEF splitting is expected to be much smaller than the splitting by the spin-orbit interaction. The degeneracy of the f multiplet is lifted into a lower multiplet with J = 5/2 and a higher multiplet with J = 7/2 due to the spin-orbit interaction, and its splitting is about 0.27 eV [9] as shown in Figure 2.6. The degeneracy of the lower multiplet is further lifted into a doublet Γ₇ and a quartet Γ₈ due to the crystal field effect with the cubic
Figure 2.4: Cross sections of the Fermi surface in CeB$_6$. 

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symmetry. Although it had been believed for a long time that the doublet is lower than the quartet in energy, Ohkawa [21] has proposed that the quartet should be lower in order to explain the exotic magnetism results [16,105] as well as the specific heat data [15]. The specific heat data shows that the entropy reaches $k_B\ln 2$ around the boundary between phase II and III, and reaches $k_B\ln 4$ at a temperature a little above the boundary between phase I and II. The $\Gamma_7-\Gamma_8$ CEF transition has been identified near 46 meV (530 K) by means of polarized Raman scattering and neutron scattering using high energy incident neutrons [13,106]. Therefore it is clear from this inelastic neutron experiment...
Figure 2.6: Energy level diagram for the 4f electrons in CeB$_6$ including the effect of spin-orbit coupling, cubic crystalline-field splitting, and applied magnetic field.
and the specific heat data that the quartet $\Gamma_8$ is lower in energy. From the anomalous temperature behavior of the $\Gamma_7$-$\Gamma_8$ transition energy observed in Raman scattering, it was concluded that a $\Gamma_8$ is the ground state that is dynamically split by approximately 30 K (2.6 meV) [13]. A similar shift of the $\Gamma_7$-$\Gamma_8$ transition energy by 1 meV to higher energy has been observed below 20 K by high-resolution neutron scattering [14]. The $\Gamma_7$-$\Gamma_8$ CEF splitting in of 545 K has been confirmed by measurements of the temperature and magnetic field dependence of the elastic constants and their quantitative fit in terms of magnetoelastic interactions [107,108]. However, A. Tomita et al. [109] could not fit their thermoelectric power data of CeB$_6$ to a calculation using the theory of Refs. [110,111] and the $\Gamma_8$ ground state splitting of 30 K.

2.7.2 Magnetic Phase Transitions

CeB$_6$ is known to have a rich phase diagram [15,16,18]. The interaction between the 4$f$ electron of a trivalent cerium ion and the electrons of the 5d conduction band gives rise to a typical dense Kondo compound behavior and to a very unusual magnetic phase diagram [17]. Various experiments for a single crystal of CeB$_6$ have been performed including transport properties [18,105,112], magnetic properties [16,105,112], NMR [113], elastic properties [114,115], specific heat [10,15,105], magnetostriction [116] and neutron diffraction [17,117]. These experiments show two magnetic transition temperatures, $T_N = 2.3$ K and $T_Q = 3.2$ K in zero field, with the three phases labeled phase I, II and III in a temperature vs. magnetic field diagram (see Figure 2.7). Each phase is itself unusual.

The magnetic phase diagram shown in Figure 2.7 was mapped out by Horn et al. [118]. It shows successive phase transitions from the paramagnetic state to the
antiferro-quarupolar (AFQ) at 3.2 K, and to the antiferromagnetic ordering at 2.3 K. Phase I and III are established as paramagnetic and antiferromagnetic, respectively [19]. Phase I exhibits a dense Kondo behavior in the resistivity [18], and its magnetization is linear with the applied field. The Kondo temperature was initially estimated as $T_K = 8$ K [18]. Later this value was significantly revised to a value of $T_K = 1$ K from the experimental data on the magnetic susceptibility versus temperature [102]. The revision was caused by an unusual picture of the crystal field splitting, revealed in the Raman and neutron spectroscopic measurements [13]. When a magnetic field is applied, a net moment is induced in Phase II. This is, in fact, observed by neutron diffraction (ND) [19,119] and NMR measurements [27]. Phase II will be discussed in detail in the next section. At very low temperatures, the magnetic dipole moments of the Ce atoms become anti-ferromagnetically ordered in Phase III. The long-range magnetic order has several sub-structures that have been observed by neutron diffraction [25] and NMR measurements [26,27]. As was mentioned before, we will not be concerned with the structure of Phase III other than to point out that at all applied magnetic field above about 2.2 T and temperatures above 2.1 K the ordering is suppressed.

The phase boundaries between Phases I and II and Phases II and III are strongly dependent on magnetic field. An explanation for this behavior was given by Ohkawa [120] taking into account the RKKY interaction for four degenerate ground states.

According to his theory CeB$_6$ is a candidate to exhibit a quadrupolar order due to RKKY-type interactions. In Phase II, the magnetization is nonlinear with field and
Figure 2.7: The magnetic phase diagram of CeB$_6$ exhibits three main phases at zero field separated by two magnetic ordering temperatures: the quadrupolar ordering temperature $T_Q = 3.2$ K and the Neel temperature $T_N = 2.3$ K. Below $T_N$, phase III is characterized by a complex magnetic ordering which is destroyed at fields larger than 1-2 T; the exact field is orientation dependent.
the Kondo behavior is sharply suppressed. The boundary field between Phase I and Phase II increases with increasing temperature and the phase transition becomes sharper. In Phase III the magnetization curve is complex and depends strongly on the crystal direction, indicating long range ordering.

2.7.3 Phase II

The ordered phases of CeB₆ are complicated but quite fascinating [121-123]. Phase II under applied magnetic field is believed to be an AFQ phase. There are some mysteries about Phase II such as why the transition temperature increases with the field and the nature of the field-induced AFQ. Although experimental studies on Phase II have a long history, their microscopic origin remains controversial.

The difficulty resolving the controversy is due to a lack of direct observation of AFQ moments. In principle they are observable by using the ND and NMR. Such experiments were actually carried out at the beginning of 1980’s. However there was a serious contradiction in the interpretations of these experiments: An usual triple-k structure was proposed by NMR measurement [27], while ND measurements suggested that the ordinary (1/2, 1/2, 1/2) AFQ is induced by the field [19,119].

So far several theories have been put forward to explain Phase II [21,124-128]. Hanzawa et al. [124] studied the phase diagram of CeB₆ in which the ground state is a Γ₇ doublet and excited CEF is a Γ₈ quartet were assumed. After their work, however, the crystal-field ground state in CeB₆ was identified to be the Γ₈ quartet. Since the transition temperature to Phase II is much lower than the Γ₇-Γ₈ excitation energy of 530 K, it is reasonable to confine the basis set to Γ₈ quartet states only.
In an early paper, Ohkawa [21] proposed that indirect exchange interactions between pairs of cerium atoms would produce a splitting of the four-fold level into \((4 \times 4)\) sixteen levels split into a group of two triplets and a group consisting of a singlet plus a nine-fold degenerate level with Phase II representing an ordering of the orbital moments. Most recently, an alternate interpretation of the neutron scattering results was given by Uimin [22]. Uimin et al. [125] have studied the transition to Phase II, assuming the point-charge model within the quartet. They argued that the quadrupolar fluctuations become large due to a special form of the interaction and that the suppression of the fluctuations by the magnetic field is responsible for the enhancement of the transition temperature. It should be noted that muon spin rotation measurements in zero applied magnetic field yield a different magnetic structure for CeB\(_6\) for both Phase II and Phase III [23,24].

Recently, Shiina et al. [127] studied the phase diagram of CeB\(_6\) in magnetic fields by extending the RKKY-type Hamiltonian for the \(\Gamma_8\) state, which was derived initially by Ohkawa [21]. They have observed that the octupole-octupole interaction is present in Ohkawa's Hamiltonian, in addition to the dipole-dipole and the quadrupole-quadrupole interactions. Shiina et al. [128] proposed a theory for CeB\(_6\) in a magnetic field by extending and slightly modifying a previous paper. The AFQ ordering induces dipoles and octupoles when the magnetic field is applied. The nature of those field-induced multipoles is studied by changing the direction of the field. It is shown that the theoretical results are consistent with the main results of ND measurements. It is also shown that the contradiction between NMR and ND measurements is resolved by
taking into account the influence of the octopoles. Thus, it is concluded that CeB₆ is the first example in which the octupoles play a crucial role on the anomalous $f$-electron ordered phase. Therefore, it is worthwhile to consider to the hyperfine field due to the multipolar moments including octupoles, which was not taken into account before. Moreover, Sakai et al. [129] pointed out that the discrepancy between ND and NMR measurements for Phase II of CeB₆ can be resolved by considering the hyperfine field due to the induced octupolar moment.

Unusual behavior of the 4f electrons is derived from the competition between localized character due to strong intra-atomic Coulomb interaction and the itinerant nature due to hybridization with the valence electrons. Therefore, it is important to know the electronic structure of the Ce 4f states. EPR is a useful method in determining the low-lying energy levels in crystals and gives detailed information about the local symmetry of a magnetic ion situated in a crystalline potential. The degeneracy and splitting of levels are functions of the crystalline symmetry. The measurement and analysis of the results of EPR and magnetization measurements on CeB₆ are the focus of the remainder of this dissertation.
CHAPTER 3

ELECTRON PARAMAGNETIC RESONANCE

3.1 Historical Background

During World War II, techniques in microwave generation and detection were developed. It was only natural that these techniques should be applied to study of energy level separations lying in the centimeter and millimeter range.

The first experimental observations of laboratory-induced transitions among the Zeeman levels of electrons were those of Zavoisky [130] reported in 1945. The initial experiments used a 25-meter wavelength to observe absorption as a function of magnetic field in substances whose line widths were ~50 gauss or larger, and a resonance line was scarcely discernible at low frequencies, which correspond to a resonance "peak" at about 4 gauss. The second series of experiments found a maximum for Cu$^{++}$ ion at 47.6 gauss, using a frequency of 133 Mc/sec (still not in what we would call the microwave range) and allowed Zavoisky to conclude in effect that g = 2. Subsequently Zavoisky [131] pushed into the microwave region and observed a clearly resolved resonance of 200 to 300 gauss width in fields of about 1000 gauss. Very soon afterward, experiments were reported by Cummerow and Halliday [132] and by Bleaney and Penrose [133]. Bagguley and Griffiths [134] performed an experiment at the Clarendon Laboratory observing the Cr$^{3+}$ resonance in a chrome alum crystal at 3.18 cm wavelength.

The EPR spectrum of several rare-earth metals was first observed by Salikhov [135]. Goodrich et al. [136] made the EPR measurements on pure polycrystalline
metallic cerium at atmospheric pressure and at temperatures 300, 196, and 77 K using a standard 1.25-cm microwave spectrometer in magnetic fields up to 26.5 kG. The ground state of the cerium atom in metallic Ce is $\Gamma_7$, and the results of the EPR spectrum are at variance with Salikhov’s [135].

3.2 Background

Electron paramagnetic resonance (EPR) is the process in which an unpaired electron in a static magnetic field starts in a lower spin up state and absorbs a resonant microwave photon, moving to the higher spin down state.

Electrons naturally have spin angular momentum, a concept that was proposed by S.A. Goudsmit and G.E. Uhlenbeck in 1925 based on experimental results and by P.A.M. Dirac in 1928 based on a theoretical solution to a relativistic wave equation. This angular momentum is described by the spin magnetic quantum number, $m_s$, which has a value of $+1/2$ or $-1/2$ for electrons. The component of spin angular momentum that is parallel to the z-axis, where $m_s = +1/2$, is known as spin up, and the component antiparallel to the z-axis, where $m_s = -1/2$, is known as spin down as shown in Figure 3.1. Electrons inside atoms exist in spin-up/spin-down pairs, unless there are an odd number of electrons, in which case there is an unpaired electron, which can experience electron spin resonance. In the absence of a magnetic field, the spin quantum number does not cause an energy level splitting, but in the presence of a magnetic field, electrons will separate into two groups according to whether their $m_s$ value is positive or negative. Electrons also have a spin magnetic dipole moment, which is in the
Figure 3.1: Energy level splitting for one electron in a magnetic field $B$ directed along the positive $z$-axis. For an electron the magnetic moment $\mu$ is opposite in sign to the spin $S$, so that $\mu = -g \mu_B S$. In the low energy state the magnetic moment is parallel to the magnetic field.

opposite direction from the spin angular momentum due to the negative charge on the electron. Therefore, it has a component antiparallel to the $z$-axis in the spin-up state and parallel to the $z$-axis in the spin-down state. When the electron is in a magnetic field $B$, it wants to line up with the field. As a result, the spin-up state, where the $z$-component of points directly opposite the $B$ field, has more energy than the spin-down state, because the spin-up state is positioned further away from alignment with $B$ and so it has a potential to rotate in order to line up with the field. This energy difference between the spin-up and spin-down states when placed in a magnetic field allows electron spin resonance to occur with an electron in the spin-down state absorbing a
photon whose energy equals the energy difference between its state and the spin-up state, thus boosting the electron to the higher energy level.

The transition is sometimes called a "spin flip," because the electron flips from the spin-down state to the spin-up state.

The energy transition that occurs in electron spin resonance is described by,

\[ h\nu = g\mu_B B, \]

which equates the energy of the absorbed photon on the left side to the energy difference between the spin-down and spin-up states on the right side. In the equation, \( h \) is Planck's constant, \( \nu \) is the frequency of the absorbed photon, \( \mu_B \) is the Bohr magneton, and \( B \) is the magnetic field strength. The factor \( g \) is the Landé g factor. It should be pointed out that the microwave photons have angular momentum \( \ell = 1 \). Therefore they only can induce transitions of \( \Delta m = \pm 1 \). This is always the case for EPR on spin \( \frac{1}{2} \) systems.

3.3 Spectroscopy

EPR is frequently considered to be in the microwave branch of spectroscopy (10^9-10^11 Hz, 30 cm-3 mm), and nuclear magnetic resonance (NMR) is usually classified in radiofrequency spectroscopy (10^6-10^8 Hz, 300 mm-3 m). In terms of observed phenomena, EPR studies the interaction between electronic magnetic moments and magnetic fields. Occasionally, EPR studies are carried out with NMR instrumentation using magnetic fields of several gauss rather than several thousand gauss. The splitting of energy levels by a magnetic field is customarily referred to as the Zeeman effect, and so we may say that EPR is the study of direct transitions between electronic Zeeman levels, while NMR is the study of direct transitions.
between nuclear Zeeman levels. In concrete terms it may be said that EPR and NMR study the energy required to reorient electronic and nuclear magnetic moments, respectively, in a magnetic field.

Differences of EPR from NMR:

• Sign convention opposite

• Variable magnetic field

• Bohr magneton, $\mu_B$, is 2000 times $\mu_N$ (lower B, higher $v$)

• Chemical shift measured by variable $g$, not relative to internal standard

• $g$ for most radicals near 2.003, but some metal-based radicals in the range $0 < g < 4$

• Hyperfine structure is due to nuclear spins.

3.4 Magnetic Moments

The magnetic moment of an electron spin $\mu_s$ is given by

$$\mu_s = \mu_B S, \quad (3.1)$$

while the magnetic moment associated with orbital momentum $\mu_l$ is

$$\mu_l = \mu_B L, \quad (3.2)$$

where the Bohr magneton $\mu_B$ defined by
\[ \mu_B = \frac{e\hbar}{2m}, \quad \text{(3.3)} \]

is a convenient unit of magnetic moment, \( S \) is the spin angular momentum operator, and \( L \) is the orbital angular momentum operator. One may write Eqs. 3.1 and 3.2 in terms of the "g" factor:

\[ \mu_s = g\mu_B S, \quad \text{(3.4)} \]
\[ \mu_i = g\mu_B L, \quad \text{(3.5)} \]

where \( g = 2 \) and 1 for the spin and orbital motion, respectively. The \textit{g factor} is the ratio of the magnetic moment to the angular momentum expressed in dimensionless units by means of the Bohr magneton. The ratio of the Bohr magneton to the unit of nuclear magnetic moments called the nuclear magneton \( \mu_N \) is

\[ \frac{\mu_B}{\mu_N} = 1836, \quad \text{(3.6)} \]

which is the ratio of the rest mass \( m_p \) of the proton to the rest mass \( m_e \) of the electron. Thus EPR energies are generally about 2000 times larger than NMR energies.

If an electron has both spin and orbital motion, then the total angular momentum \( J \) is obtained by the vector addition.
\[ \mathbf{J} = \mathbf{L} + \mathbf{S}, \quad (3.7) \]

where \( \mathbf{J} \) has the possible magnitudes \( |L - S|, |L - S + 1|, \ldots, |L + S| \).

As a result of Eqs. 3.1 and 3.2 the vector addition of the orbital and spin components to the magnetic moment gives a value

\[ \mu = g\mu_B \mathbf{J}, \quad (3.8) \]

for the overall magnetic moment, where the Landé g factor has the form

\[ g = \frac{3}{2} + \frac{S(S+1) - L(L+1)}{2J(J+1)}. \quad (3.9) \]

In solids the electronic orbital motion interacts strongly with the crystalline electric fields and becomes decoupled from the spin, a process called "quenching". The more complete the quenching, the closer the \( g \) factor approaches the free electron value. For example, \( g = 2.0036 \) in the free radical \( \alpha, \alpha' \)-diphenyl-\( \beta \)-picryl-hydrazyl (DPPH), which is very close to the free-electron value of 2.0.

In most EPR experiments the value of \( g \) is determined. In addition, from the EPR line shapes, the relaxation time back to the ground state can be determined. Relaxation times and line widths are discussed in the next section.
3.5 Relaxation Times and Line Widths

A variable-temperature EPR study can provide a great deal of information about a spin system and its interaction with its environment. To first order, the g factor, hyperfine interaction constants, and other terms in the Hamiltonian are independent of temperature. The line shape, line width ΔH, and the relaxation times are the principal quantities that are sensitive to the temperature.

In many cases, the resolution of the fine structure and hyperfine structure is limited by the width in field or frequencies over which the absorption lines are observed. This line width is dependent on the interaction between the paramagnetic ions themselves, and on inhomogeneities in the crystal lattice. The most important sources of broadening are: (1) spin-lattice relaxation; (2) dipolar interaction between spins of the same kind; (3) dipolar interaction between unlike spins, that is, between spins with different resonance frequencies; (4) exchange interactions; (5) saturation by the radiation field; (6) hyperfine structure interaction; (7) inhomogeneities in the crystal lattice; (8) inhomogeneities in the applied magnetic field. Some of these factors will be dealt in this chapter.

3.5.1 Spin-lattice Relaxation Time

The spin-lattice relaxation time measures the energy transfer from the paramagnetic ions to the surroundings, that is to say, to the crystal lattice. This relaxation time T₁, often called the longitudinal relaxation time, is defined for two energy levels by

\[
\frac{d}{dt}(\Delta N - \Delta N_0) = -\frac{(\Delta N - \Delta N_0)}{T_1},
\]

(3.10)
where $\Delta N$ is the population difference between the two levels caused by the resonant absorption; $\Delta N_0$ is this difference at equilibrium. The differential equation expresses the rate at which the system approaches the equilibrium after having been disturbed by the absorption of energy. Here $\Delta N_0$ is defined by the Boltzmann distribution and is given by

$$\Delta N_0 = N \tanh \left( \frac{h \nu}{2k_B T} \right), \quad (3.11)$$

where $N$ is the total population of the two levels. For microwave frequencies and high temperatures such that $(h \nu / 2k_B T) \ll 1$,

$$\Delta N_0 \approx \frac{Nh \nu}{2k_B T}. \quad (3.12)$$

Assume now that the equilibrium distribution is being disturbed, for example, by resonance absorption. What mechanisms are operative to restore the equilibrium distribution? The first discussion of such mechanisms by Waller [137] was based on modulation of the spin-spin interaction by the phonons, which induces oscillatory components in the distances between paramagnetic ions. It should be noted that this was before EPR was discovered. Waller distinguished two processes in such interactions.
**Direct process.** A phonon of the same energy \((\hbar \omega)\) as the spin quantum required for a resonance transition is observed by the spin system, resulting in an “up” transition in Figure 3.1; or a phonon is emitted, accompanied by a “down” transition within the spin system.

**Raman process.** A phonon of any frequency \((\omega_p/2\pi)\) may interact with a spin, causing a transition (up or down) within the spin system, the phonon being scattered with a different frequency \((\omega_p/2\pi)\pm \nu\) respectively, where \(\nu\) is the magnetic resonance frequency. This is known as an indirect process and is predominant at high temperatures as shown in Figure 3.2.

If we regard the direct process as a first order (one phonon) process, then in comparison the Raman process is a second order (two phonon) process with a correspondingly smaller coupling of the phonons to the spin system.

The theory of Waller, based on modulation of the magnetic dipolar spin-spin interaction, led to relaxation times appreciably longer than those observed experimentally. A more potent mechanism and one which, unlike that of Waller, is independent of the degree of concentration of the magnetic ions, is modulation of the ligand field by the lattice vibrations.

The foundations of the quantitative formulation of the theory of spin-lattice relaxation through modulation of the ligand field were laid by Kronig [138] and Van Vleck [139], and have been extended by many others, notably Orbach [140]. There are many complications to be considered, but here we confine ourselves to the temperature dependence. In the majority of cases this can be written in the form [141]
Figure 3.2: Level schemes for spin-lattice relaxation theory. (i) Orbach process, (ii) Raman process (non-Kramers), (iii) Raman process (Kramers ions).

\[
\frac{1}{T_1} = a \coth \left( \frac{h \nu}{2k_B T_0} \right) + b T_0 + \frac{c}{\exp \left( \frac{\Delta}{k_B T_0} \right) - 1},
\]

(3.13)

where the various terms arise from different processes that contribute simultaneously to the relaxation rate, that is, to \((1/T_1)\). Briefly these processes are as follows.

1. **Direct process**, involving phonons of the same energy as the magnetic resonance quantum \(h \nu\), which gives the first term in Eq. 3.13. The two limiting cases are:
\[ \frac{\hbar v}{k_B T_0} \ll 1, \text{ for which } \frac{1}{2} \coth \left( \frac{\hbar v}{k_B T_0} \right) \to \left( \frac{k_B T_0}{\hbar v} \right), \text{ which is the average number of quanta per phonon mode in the classical high temperature limit;} \]

\[ \frac{\hbar v}{k_B T_0} \gg 1, \text{ for which } \coth \left( \frac{\hbar v}{k_B T_0} \right) \to 1, \text{ giving a constant spin-lattice relaxation time determined by the rate of spontaneous emission of phonons from the upper state when phonons of energy } \hbar v \text{ are no longer thermally excited.} \]

2. **Raman process**, a two-phonon process in which all phonons can take part, giving the strongly temperature dependent second term in Eq. 3.13. Typical values of the exponent \( n \) are:

- non-Kramers doublet, \( n = 7 \);
- Kramers doublet, \( n = 9 \);
- multiplet with small splitting, \( n = 5 \).

3. **Orbach process**, giving the third term. Suppose the magnetic ion has a set of energy levels such as that shown in Figure 3.2(i), where there are two low-lying states and an excited states \(|c\rangle\) whose energy is less than the maximum phonon energy, \( \omega_m \).

It is than possible for an ion in state \(|b\rangle\) to absorb a phonon of the appropriate frequency by a direct process, and be excited to the state \(|c\rangle\). In this state it emits a second phonon by spontaneous or induced emission and falls down to state \(|a\rangle\). This gives an indirect transfer of ions from state \(|b\rangle\) to \(|a\rangle\), and constitutes a relaxation process that may be faster than the direct transfer from state \(|b\rangle\) to \(|a\rangle\) because of the much higher density of phonons of energy \( \Delta \). This process is also strongly temperature-dependent, being determined by the number of phonons of energy \( \Delta \).
available to the excite the ion to the upper state at $\Delta$. When $\Delta \gg k_B T_0$, the last term in Eq. 3.13 approximates to $\exp(-\Delta/k_B T_0)$.

### 3.5.2 Exchange Interaction

Line width measurements in crystals containing large concentration of paramagnetic ions hardly ever agree with the theory of dipolar broadening. One of the main reasons for this is the exchange interaction between electrons.

Van Vleck [142], Pryce and Stevens [143] and Anderson [144,145] have calculated the combined effect of exchange and dipolar interaction on the line width. Their calculations can be summarized as follows [8].

1. The spins are all identical and $S = \frac{1}{2}$. Van Vleck’s calculations show that the isotropic exchange interaction contributes to the fourth moment and not to the second moment. Since the total of the line cannot change, the effect is that the center part of the line is narrowed and tails broadened. This peaking of the line shape is called *exchange narrowing*.

2. The spins are not identical. This may occur when the ions do not process about parallel axes, as for example in the crystals where there is a zero field splitting of the energy levels. In this case, the isotropic exchange interaction contributes to the second moment and the line width is broadened. In general, both exchange broadening and narrowing is present and the resultant line width depends on the relative contribution of each type of interaction.

3. Strong exchange interaction between dissimilar ions. The only case considered so far is that of $S = \frac{1}{2}$. For a slow rate of exchange, the resonance spectrum...
of different magnetic types of ions in a unit cell of distinct resolved lines having different g values, the exchange will contribute to the broadening of the lines. At very strong exchange, the line will show exchange narrowing.

4. Exchange interaction between isolated pairs of ions. Occasionally, two magnetic ions may be nearest neighbors in diluted samples. There will be an exchange interaction between these two. The two ions may be considered as an isolated diatomic molecule in a crystal.

3.5.3 Temperature Dependence of Line Width

A great deal of information can be obtained from a careful analysis of the width and shape of a resonant absorption line. The microwave power level is sufficiently low so that saturation is avoided and the modulation amplitude is much less than the line width. The integrated area A of a resonant absorption line is proportional to the number of spins, and the measured moments of the lines are physically significant in terms of the theories of Van Vleck [142] and others.

If narrow band amplifier and phase sensitive detector are tuned to the modulation frequency and the modulation amplitude \( H_{\text{mod}} \) is much less than the line width, then the recorded line shape becomes the first derivative \( Y' \) of the absorption line \( Y \)

\[
Y' = \frac{dY}{dH}. \tag{3.14}
\]

If the line shape is unsymmetrical, then one may treat each area separately. The first derivative line shape formula may also be put integral form:
The area and nth moment \( \langle H^n \rangle \) is obtained through integrating by parts

\[
Y(H) = \int_{-\infty}^{H} Y'(H) dH.
\]

(3.15)

The area and nth moment \( \langle H^n \rangle \) is obtained through integrating by parts

\[
A = \int_{-\infty}^{\infty} (H - H_0) Y'(H) dH,
\]

(3.16)

since for all line shapes of finite area \( \lim_{H \to \pm \infty} (H-H_0)Y = 0 \). The nth moment [146] is given by

\[
\langle H^n \rangle = \frac{-1}{n+1} \int_{-\infty}^{\infty} (H - H_0)^{n+1} Y' dH.
\]

(3.17)

Using above equation the moments can be calculated for each temperature.

3.6 Information Gained From EPR

To be more informative an EPR spectrum of a particular paramagnetic system can be recorded at several temperatures, several frequencies, and several microwave powers. Sometimes one may employ the EPR spectrum to identify an unknown transition-metal ion or lattice effect, or it may distinguish between several valence states of the same ion. The EPR spectrum frequently identifies the lattice site and symmetry of the paramagnetic species, particularly if single crystal data are available.
Considerable information can be obtained about the nuclei in the immediate neighborhood of the absorbing spin, and sometimes relaxation-time data detect long-range effects. Diffusion constants, correlation times, and the type of hydration can be determined from the EPR spectra of the solutions. Chemical bonds in molecules and crystals sometimes may be characterized by EPR studies. The effective mass of atoms in semiconductors may be deduced. EPR studies furnish detailed information on ferromagnetic, antiferromagnetic, and ferrimagnetic materials.

By measuring the angular dependence of the magnitude of the g factor, the symmetry and strength of the crystalline field acting on the paramagnetic ions can be determined. In the metals the situation is complicated by the interaction of the magnetic electrons with the conduction electrons. Measurements of the EPR spectrum in metals doped with rare-earth ions have shown that information about the exchange interaction between the 4f and the conduction electrons can be obtained [147]. A measurement of the EPR spectrum of the 4f electrons in metallic cerium, then, is expected to yield information about both the local symmetry and the exchange interactions in this metal.

3.7 Relationship of EPR with Magnetic Susceptibility

An EPR measurement consists of the simultaneous determination of the microwave frequency $v$ and the magnetic field $H$. These data are used to calculate the g factor from the relation

$$g = \left(\frac{\hbar}{\mu_B}\right) \left(\frac{v}{H}\right),$$

(3.18)
where the constant of proportionality is the ratio of the Planck's constant to the Bohr magneton. A magnetic susceptibility, $\chi$, measurement carried out with a paramagnetic sample entails the determination of ratio of the total magnetic moment of the sample to the strength of applied field of this measurement is made as a function of the absolute temperature $T$. The data can be used to calculate the susceptibility $\chi_0$, the Weiss constant $\theta$, and the $g$ factor by means of the Curie-Weiss law

$$\chi_0 = \frac{N^2 g \mu_b^2 S(S + 1)}{3 k_B (T + \theta)}, \quad (3.19)$$

where $S$ is the spin, $k_B$ is the Boltzmann's constant, and $N$ is the number of spins in the sample. This is the spin-only formula used for a quenched orbital angular momentum. In the absence of quenching one replaces $S$ by $J$ where

$$J = L + S. \quad (3.20)$$

The both EPR and the magnetic susceptibility methods can provide the $g$ factor. The EPR technique singles out each ion and electronic state and resolves the corresponding spectra, while the magnetic susceptibility technique measures an average of the susceptibilities of all the paramagnetic states in the sample. EPR provides additional information concerning hyperfine interactions with nuclear spins. Both methods furnish information on zero-field splittings, with the EPR results being more
specific. The Weiss constant $\theta$ determined by magnetic susceptibility measurements may be employed to evaluate the exchange integral (exchange energy) $J$ between two paramagnetic ions by the approximation

$$\theta = \frac{2zS(S+1)J}{3k_B},$$

where $z$ is the number of paramagnetic nearest-neighbor ions exchange-coupled to each paramagnetic ion. One should not confuse this use of $J$ with the total angular momentum. The value of $\theta$ corresponds to either the Curie temperature $T_c$ for ferromagnets when $J$ is positive or the Néel temperature ($T_N$) for antiferromagnets when $J$ is negative. It must emphasized that equating $\theta$ to either $T_c$ and $T_N$ is approximation, since in practice usually $T_c \neq \theta$, and often $\theta$ exceeds $T_c$ by a factor of 2 to 4.
CHAPTER 4

EXPERIMENTAL PROCEDURE

4.1 Introduction

This chapter describes the 35, 95 and 220 GHz EPR spectrometers and the SQUID magnetometer used to carry out the present work. The method by which the samples were made, characterized, and also described. This work was performed in the Low Temperature Physics Laboratory at Louisiana State University, Baton Rouge, Louisiana and the National High Magnetic Field Laboratory in Tallahassee, Florida.

The measurements reported here were made on small single crystals (CeB$_6$ and EuB$_6$) in the shape of flat plates having approximate dimensions of 0.25 mm x 0.1 mm x 1 mm long. Each of these dimensions was along a [100], or equivalent, axis of cubic structure, and the magnetic field was applied in the plane of the plate parallel to the [100] for the magnetization measurements and either perpendicular to or in the plane of the plate for the EPR measurements.

The single crystal samples of both CeB$_6$ and EuB$_6$ used in this investigation were grown at Florida State University by Z. Fisk. The method used is commonly referred to as the aluminum flux technique [148]. Starting with the correct atomic weigh percent mixtures of the RE and B powder as 5% of a total REB$_6$ + Al mixture, the total amount was heated under a 500 Torr Argon atmosphere in an alumina crucible to 1400 °C where the solution was completely melted. The solution was slowly cooled over a period of 3 to 4 weeks to below the solidification temperature of the hexaboride,
then rapidly brought to room temperature. The pure Al flux was removed by etching in a saturated solution of NaOH leaving many hexaboride crystals with dimension of mm size. No visible signs of Al inclusion in the crystals were evident upon magnification. The crystals are of high quality and close to stoichiometry, as is evidenced by the observation of the dHvA effect [103]. The residual resistivity is high, of order of several $\mu\Omega\cdot cm$ since the resistivity is dominated by the Kondo effect and decreases only slowly below $T < 2$ K [149,150].

The sample formed part of the end plate of either a rectangular or a cylindrical resonant cavity with the rf magnetic field in the cavities perpendicular to the applied field. In order to mount the electrically conducting sample on the copper end plate of the cavity a circular depression slightly deeper than the sample thickness and slightly larger than the sample dimensions was machined in the plate. Pure In was melted into the depression and the sample pressed into it before cooling. The entire surface consisting of Cu, In, and CeB$_6$ or EuB$_6$ was then mechanically polished to expose the sample and have a flat conducting surface on the end plate. The sample in this manner was subsequently placed on the microwave cavity and enclosed inside a vacuum jacket before appreciable oxidation could occur. For the angular dependent measurements, the cavity end plate was rotated with the applied external field remaining in the plane of the sample. One way to conveniently rotate the sample requires the construction of a gear system that allows the user to modify the sample orientation from a room temperature control on top of the sample probe. Thus the sample orientation can be changed without pulling the probe from the cryogenic system. Temperatures were
measured using a calibrated Cernox thermometer attached to the resonant cavity.

Most of the EPR measurements were made at 35 GHz using a standard microwave frequency-locked spectrometer, a superconducting magnet, and modulation coil.

4.2 EPR Spectrometers

4.2.1 The 35 GHz Spectrometer

In the course of this thesis, the 35 GHz EPR spectrometer in the Low Temperature Physics Laboratory at LSU was used and operated at fields up to 5 T. The spectrometer operates at fixed frequency and the spectrum is scanned by a linear variation of the static magnetic field.

The microwave power was supplied by a 150 mW OKI Klystron or by a 145 mW Central Microwave Gunn effect oscillator. Two slightly different spectrometer configurations were used in order to achieve the best results using each oscillator. These are shown in Figure 4.1. The Klystron has a center frequency of 35 GHz with a mechanical tuning range of ± 3 GHz around the center frequency. In the Klystron system, the operation frequency was frequency modulated and the output voltage from a detector fed back to lock the Klystron frequency to that of the resonant cavity. For this purpose a Teltronics KSLP stabilizer operating at 27 kHz was used for automatic frequency control (AFC). The input impedance of the KSLP is low compared to that of the lock-in amplifiers used for detection of the field modulated signal and so a separate 1N53 detector diode was supplied to drive the AFC. This was mounted on a 20 dB multihole directional coupler. The circulating element used in this system was a three-
Figure 4.1: (a) Klystron system, (b) Gunn oscillator system.
port circulator. The noise level and signal quality of this system were very sensitive to the settings of the AFC. This often had to be retuned between magnetic field sweeps. The AFC was operated in the reverse AC lock mode. Lowest noise operation was achieved with the modulation drive level and the gain set as low as possible. This setting should be sufficient to give approximately a ±10 V correction range. It is critical that the 30 V battery in the AFC used, as a correction voltage source be fresh. The AFC can be tuned by watching the noise level on the mixer output of the lock-in amplifier and adjusting the gain and phase until the noise level is sufficiently low.

The change to a Gunn oscillator based system was partly motivated by the difficulties in consistently obtaining good results with Klystron. The Gunn oscillator is a Central Microwave CMF720P and has center of frequency of 35 GHz with a mechanical tuning range of ±1.5 GHz around the center frequency. The mechanically tuned oscillator has relatively narrow tuning range as compared to a Klystron making it necessary to construct the resonant cavity carefully so that its resonance falls within the tuning range of the Gunn oscillator. This factor presents some small difficulties in resonant cavity development where a wide tuning range is often desirable and all cavity development was done using the Klystron.

Although the Gunn oscillator was not expressly designed for electrical tuning, it actually has a small electrical tuning range on the order of ±100 MHz. This is achieved by varying the supply voltage to the Gunn oscillator around its central value. In practice, not all of this range is useful since varying the drive voltage causes an amplitude change as well. It is possible, however, to use this capability to provide an AFC.
The AFC works on the same principal as that used with the Klystron. The frequency of the microwave oscillator is first adjusted mechanically as closely as possible at the cavity resonance. This is done by frequency modulating the oscillator and looking for the resonant dip with an oscilloscope. This is somewhat more difficult to do with the Gunn oscillator since it is not possible to sweep over as wide a range as with the Klystron. The wide bandwidth of the Klystron is one of the characteristics, which makes very useful in cavity development. Another tuning method that is very useful with the Gunn oscillator is to look for a null reading on the lock-in amplifier with a phase shift of 0°. This will occur when the frequency is being modulated symmetrically around the cavity resonance. The null reading at the lock-in when the oscillator is tuned to the cavity resonance occurs because the frequency modulation varies oscillator frequency over a small range around the cavity resonant frequency. The amplitude of the reflected power from the cavity increases as the frequency moves away from the resonance in either direction. The result is that the signal produced is exactly twice the modulation frequency. Provided that there are no phase shifting effects in the system, the frequency doubling will give a null reading on the lock-in at a 0° phase shift and will shift to positive or negative reading as the signal becomes asymmetrical with a frequency shift away from resonance. The system polarities and phases should be set up so that an increase in frequency causes a negative output since the Gunn oscillator frequency is directly proportional to the supply voltage. The output of the lock-in can then be used to supply a correction voltage to shift the oscillator frequency back to the resonance.
This AFC is much easier to tune than that used in the Klystron system. It is extremely stable and requires almost no retuning during a run. As with the Klystron stabilizer, the AFC operates best with as low a modulation drive as possible and with as little correction gain as it is possible to use while still maintaining stability.

4.2.2 Magnet System

The magnet used in the present work was a 5 Tesla superconducting magnet that was built by Westinghouse. It is driven by a programmable power supply that has a built in sweep control. The solenoid consists of a base coil of 19,330 turns and two correction coils of 1,147 turns each. The coils are in series electrically. The conductor is a 0.254-mm diameter niobium base alloy, copper clad and insulated with an epoxy enamel. At rated field the inductance of the solenoid is 11.5 henries with a corresponding stored energy of 10,351 joules. Rated field uniformity is 0.01% within a sphere of 1 cm diameter around the magnet center.

The applied field was calibrated from the EPR signal of the DPPH placed at the sample position. A sample trace of the EPR signal is given in Figure 4.2. Since the EPR signals were obtained using the magnetic field modulation technique, what is actually recorded in Figure 4.2 is the first derivative of the EPR resonance with respect to the magnetic field.

Thus the field value of the EPR resonance peak power absorption is the same as the field value of the zero crossing of the first derivative signal. The magnetic field calibration was performed by calculating the field at which the zero crossing should occur from the frequency of the resonant cavity and the g-splitting factor of the DPPH. For the DPPH, the g factor is 2.0037 corresponding to a resonance field of 1.248 T for
Figure 4.2: First derivative of the EPR resonance of DPPH with respect to the magnetic field at 34.69 GHz.

the frequency 35 GHz. The magnetic field value was obtained by measuring the current passing through a calibrated shunt (100 mV, 50 Amps) resistor which was connected in series with the magnet. The calibration factor between the magnetic field in Tesla and the voltage drop across the shunt resistor is 0.0594 T/mV.

When sweeping the external magnetic field, the field shows hysteresis between up and down sweeps. This effect is due to trapped flux in the magnet, which adds to the field in one sweep direction and subtracts in the other. One can get around this by sweeping the field up and down and taking the average value of the resonance fields of both sweep directions.
4.2.3 Modulation Coil

To get high sensitivity of the resonance signal, the field modulation method with the modulation field being provided by a low impedance coil placed inside the main magnet was used. This technique requires the application of a small time varying magnetic field in addition to the steady state field. The coil consisted of 212 turns per layer and 6 layers of #26 copper wire (0.406 mm in diameter) wound on the stainless steel vacuum can surrounding the resonant cavity and was 43.18 mm in diameter and 86.36 mm long. The windings were embedded with epoxy to ensure that the wires of the coil were immobile. The coil resistance is 23.2 ohm at room temperature, 4.1 ohm at liquid nitrogen temperature (77K), and 2.1 ohm at liquid helium temperature (4.2 K).

In order to get 100 G modulation for a given thickness of wire, the resistance of the wire per unit length, the number of turns and layers, and the current that passes through the coil was calculated. The details of the modulation field calculations written by Dr. Donavan Hall are given in Appendix A. After winding the modulation coil, it was calibrated using an ac current. The output voltage from a calibrated pick up coil of known cross-sectional area (A) and number of turns (N) placed at the center of the modulation coil was recorded for a measured ac currents running through the coil. From the measured voltage amplitude the field can be calculated since

\[ V = -\frac{d\Phi}{dt} = -NA \frac{dB}{dt} \]

When \( B = B_0 \sin \omega t \), \( V = -NAB_0 \omega \cos \omega t = V_0 \cos \omega t \). Thus, \( B_0 = \frac{V_0}{NA \omega} \). This was repeated for ac currents at different frequencies. The theoretical calculations and the experimental results were found to be in good agreement.

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agreement with each other. For example, in order to get 100 G modulation field from
the modulation coil, the calculations showed that 0.426 mA AC current would be
needed and the experimental measured value was 0.420 mA as shown in Figure 4.3.
Therefore, these two values are in good agreement with each other. The modulation
coil was driven from the reference output of detection lock-in through a McIntosh 240
power amplifier.

The line widths and peak positions of the EPR spectral lines are very sensitive to
the effects of over-modulation and the modulation field values were carefully set to
avoid this. The modulation field setting to be used was found by reducing the
modulation until no additional narrowing of the EPR line occurred. The modulation

Figure 4.3: Calibration for the modulation coil used in the experiment.
fields used were typically on the order of 50 G outside the vacuum can at a frequency of 40 Hz. There is some attenuation of this field due to the metallic vacuum can and microwave resonant cavity. However, by using low modulation frequencies, these absorption problems are minimized.

4.2.4 The 95 and the 220 GHz Spectrometers

The multi-frequency high-field EPR spectrometer at the National High Magnetic Field Laboratory (NHMFL) in Tallahassee, FL was designed and built to cover a broad range of frequencies (23 GHz – 3 THz) and operates at fields up to 17 T.

In order to cover the broad band of frequencies 23 GHz to 3 THz, different sources are used depending on the application: a microwave synthesizer, Gunn oscillators and a Far-Infrared (FIR) laser. Dividing the above range of frequencies into low, intermediate and high frequency regimes, each of these sources serves to span a particular regime.

The intermediate frequency region (95 to 550 GHz) is covered with two Gunn oscillators with different fundamental frequencies, one emitting at 110 GHz and the other at 95 GHz. Both oscillators are tunable within a few GHz, specifically in the intervals 92.5 to 98 GHz and 107 to 112 GHz. Higher frequencies are obtained by harmonic generation, and therefore each of these oscillators comes with a Schottky harmonic generator and a set of output high pass filters which, depending on the harmonic of interest, allows one to filter out the lower harmonics. The Gunn oscillator fundamental frequency is measured and locked to a frequency counter (EIP 578B). A bolometer was used as a detector. The bolometer in use in the spectrometer incorporates a fast Indium Antimonide hot electron bolometer with broad band

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magnetically enhanced performance (QMC Instruments LTd.). No AFC is used because there is no resonant cavity to which the source must match in frequency.

The 95 and 220 GHz EPR measurements were performed at NHMFL. Here no resonant cavity was used and the measurements were again made using magnetic field modulation with the field applied perpendicular to the plane of the sample along a [100] axis of the crystal using a superconducting magnet. The spectrometer was operated in the reflection mode with the sample mounted on a plate terminating the waveguide. In the reflection mode, microwaves hit the sample and reflection from the sample is detected. The wave guide used in these experiments was brass. The magnet in the spectrometer is a Teslatron designed by Oxford Instruments. It can reach to a maximum field of 15 T at 4.2 K and 17.1 T when cooled down to 2.2 K by pumping on He\(^4\).

A modulation coil, 50 mm in length, is wound around a G-10 tube and fitted around the wave-guide where the sample sits. It serves to modulate the external static magnetic field and can deliver modulation fields up to ± 25 G peak to peak at a frequency of 10 kHz. Attenuation problems are much less in this case and higher modulation frequencies can be used to get above the 1/f noise in the detector.

4.2.5 Operation and Data Acquisition

All of the experiments performed on various samples used the field modulation with lock-in detection technique. The signal at the modulation frequency from the detector is fed into a lock-in amplifier and the spectra were recorded using a Labview program that reads the DC output of the lock-in amplifier. It also reads the current produced by the magnetic field power supply and converts it into field values. The
resultant signal and hence the recorded spectrum is the first derivative with respect to
the magnetic field of the signal detected at the detector. A block diagram of the entire
spectrometer is given in Figure 4.4. A commercially available program, Kaleida
Graph, was used to analyze the data that is described in this chapter.

\subsection*{4.3 Magnetization Measurements}

Magnetization measurements were performed using a superconducting quantum
interference device (SQUID) magnetometer in the Low Temperature Physics
Laboratory at Louisiana State University.

The normal measurement process used in the Magnetic Property Measurement
System (MPMS) has three detection coils that are wound in a second-derivative
configuration in which the upper and lower single turns are counterwound with respect
to the two-turn center coil. The superconducting detection coils are located outside the
sample chamber and at the center of the magnet. This configuration strongly rejects
interference from nearby magnetic sources and lets the system function without the
need for a superconducting shield around the SQUID sensing loop. MPMS is to
position the sample below the detection coils with the sample transport set at its lower
limit of travel and then to raise the sample through the coils while measuring the output
of the SQUID detector. In its initial position, the sample should be far enough below
the detection coils so that the SQUID does not detect the sample moment. The sample
is then typically measured by repeatedly moving the sample upward some distance and
reading the voltage from the SQUID detector.
Figure 4.4: Block diagram of the 35 GHz EPR spectrometer.
Standard SQUID magnetization measurements were performed with the field applied parallel to a [100] axis aligned in the plane of the sample in order to measure the overall magnetization of the sample both as a function of temperature and applied field. Field dependent measurements between zero and 5.5 T were made at temperatures between 4 and 300 K.

In the EPR measurements, the electrons contributing to the signal are exposed to the total internal field inside the sample, $B = H_{\text{ext}} + (1-D)4\pi M$, where $H_{\text{ext}}$ is the externally applied magnetic field, $D$ is the sample demagnetization factor, and $M$ is the magnetization. The results of these measurements show that the difference between the magnetic induction $B$ that the electrons see and the applied external field $H_{\text{ext}}$ was 0.9% at low temperature.

4.4 Data Analysis

4.4.1 Extracting the g Value and the Relaxation Time from EPR Spectra

The first paramagnetic resonance absorption in metals due to conduction electrons was observed by Griswold et al. [151]. At that time there was no theory to take the diffusion of the electrons properly into account and therefore exact $g$ values and relaxation times could not be obtained. The theory of the EPR line shapes obtained from conduction electrons in metals was worked out by Dyson [152] and confirmed experimentally by Feher and Kip [153] in their extension of the original work of Griswold et al [151].

The main parameters in Dyson's theory are: $T_D$, the time an electron takes to diffuse through the skin depth $\delta$, the time $T_T$ that it takes for the electron to traverse the sample, the electron spin-lattice relaxation time $T_1$, and the electron spin-spin
relaxation time $T_2$ (for metals $T_1 = T_2$). In our case, $T_T \gg T_D \gg T_2$ and $T_T$ and $T_D$ are
$\infty$ which corresponds to thick films with slowly diffusing magnetic dipoles. The
Dysonian line shapes for this condition are given [146] by the relation

$$P = \left[ \frac{\omega H_i^2}{4} A \delta \omega_0 \chi_0 \frac{T_i}{T} \right] \left[ \frac{1}{2} \frac{1-T_i(\omega-\omega_0)}{1+T_i^2(\omega-\omega_0)^2} \right]$$

(4.2)

where $P$ is the absorbed power, $H_i$ is the microwave magnetic field amplitude, $\chi_0$ is the
paramagnetic part of the static susceptibility, $A$ is the sample surface area, $\delta$ is the skin
depth, and $\omega_0 = g\mu_B H_0/\hbar$ is the resonant frequency. The first derivative of the absorbed
power with respect to frequency is also given [146] by

$$\frac{dP}{d\omega} = \left[ \frac{\omega H_i^2}{4} A \delta \omega_0 \chi_0 T_i \right] \left[ \frac{T_i^3(\omega-\omega_0)^2 - 2T_i(\omega-\omega_0) - 1}{4(1+T_i^2(\omega-\omega_0)^2)^2} \right]$$

(4.3)

where $dP/d\omega$ is the power absorbed per unit angular frequency.

4.4.2 Susceptibility Calculation

In order to understand the temperature and field dependent magnetization
measurements on CeB$_6$ the susceptibility $\chi$, is calculated from the field dependent
magnetization measurements at each temperature. It is seen that a linear dependence of
$1/\chi$ on temperature does not occur as would be expected from the 4f electron in CeB$_6$
behaving in a simple non-interacting manner. Several previous experiments [13], [14]
have shown that the four degenerate $\Gamma_8$ states are split into two states separated in energy by an amount $\Delta = 30$ K. Several models have been given for the interaction causing this splitting. The suggested possible models include a dynamic Jahn-Teller effect involving acoustic phonons and a hybridization-mediated anisotropic coupling of the 4f wave functions to the p-like boron or 5d-type cerium wave functions [13]. In addition, exchange coupling may be present. The local f electrons are coupled through interaction with the conduction electrons with a coupling strength $J$. The interaction between the f and conduction electrons results in an indirect coupling of the local f moments to one another. This type of indirect interaction between the local f electrons is called the RKKY interaction. To extract the splitting of two $\Gamma_8$ doublets and the exchange field, if present, from our $1/\chi$ versus $T$ data, Dr. Dana Browne has derived an expression for the magnetic susceptibility for CeB$_6$. A copy of Dr. Browne's complete calculation is given in Appendix B.

In the remainder of this section the work of Dr. Browne is summarized. It is first assumed that the splitting causes two doublets, $|a\pm\rangle$ and $|b\pm\rangle$ to occur and that the $|a\pm\rangle$ and $|b\pm\rangle$ orbitals are simply split without any mixing. This $|a\pm\rangle$ and $|b\pm\rangle$ levels are given by the standard expressions for levels within the $\Gamma_8$ configuration as listed in the first set of equations in Appendix B. Then the susceptibility is given by

$$\chi = \frac{N g^2 \mu_B^2}{V \frac{121}{36} + \frac{1}{4} e^{-\mu_A} + \frac{25}{36} e^{-\mu_B} + \frac{40}{9} (1 - e^{-\mu_B}) \frac{1}{\beta W}}{Z},$$

(4.5)
when the $|a\pm\rangle$ level lie lowest, and

$$
\chi = \frac{N g^2 \mu_B^2}{V k_B T} \left\{ \frac{1}{4} + \frac{121}{36} e^{-\mu_\alpha} + \frac{25}{36} e^{-\mu_\nu} + \frac{40}{9} \frac{e^{-\mu_\alpha} - e^{-\mu_\nu}}{\beta W} \right\},
$$

(4.6)

if the $|b\pm\rangle$ orbitals lie lowest. Here $\Delta$ is the energy splitting of the two sets of levels, $W$ is the energy separation between $\Gamma_8$ and $\Gamma_7$, and $Z = \sum_\alpha e^{-\beta \mu_\alpha}$ where $\alpha$ runs over all of the levels.

Using previously measured values for $\Delta$ and $W$ and plotting the inverse of Equation 4.6, $1/\chi$ versus $T$, when the small-moment $|b\pm\rangle$ levels form the ground state there is a hump in the curve near $T = \Delta$ which is not seen in the data as shown in Figure 4.5. The hump comes from the large moment of the excited $|a\pm\rangle$ levels being depopulated below 30 K. Hence we see that we can not have the ground state that consists of a rather small moment with a larger moment state at higher energy. The true ground state must either be $|a\pm\rangle$ pair; or have a lot of the $|a\pm\rangle$ levels mixed into their overall wavefunction. A plot of Equation 4.5 along with the data is shown in Figure 4.6. As can be seen having the $|a\pm\rangle$ levels lowest in energy gives a closer representation of the data, but the actual fit to the data is not as close as can be achieved through further consideration of mixing of the levels.
Figure 4.5: $1/\chi$ versus temperature of CeB$_6$ if $|b\pm\rangle$ levels lie lowest. The solid line shows the fit to the data using Eq. 4.5.

Figure 4.6: $1/\chi$ versus temperature of CeB$_6$ if $|a\pm\rangle$ levels lie lowest. The solid line shows the fit to the data using Eq. 4.6.
Next, the possible mixing of the levels is taken into account. In general, if one assumes the $\Gamma_8$ orbitals are mixed in some arbitrary way, there would have to be van Vleck terms between all the levels. A possible mixing with the $\Gamma_7 \; |c\pm\rangle$ levels also is included in the calculation. This assumption increases by one the number of parameters in the interactions. The main fact included in Browne’s calculation that has not been included in previous published calculations is that the interaction Hamiltonian must obey time reversal symmetry. After a complete calculation, the expression for the susceptibility is given by contributions from three sets of levels: $a$ and $b$ from the split $\Gamma_8$ and $c$ from the $\Gamma_7$. The result is:

$$\chi_{\text{tot}} = \chi_a + \chi_b + \chi_c,$$

(4.7)

where

$$\chi_a = \frac{N}{V} \mu_B^2 \left( g_a^2 \beta + C_{ab} + C_{ac} \right) \frac{1}{Z},$$

$$\chi_b = \frac{N}{V} \mu_B^2 \left( g_b^2 \beta - C_{ab} + C_{bc} \right) e^{-\beta V},$$

and

$$\chi_c = \frac{N}{V} \mu_B^2 \left( g_c^2 \beta - C_{ac} - C_{bc} \right) e^{-\beta V} \frac{1}{Z}.$$

The $g$ factors for the three levels are given by:
\[ g_a = \frac{1}{7} \sqrt{121 \cos^4 \theta + 66 \cos(2\phi) \sin^2 \theta \cos^2 \theta + 9 \sin^4 \theta}, \quad (4.8) \]

\[ g_b = \frac{1}{7} \sqrt{9 \cos^4 \theta + 66 \cos(2\phi) \sin^2 \theta \cos^2 \theta + 121 \sin^4 \theta}, \quad (4.9) \]

and

\[ g_c = \frac{5}{7}. \quad (4.10) \]

It should be noted that the measured \( g \) factors will be the twice these numbers. The van Vleck terms are

\[ C_{ab} = \frac{260 - 132 \cos(2\phi)}{49\Delta} \sin^2 \theta \cos^2 \theta, \quad (4.11) \]

\[ C_{ac} = \frac{160 \cos^2 \theta}{49W}, \quad \text{and} \quad C_{bc} = \frac{160 \sin^2 \theta}{49(W - \Delta)}, \quad (4.12) \]

assuming the \( |A \pm \rangle \) levels lie lowest. In these expression the interaction strengths are parametrized by two angles, \( \theta \) for the \( \Gamma_8 \) interaction and \( \phi \) for the \( \Gamma_8 - \Gamma_7 \) interaction.

As a further refinement, Browne also included the effect of the indirect exchange interaction between \( f \) electrons on different sites. Using a standard mean
field approach and assuming that the mean moments induced in the material add to the local field, the susceptibility is given in Appendix B is found to be

\[ \chi = \chi_c + \frac{\chi_a + \chi_b + \chi_a \chi_b (2J_{ab} - J_{aa} - J_{bb})}{1 - \chi_a J_{aa} - \chi_b J_{bb} + \chi_a \chi_b (J_{aa} J_{bb} - J_{ab}^2)} \]  \hspace{1cm} (4.13)

where the \( J_{ij} \) are exchange constants and they satisfy \( J_{ij} = J_{ji} \) and no exchange interactions exist between the \( \Gamma_8 \) and \( \Gamma_7 \) levels. If one further assumes that all of the exchange interactions are the same so that \( J_{aa} = J_{bb} = J_{ab} = J \), the expression is reduced to

\[ \chi = \chi_c + \frac{\chi_a + \chi_b}{1 - J(\chi_a + \chi_b)} \]  \hspace{1cm} (4.14)

The result is a five-parameter model (\( \theta, \phi, \Delta, W \) and \( J \)) for the susceptibility, provided that the free ion moment is unaffected in the compound. The discussion and fit are given in Chapter 5.
CHAPTER 5

EPR AND SUSCEPTIBILITY MEASUREMENT RESULTS

5.1 Magnetization Measurements on CeB$_6$

The results of the magnetization and EPR measurements made on single crystal of CeB$_6$ are given in this chapter. These results are compared to other existing data on CeB$_6$.

The SQUID magnetization measurements were made at 16 different temperatures between 4 and 300 K. At each temperature the magnetic field was applied parallel to the [100] crystal axis and was varied from 0 to 1 T in 0.01 T increments then from 1 to 5.5 T in 0.05 T increments. Representative plots of this type data are shown in Figure 5.1. At 4 and 5 K the transition from Phase I to Phase II is observed, and all of the data in Phase I is linear in field. This linearity was checked by plotting values of M/H versus H as shown in Figure 5.2. The deviations from constant values are less than 2.5% at all fields above 0.5 T at all temperatures. Below 0.5 T some deviation in values of M/H are seen due to the unknown trapped flux of order 50 Gauss in the superconducting magnet used to make the SQUID measurements. Therefore only the measured values between 1 and 5.5 T were used to calculate the susceptibility at temperatures above 5 K, and a correction for the trapped flux was made in the range of 0.5 to 1.3 T and 2.2 T for the 4 and 5 K data respectively. The slope of each measured curve was used to calculate the susceptibility, $\chi$, as shown in Figure 5.3. The calculated values of $1/\chi$ as a function of temperature are shown in

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Figure 5.1: Magnetization $M$ as a function of external field $H$ parallel to the [100] direction for several different temperatures.

Figure 5.4. Above 100 K, this curve is in nearly linear, but below 100 K it deviates considerably from a Curie-Weiss behavior.

Several previous papers [13], [14] have shown that two of $\Gamma_8$ states are split by an interaction in Phase II. Here we make the assumption that the four-fold degenerate $\Gamma_8$ level remains split in the paramagnetic phase (Phase I) and that the overall magnetization due to the $\Gamma_8$ level arises from two levels, each two-fold degenerate, split
Figure 5.2: $M/H$ versus applied magnetic field $H$ at 10 K.

Figure 5.3: Magnetization as a function external field. The solid line is to calculate susceptibility values.

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Figure 5.4: The inverse paramagnetic susceptibility of CeB$_6$ as a function of temperature. The solid line was calculated using Equation (4.14).

by less than 50 K. As stated before (Chapter 4) to calculate the actual susceptibility, the effect of the exchange interaction between sites was included. Assuming that there are no exchange interactions except those between the $|a\pm\rangle$ and $|b\pm\rangle$ states and that $J_{aa} = J_{bb} = J_{ab} = J$, we fit Equation 4.14 to the temperature dependence of inverse susceptibility. The fact that only one resonance line is observed in the EPR measurements at all frequencies indicates that the values of $\theta$ and $\phi$ in Equation
(4.14) are $\pi/2$ and 0 respectively. This is because when these values are taken, both $g_a$ and $g_b = 2$ in Equations 4.8 and 4.9. The meaning of $\phi = 0$ is that there is no coupling between the $\Gamma_7$ and the $\Gamma_8$ ground state levels. The meaning of $\theta = \pi/2$ is that the four states $|a \pm\rangle$ and $|b \pm\rangle$ are equally mixed in the two doublets giving both of them the same $g$ value and only one EPR line near $g = 2$ is expected.

Upon using values of $\theta = \pi/2$ and $\phi = 0$ and the spectroscopically measured CEF splitting value of $W = 530$ K, the expression for $\chi$ then has only two adjustable parameters, the $\Gamma_8$ splitting $\Delta$ and the exchange parameter $J$. The solid line in Figure 5.4 shows the result of fitting this data to Equation (4.14) with $\Delta$ and $J$ being determined from the fit. From this fit, it is found that the energy separation between the two $\Gamma_8$ levels is $34.2 \pm .1$ K, and the exchange field calculated from $J$ is $0.024 \pm 0.006$ T in the paramagnetic phase. All previous estimates of the splitting of the $\Gamma_8$ level of 30 K have been for Phase II, but the current results indicate that this splitting persists to high temperatures. We have attempted to use $\theta$ as an additional adjustable parameter and find a value of $50 \pm 3^\circ$ and little change in either $\Delta$ or $J$. Considering the fact that there are only 16 data points to be fit with three adjustable parameters in this case, the use of $45^\circ$ is well justified.

Next we calculated values of $1/\chi$ as a function of temperature for limited field ranges of 0.5 T from 1 to 5.5 T. In fitting this data the value of $\Delta$ was fixed at $34.2$ K and the exchange parameter is extracted at each field. The result of the field
dependence of the exchange field is shown in Figure 5.5. As can be seen there is small peak in J as a function of field between 3.5 and 4 T. The exchange field and g values will be discussed in the next section.

From the previous magnetization measurements in magnetic fields up to 15 T [16,118,154] the data was analyzed on the basis of the $\Gamma_7$ level being lowest in energy and a magnetic moment of the ground state of about $1.0 \mu_B$ was found. Their value exceeds $0.71 \mu_B$ for a pure $\Gamma_7$ ground state, and was attributed to an admixture

![Figure 5.5: Values of the exchange field as a function of field from the susceptibility data.](image-url)
of the Γ₄ level into the Γ₇ ground state [16]. In view of the more recent findings showing the Γ₈ states to be lower in energy, this explanation has to be ruled out. The magnetization data, in fact, suggest a Γ₈ ground state, since the degenerate Γ₄ level gives a magnetic moment of 1.54 μₜ [13]. With the new CEF level scheme and Γ₈ splitting of about 30 K, the magnetic susceptibility data [16] was fit between 3.3 and 700 K without any adjustable parameter except a reduction factor of 1.29 for the total susceptibility by Zirngiebl et al [13]. This result is in good agreement with our result of Γ₈ splitting of 34 K.

5.2 EPR Measurements

A typical example of the single resonance line shapes observed at 37 GHz is shown in Figure 5.6. It should be remembered that the observed voltages are proportional to the field derivative (dP/dB) of the power absorption rather than to the direct power absorption, P. We first note that in the field range 0 to 5 T at 37 GHz and 1 to 9 T at both 95 and 218 GHz a single resonant line is observed at all temperatures, frequencies, and angles of applied field over these field ranges. This fact is at variance from what is expected for a pure unsplit Γ₄ level for the 4f electron where as many as three lines with g factors of 6/7, 2 and 22/7 are expected for the field applied parallel to the [100] where the extensive field sweeps were made. At 37 and 95 GHz the field range is sufficient to observe all three of the possible resonances, and at 218 GHz two (22/7, 2) would have been in the field range.

Because the samples are metallic we have fit the data to a Dysonian line shape in the limit of the diffusion time being infinite for these localized moments, and the fits
are shown as solid lines in Figures 5.7 and 5.8. From a least squares fit of Equation 4.3 to the data both the g factors and spin-lattice relaxation time, $T_1$, were extracted for all temperatures, frequencies, and angles of applied field. Assuming no exchange field and using the fitting procedures described above and in Section 4.4.1, g factors obtained from the single line $\mathbf{H} \parallel [100]$ are $1.98 \pm 0.03$ at 37 GHz, $2.50 \pm 0.01$ at 95 GHz, and

![Figure 5.6: First derivative of the resonance absorption at 5 K in CeB$_6$ with the field parallel to the [100] direction at 37 GHz.](image)

Figure 5.6: First derivative of the resonance absorption at 5 K in CeB$_6$ with the field parallel to the [100] direction at 37 GHz.
Figure 5.7: First derivative of the resonance absorption at 100 K in CeB$_6$ with the field parallel to the [100] direction at 37 GHz. The solid line was calculated using equation (4.3).

2.36 ± 0.01 at 218 GHz. These measured g factors, or resonant fields are temperature independent to within the quoted error at all temperatures measured. From these results it can be seen that the Zeeman splitting of the ground state level is non-monotonic in field (frequency). This result will be discussed later.

There is a slight anisotropy of the g factor measured at 37 GHz, for rotations of 45° in the (100) plane and this result is shown in Figure 5.9. This anisotropy may arise
Figure 5.8: First derivative of the resonance absorption at 100 K in CeB$_6$ with the field parallel to the [100] direction at 95 GHz. The solid line was calculated using equation (4.3).

from either an anisotropic exchange mechanism or a direction dependent splitting of the Zeeman levels in the presence of the CEF. If the interactions causing the splitting is anisotropic, then for other directions the value of $\theta$ may not be $\pi/2$ causing a decrease in the measured g factor.

While all of the g factors measured using the fitting procedures are temperature independent, the values of $T_1$ are not. In Figure 5.10 $T_1$ measured at 37 and 95 GHz
are given as a function of temperature respectively. At 37 GHz $T_1$ is found to increase by a factor of 2 between 4 and 60 K, then become practically temperature independent to 300 K. A similar behavior is observed at 95 GHz with the temperature independence occurring at slightly high temperatures. As can be seen $T_1$ becomes slightly longer with increasing temperature as would be expected from exchange narrowing of the line. Therefore, we calculated the first moments of the line shapes (see Chapter 3) at 37 and 95 GHz for each temperature using equation (3.17) as shown in Figures 5.11.

Again we make the assumption that there is a single exchange interaction parameter, $J$, and fit the data above 30 K to the expression of the expected result from
Figure 5.10: The spin-lattice relaxation time measured at 37 and 95 GHz as a function of temperature.

For a spin \( \frac{1}{2} \) system with all spins identical [141]:

\[
h\langle \Delta \nu \rangle = -\frac{3J}{4} \tanh \left( \frac{g\mu_B H}{2k_B T} \right),
\]

with results being the solid line in Figure 5.11. Here J is an average exchange parameter. In Figures 5.11 the fits with J as the only adjustable parameter to this expression for temperatures above 30 K is shown both for the 37 and 95 GHz data. The exchange field determined from the fits are 0.033 \( \pm \) 0.005 T at 1.36 T and
$0.048 \pm 0.004 \text{T at } 2.7 \text{T.}$

Below 30 K the data deviates substantially from this expression. The probable reasons for this deviation are twofold: a.) the higher energy doublet is depopulating below 30 K, and b.) the Dysonian line shape is for temperatures much larger than the splitting between the Zeeman levels, which begins to break down below 30 K. We have not attempted any further analysis of this low temperature data.

As stated before, from the inverse susceptibility fit the exchange field and $g_a = g_b$ are found to be 0.024 T and 2, respectively. When $\theta = 45^\circ$ and $\phi = 0^\circ$ in
Equations (4.9) and (4.10) we should observe only one resonance because both $g_a = g_b = 2$. From the 37 GHz EPR measurements the g factor is found to be $1.98 \pm 0.03$ at 1.36 T. The antiferromagnetic exchange field of 0.024 T needs to be subtracted from the applied field in the EPR data to give an accurate value. When this subtraction is done and the line shape fit recalculated the g factor measured at 37 GHz turns out to be $2.01 \pm 0.03$, or in very good agreement with the assumption of equal mixing of the two levels in the $\Gamma_8$ doublets.

What does not fit well with this overall picture is the non-monotonic increase of the g factors at 95 and 218 GHz. The exchange-coupled model for the structure of Phase II of Ohkawa [21] predicts a g factor of 2 for the ground state of the coupled system, but no field dependence of the doublet levels was calculated. While we do not understand the mechanism that gives rise to this change, we doubt that it is due to a field dependent exchange because the J values calculated (see Figure 5.5) from the susceptibility as a function of field are too small account for it. On the other hand the J values have a peak in the same field range where the g factor is largest.

In addition, we point out that there is some correlation with what happens at low temperatures in the conduction electron system. Here the electronic component of the specific heat, $\gamma$, is greatly enhanced, presumably by electron-electron interactions, and changes with applied magnetic field non-monotically [94], [104] (see Figure 2.5). There is a peak in the values of $\gamma$ near 3 T where the measured g factor is largest. The fields at which the EPR data was taken span the peak in the specific heat measurements with $g = 2.01$ at 1.34 T rising to 2.55 at 2.67 T, then falling to $g = 2.39$ at 6.57 T. Thus
it appears that whatever the mechanism causing the increased mass in the conduction
electron system also may be causing a change in the 4f electron g factor.

5.3 Conclusion

We have performed extensive magnetization and EPR measurements on CeB₆ from which the following conclusions are drawn.

- The lowest lying four-fold degenerate $\Gamma_8$ level is split into two identical doublets with equal mixing of the four original states.
- There is only one observable EPR signal at applied fields between 0 and 5 T whereas for a $\Gamma_8$ level there should be three. This result is consistent with the $\Gamma_8$ being split into two doublets with the same g factor.
- There is an indirect exchange interaction between 4f electrons on different sites that has an effect on the field dependence of the measured g factors and the magnetic susceptibility.
- The g factor for this transition is independent of temperature between 4 and 300 K, depends on magnetic field (measurement frequency) in a non-monotonic manner, and depends slightly on crystal orientation with respect to the applied direction in the (100) plane.
- Spin-lattice relaxation time becomes slightly longer with increasing temperature as would be expected from exchange narrowing of the line.
- A peak in the magnetic field dependence of the values of the electronic specific heat, the 4f g factors and the indirect exchange all occur near applied fields of 3 T.
Overall the split $\Gamma_8$ level structure determined here should be useful in future considerations of the mechanisms causing the splitting of the $\Gamma_8$ level and the interactions of the 4f electrons with the conduction electrons.
CHAPTER 6

EPR MEASUREMENTS ON EUB₆

6.1 EPR Measurements on EuB₆

The measurements reported here were made on small single crystal EuB₆ (0.38 mm x 0.25 mm x 0.76 mm) which were grown in a molten Al flux crystallizing about at 1400 °C.

The EPR measurements were made using the 35 GHz spectrometer described in Chapter 4 in the temperature range from 10 K to 150 K, with 10 K increments. A typical example of the resonance line pattern, observed at 34.69 GHz with the dc magnetic fields applied parallel to the sample disk plane, is shown in Figure 6.1. For the EuB₆ single crystal, at all temperatures and angles of applied field, the EPR spectrum shows one single line with a Dysonian shape, characteristic of an electrically conductive sample with stationary localized spins. All the spectra are well fitted to a single resonance line of Dysonian shape and the fit is shown as a solid line in Figure 6.1. From the Dysonian shape fit, the g value and relaxation time were extracted. As shown in Figure 6.2, the g factor corresponding to the Eu²⁺ resonance is equal to 1.98 ± 0.01 and it is independent of temperature within the quoted error at all temperatures measured which is consistent with previous results by other people [42,155,156]. However, the spin-lattice relaxation time is temperature- dependent. The relaxation time increases with increasing temperature as shown in Figure 6.3, and the resonance line width, ΔHpp, increases with decreasing temperature is shown in Figure 6.4 [43,44,
Figure 6.1: Derivative with respect to magnetic field of the power absorbed in EuB$_6$ versus magnetic field at 40 K at 35 GHz. The solid line shows the fit to the data using Equation 4.3.

Figure 6.2: g versus temperature for EuB$_6$ at 35 GHz.
Figure 6.3: Spin-lattice relaxation time versus temperature for EuB₆ at 35 GHz.

This increase could be due to the occurrence of critical fluctuations in the spin system. Above 100 K the critical spin fluctuations become unimportant and the line width is almost independent of temperature. In addition, no anisotropy in the g-value was observed for field rotations of the [100] plane at all temperatures [43]. These results are in good agreement with previous experimental results.
Figure 6.4: Thermal variation in the half-width at half maximum power absorption for EuB$_6$.

6.2 Conclusion

EPR measurements were made using the Q band (35 GHz) spectrometer in the temperature range from 6 to 150 K. These resonances for EuB$_6$ single crystal have following special features.

- A single line is observed at all temperatures.
- The $g$ factor in Eu is temperature-independent.
- Dysonian line shape is observed due to metallic conductivity.
- No anisotropy is measured at all temperatures.
• The line width becomes broader as temperature decreases.

• The spin-lattice relaxation time increases with increasing temperature at low temperatures but at high temperatures it becomes temperature-independent.

The purpose of these measurements was to provide a check on the experimental measuring technique and data analysis. Good agreement between the presents results and published results is found.
CHAPTER 7

CONCLUSION

The sixfold degenerate ground state of Ce$^{3+}$ ($J = 5/2$) splits into a $\Gamma_8$ quartet and a $\Gamma_7$ doublet. The $\Gamma_8$ was known to be the ground state from published inelastic magnetic neutron scattering and by the measurements of the magnetization. However, information about the ground state of 4f electronic structure in CeB$_6$ has been very unclear. To our knowledge the current research the first attempt to understand the 4f electronic structure in CeB$_6$ using EPR. We have done extensive temperature and angular dependent EPR measurements on a single crystal of CeB$_6$ in the paramagnetic phase from 5 to 300 K at different microwave frequencies (35, 95, and 220 GHz). Angular dependent EPR measurements were made only at 35 GHz using a standard microwave frequency-locked spectrometer, superconducting magnet, and magnetic field modulation. These measurements are supplemented by temperature and field dependent DC SQUID magnetometer measurements of the sample magnetization.

As a result of the EPR and magnetic susceptibility measurements made in this work, a theory of the ground state energy level scheme for the Ce 4f electron in CeB$_6$ was developed by Professor D. Browne. In analyzing the experimental results on the basis of this theory the following conclusions were reached.

- The ground state 4 fold degenerate $\Gamma_8$ level is split by interaction acting on the 4f electron into two, 2 fold degenerate levels, separated in energy by 34 K.
- A 34K splitting of the crystal field ground state $\Gamma_8$ level of the 4f electron in Ce
exists at all temperature up to 300 K.

- Exchange interaction between 4f electrons are found to exist and give rise to an internal exchange field of 0.024 T.
- On the basis of this model most of the experimental data for EPR and temperature dependent magnetic susceptibility is explained.
- There is one observable EPR signal at applied fields between 0 and 5 T at 37 GHz and, 1 and 9 T at 95 GHz.
- The two doublets exhibit equal mixtures of the original wave function of the quartet and both have the same g factor of approximately 2.
- The g factor for this transition is independent of temperature between 5 and 300 K, depends on magnetic field (measurement frequency) in a non-monotonic manner as shown in Table 7.1 and depends slightly on crystal orientation with respect to the applied field direction in the (100) plane as shown in Table 7.2.
- The field dependent 4f electron g factor and a field dependent exchange constant measured are not explained by the current theory, but are consistent with the magnetic field dependence of the conduction electron effective mass measured by other.

Table 7.1: Microwave frequency dependence of the g factor.

<table>
<thead>
<tr>
<th>Measured g factor</th>
<th>Measurement Frequency (GHz)</th>
<th>Resonant Field (T)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.98</td>
<td>37</td>
<td>1.36</td>
</tr>
<tr>
<td>2.50</td>
<td>95</td>
<td>2.70</td>
</tr>
<tr>
<td>2.36</td>
<td>218</td>
<td>6.60</td>
</tr>
</tbody>
</table>
Table 7.2: Angular dependence of g factor in the (100) plane.

<table>
<thead>
<tr>
<th>Angle from (100) plane</th>
<th>Measured g factor</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>1.98</td>
</tr>
<tr>
<td>10</td>
<td>1.95</td>
</tr>
<tr>
<td>20</td>
<td>1.94</td>
</tr>
<tr>
<td>30</td>
<td>1.94</td>
</tr>
<tr>
<td>40</td>
<td>1.95</td>
</tr>
<tr>
<td>45</td>
<td>1.96</td>
</tr>
</tbody>
</table>

- The spin-lattice relaxation time becomes slightly longer with increasing temperature as would be expected from exchange narrowing of the line.

Overall this is the most direct set of measurements of the ground state properties of the Ce 4f electron in CeB$_6$ that has been carried out to date.

In addition, EPR measurements were made on EuB$_6$ that are in good agreement with published results and provided a check on the technique used.
REFERENCES


APPENDIX A

CALCULATIONS FOR THE 100 GAUSS MODULATION COIL

The calculations are done for #26 Cu wire with 6 layers as follows:

Wire diameter: \( d = 0.4049 \text{ mm} \), \( \mu_0 = 4\pi 10^{-7} \text{ N/A}^2 \)

Wire diameter with insulation: \( d = 0.406 \text{ mm} \)

Resistant/length: \( R_k = 133.9 \Omega/\text{km}, \quad R_m = \frac{R_k}{1000} \Omega/\text{m} \)

Resistivity: \( \rho_\mu = 1.7241 \mu\text{cm (annealed)} \)

\[ \rho = \frac{\rho_\mu}{100} \times 10^{-6} \text{ m} \]

Diameter of coil: \( D_E = 1.7 \text{ in.}, \quad D = D_E \times 25.40 \text{ mm} \)

Length of coil: \( H_E = 3.4 \text{ in.}, \quad H = H_E \times 25.40 \text{ mm} \)

Beta: \( \beta = \frac{H}{D} \), \( D = 43.18 \text{ mm} \)

Number of turns/layer: \( N_1 = \frac{H}{d_i}, \quad N_1 = 212.709 \text{ turns} \)

Length of wire: \( L_1 = N_1 \times \frac{2\pi D}{2}, \quad L_1 = 2.885 \times 10^4 \text{ mm} \)

Number of layers: \( I = 6 \)

Resistance: \( R = \frac{\rho L_1 \times I \times 1000}{\pi \times \left(\frac{d}{2}\right)}, \quad R_r = \frac{R_m \times L_1 \times I}{1000} \)
R = 23.182 Ω, \hspace{1cm} R_T = 23.182 Ω

Diameter of dewar tail: \hspace{1cm} D_{Te} = 1.5 \text{ in.}, \hspace{1cm} D_T = D_{Te} \times 25.40 \text{ mm}

Insulation thickness: \hspace{1cm} \ell_{Te} = 0.001 \text{ in.}, \hspace{1cm} \ell_T = \ell_{Te} \times 25.40 \text{ mm}

Total diameter of tail and coil: \hspace{1cm} D_T + 2 \ell_T + d_i \times 2 \times I = 43.023 \text{ mm}

Target modulation amplitude: \hspace{1cm} B_T = 100 \text{ Gauss (peak)}

\[ B = \left( \frac{\beta}{\sqrt{1 + \beta^2}} \right) \mu_0 \frac{I}{d_i}, \quad B_I = \frac{B_T}{I} \]
\[ I = \frac{B}{\sqrt{1 + \beta^2}} \frac{\mu_0}{\beta} d_i \]

Current:
\[ I = \frac{B_I}{10000} \frac{\sqrt{1 + \beta^2}}{\beta} \left( \frac{d_i}{1000} \right) \]

\[ I = 0.602 \text{ Amps (peak)} \quad \quad \quad V = I \times R_T = 13.956 \text{ V} \]

\[ I_{rms} = \frac{I}{\sqrt{2}}, \quad \quad \quad V_{rms} = I_{rms} \times R_T \]

\[ I_{rms} = 0.426 \text{ Amps} \quad \quad \quad V_{rms} = 9.869 \text{ V} \]

Power:
\[ P = I^2 \times R_T = 8.402 \text{ Watts (rms)} \]
\[ P/2 = 4.201 \text{ Watts (rms)} \]

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THEORETICAL ANALYSIS OF CeB₆ SUSCEPTIBILITY DATA

All of the following analysis was done by Professor D. Browne. It is assumed that only the $J = 5/2$ multiplet of the f-level is occupied by a single electron. The Landé $g$ factor for the $J = 5/2$ multiplet is $6/7$. In addition, it is known that the crystal field induces a $W = 530 \, \text{K}$ splitting of the $J = 5/2$ level into a $\Gamma_7$ doublet and a $\Gamma_8$ quartet.

First it is assumed that the f-levels on different sites do not interact and there is no splitting of the $\Gamma_9$. In this case the eigenstates of all six levels are:

<table>
<thead>
<tr>
<th>Symmetry</th>
<th>Notation</th>
<th>Wavefunction</th>
<th>$\langle J_z \rangle$</th>
<th>$\langle J_z^2 \rangle$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\Gamma_7$</td>
<td>$</td>
<td>c+\rangle$</td>
<td>$\frac{3}{2} - \sqrt{\frac{1}{6}}</td>
<td>\frac{5}{2}\rangle$</td>
</tr>
<tr>
<td>$</td>
<td>c-\rangle$</td>
<td>$-\frac{3}{2} - \sqrt{\frac{1}{6}}</td>
<td>\frac{5}{2}\rangle$</td>
<td>$\frac{5}{6}$</td>
</tr>
<tr>
<td>$\Gamma_8$</td>
<td>$</td>
<td>b+\rangle$</td>
<td>$\frac{5}{2} + \sqrt{\frac{1}{6}}</td>
<td>\frac{3}{2}\rangle$</td>
</tr>
<tr>
<td>$</td>
<td>b-\rangle$</td>
<td>$\frac{5}{2} + \sqrt{\frac{1}{6}}</td>
<td>\frac{3}{2}\rangle$</td>
<td>$-\frac{11}{6}$</td>
</tr>
<tr>
<td>$</td>
<td>a+\rangle$</td>
<td>$\frac{1}{2}$</td>
<td>$\frac{1}{2}$</td>
<td>$\frac{1}{4}$</td>
</tr>
</tbody>
</table>
Several previous experiments have shown that two of the $\Gamma_8$ states are split by some interaction to lie above the second pair of $\Gamma_8$ states by an amount $\Delta$. Without consideration of the mechanism causing the splitting it is assumed that the degeneracy of the quartet is lifted. It is further assumed that the interaction causes the $|a\pm\rangle$ and $|b\pm\rangle$ doublets to split without any mixing between them. Since this interaction produces only a 30 K splitting and the $\Gamma_7$ level is much higher in energy (530 K) that it is further assumed that the effect of this interaction on the $\Gamma_7$ orbitals can be ignored.

Now, in the above basis, which diagonalizes the spin-orbit and the crystal field terms in the Hamiltonian, the magnetic moment operator $M = \sum_i \mu_i (L_i + 2S_i)$ is not diagonal. It has off-diagonal components $\langle a \pm | M_z | c \pm \rangle = \mp 4\sqrt{5}/7$. Thus the application of the field mixes the wave functions of different multiplets, adding an additional van Vleck term [134] to the susceptibility. The aim is to find

$$\langle M \rangle = \frac{\text{Tr}[e^{-\beta H} M]}{\text{Tr}[e^{-\beta H}]}.$$  \hspace{1cm} (1)

Here the Hamiltonian is $H = H_{SO} + H_{CF} - M_2 h$ where $H_{SO}$ is the spin-orbit and $H_{CF}$ the crystal field parts of $H$, and $h$ is the applied magnetic field. The perturbed energies and eigenfunctions to first order in the applied field $h$ were computed, and then put into the
formula for the susceptibility \( \chi = \left( \frac{1}{V} \right) \left( \frac{\partial \langle M^2 \rangle}{\partial H} \right) \).

The calculation is begun by assuming that the \(|a\pm\rangle\) and \(|b\pm\rangle\) orbitals are simply split without any mixing of a and b orbitals. The splitting is given by an amount \(\Delta\), and the \(\Gamma_7\) orbitals lie an amount \(W\) above the ground state orbitals. We can have either the large moment \(|a\pm\rangle\) orbitals or the smaller moment \(|b\pm\rangle\) orbitals as the ground states. If one inserts the results above for the diagonal matrix elements, and also uses \(\langle c + |M_z| a^+ \rangle = -4\sqrt{5}/7\) the susceptibility is given by

\[
\chi = \frac{N g_j^2 \mu_b^2}{V k_b T} \frac{121}{36} + \frac{1}{4} e^{-\mu_1} \frac{25}{36} e^{-\mu_2} + \frac{40}{9} \left(1 - e^{-\mu_2}\right) \frac{1}{\beta W}, \tag{2}
\]

when the \(|a\pm\rangle\) levels lie lowest in energy, and

\[
\chi = \frac{N g_j^2 \mu_b^2}{V k_b T} \frac{1}{4} \frac{121}{36} e^{-\mu_1} + \frac{25}{36} e^{-\mu_2} + \frac{40}{9} \left(e^{-\mu_2} - e^{-\mu_2}\right) \frac{1}{\beta W}. \tag{3}
\]

if the \(|b\pm\rangle\) levels lie lowest.

Next, the possible mixing of the states is addressed. No assumption is made about the origin of the splitting, but it is required that the effective on-site potential obey time-reversal symmetry. Because the \(\Gamma_7\) \(|c\pm\rangle\) levels are much higher in energy

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than the 30 K splitting, one assumes that the interaction that mixes the \( \Gamma_8 \) levels does not couple them to the higher energy \( \Gamma_7 \) orbitals. This choice simply reduces the number of free parameters in the interaction.

Next the consequences of time-reversal symmetry are examined. The time reversal operator \( \mathcal{T} = R_y K \), where \( K \) is the complex conjugation operator and \( R_y \) represents a rotation of the spin by \( \pi \) about the \( y \)-axis. If one applies it to the \( 5/2 \) wavefunctions, using the fact that \( Y_{lm}^* = (-1)^m Y_{l,-m} \), one finds that \( \mathcal{T}|b\pm\rangle = \mp|b\mp\rangle \) and similarly for \( |a\pm\rangle \). Thus each pair of levels transforms under time-reversal just like a pair of spin-1/2 states. Time reversal invariance requires \( \mathcal{T} \mathcal{H} = \mathcal{H} \mathcal{T} \), or \( \mathcal{H} = \mathcal{U} \mathcal{H}^* \mathcal{U} \), where \( \mathcal{U} \) is

\[
\mathcal{U} = \begin{pmatrix} 0 & -i & 0 & 0 \\ i & 0 & 0 & 0 \\ 0 & 0 & 0 & -i \\ 0 & 0 & i & 0 \end{pmatrix}
\]

from which one deduces that the form of \( \mathcal{H} \), up to an overall shift in energy, can be written

\[
\mathcal{H} = \begin{pmatrix} a & 0 & c & d \\ 0 & a & -d^* & c^* \\ c^* & -d & b & 0 \\ d^* & c & 0 & b \end{pmatrix}
\]
The energies are given by $(a + b)/2 \pm \sqrt{((a - b)/2)^2 + |c|^2 + |d|^2}$. Each level is doubly degenerate as expected. This form is more general than one proposed in [Ohkawa, 1985 #90] as the most general Jahn-Teller coupling to a lattice vibration.

One can adjust the phase of the wave functions to make $c$ and $d$ real and positive, so that the Hamiltonian then can be written using two variables $\theta$ and $\phi$ such that: $a = \Delta \sin^2 \theta$, $b = \Delta \cos^2 \theta$, $c = \frac{1}{2} \Delta \sin 2\theta \cos \phi$, and $d = \frac{1}{2} \Delta \sin 2\theta \sin \phi$. In this notation the ground state eigenfunctions are

$$|A+\rangle = \cos \theta |a+\rangle - \sin \theta (\sin \phi |b+\rangle + \sin \phi |b-\rangle),$$

$$|A-\rangle = \cos \theta |a-\rangle + \sin \theta (\sin \phi |b+\rangle - \cos \phi |b-\rangle),$$

and the two excited state eigenfunctions with energy $\Delta$ above the ground state are

$$|B+\rangle = \sin \theta |a+\rangle + \cos \theta (\cos \phi |b+\rangle + \sin \phi |b-\rangle),$$

$$|B-\rangle = \sin \theta |a-\rangle - \cos \theta (\sin \phi |b+\rangle - \cos \phi |b-\rangle).$$

Provided that $\theta < \pi/4$, the ground state is predominantly made up of the higher-moment $|a \pm\rangle$ state.
If the $\Gamma_8$ to $\Gamma_7$ interactions are important, then $d \neq 0$. However, one can begin with $d = 0$ (or $\phi = 0$), and the following expression for the susceptibility is obtained

$$\chi_{\text{tot}} = \chi_a + \chi_b + \chi_7 = \frac{m_a + m_b + m_7}{\hbar}$$

where

$$\chi_a = \frac{N}{VZ} g_j^2 \mu_b^2 \left( g_a^2 \beta - C_{ab} + C_{ac} \right),$$

$$\chi_b = \frac{N}{VZ} g_j^2 \mu_b^2 \left( g_b^2 \beta - C_{ab} + C_{bc} \right) e^{-\beta_3},$$

$$\chi_c = \frac{N}{V} g_j^2 \mu_b^3 \left( g_c^2 \beta - C_{ac} - C_{bc} \right) e^{-\beta_3} / Z.$$  

Here the $C_{av} = 2|\langle \alpha | M_z | \nu \rangle|^2 / (\varepsilon_\nu - \varepsilon_\alpha)$ are the van Vleck terms and the $g$ factors are:

$$g_\alpha^2 = |\langle \alpha | M_z | \nu \rangle|^2, \quad \alpha = a, b, c.$$  

When the $\Gamma_8 - \Gamma_7$ interactions are important, i.e. for $d \neq 0$, the situation more complicated since the application of the magnetic field requires doing degenerate perturbation theory because the magnetic field couples degenerate levels. The results of this calculation give the same form as in the non $\Gamma_8 - \Gamma_7$ interaction case, but the $g$ factors and van Vleck terms are modified to be:

$$g_\alpha = \frac{1}{7} \sqrt{121 \cos^4 \theta + 66 \cos(2\phi) \sin^2 \theta \cos^2 \theta + 9 \sin^4 \theta},$$
\[ g_b = \frac{1}{7} \sqrt{9 \cos^4 \theta + 66 \cos(2\phi) \sin^2 \theta \cos^2 \theta + 121 \sin^4 \theta}, \]

and

\[ g_c = \frac{5}{7}, \]  

(7)

\[ C_{ab} = \frac{260 - 132 \cos(2\phi)}{49\Delta} \sin^2 \theta \cos^2 \theta, \]

\[ C_{ac} = \frac{160 \cos^2 \theta}{49W}, \quad C_{bc} = \frac{160 \sin^2 \theta}{49(W-\Delta)}, \]

if the \(|A\pm\rangle\) levels lie lowest in energy. In these expression a measured g factor is twice the value given here.

To calculate the actual susceptibility, one needs to put in the effect of exchange interaction between sites. To include the exchange one uses the standard mean field approach and assumes that the mean moments induced in the material add to the local field.

Let \(m_a\) and \(m_b\) be the moments produced in the lower and upper doublets, and \(m_c\) is the moment produced by the \(\Gamma_7\) doublet. Hence one finds

\[ m_a = \chi_a (h + J_{aa} m_a + J_{ab} m_b + J_{ac} m_c), \]

\[ m_b = \chi_b (h + J_{ba} m_a + J_{bb} m_b + J_{bc} m_c), \]

\[ m_c = \chi_c (h + J_{ca} m_a + J_{cb} m_b + J_{cc} m_c), \]
where the $J_{ij}$ are exchange constants and they satisfy $J_{ij} = J_{ji}$. These linear equations then should be solved and if it is further assumed that there are no interactions except between the $|a\pm\rangle$ and $|b\pm\rangle$ states, the total susceptibility

$$\chi = \chi_\gamma + \frac{\chi_a + \chi_b + \chi_a \chi_b \left(2J_{ab} - J_{aa} - J_{bb}\right)}{1 - \chi_a J_{aa} - \chi_b J_{bb} + \chi_a \chi_b \left(J_{aa} J_{bb} - J_{ab}^2\right)}.$$  

If one further assumes $J_{aa} = J_{bb} = J_{ab} = J$,

$$\chi = \chi_\gamma + \frac{\chi_a + \chi_b}{1 - J(\chi_a + \chi_b)} \quad (8)$$

This the final form of $\chi$ and when Equations (6) and (7) are inserted it is used to analyse the susceptibility data.
APPENDIX C

TABLE OF DATA FILES

<table>
<thead>
<tr>
<th>Sample</th>
<th>File Name</th>
<th>Temperature (K)</th>
<th>Frequency (GHz)</th>
<th>Field Range (T)</th>
</tr>
</thead>
<tbody>
<tr>
<td>EuB₆</td>
<td>EPR OF EUB₆</td>
<td>5-150</td>
<td>34.6</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>EUB₆-20K-35</td>
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<td>34.6</td>
<td>0.8-1.5</td>
</tr>
<tr>
<td></td>
<td>EUB₆-30K-35</td>
<td>30</td>
<td>34.6</td>
<td>0.8-1.5</td>
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<td>EUB₆-40K-35</td>
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<td>34.6</td>
<td>0.8-1.5</td>
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<td>MAGNETIZATION</td>
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<td>SUSCEPTIBILITY</td>
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<tr>
<td>FIRST MOMENT-37</td>
<td>5-150</td>
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<td>-</td>
<td></td>
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<td>95</td>
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VITA

Cabir Terzioglu was born on May 1, 1965, in Rize, Turkey, to Rifki and Zinnet Terzioglu. He graduated with a bachelor of science degree in physics in 1988 from Karadeniz Technical University in Trabzon, Turkey. He entered the master’s program in physics at the Karadeniz Technical University, Trabzon, in 1989. He worked as a research assistant for three and half years at Karadeniz Technical University. He earned the degree of Master of Science in physics in December 1992. After this, he began his doctoral study at Karadeniz Technical University. After finishing his class requirements, he decided to come to the United States of America to do his graduate study at Louisiana State University. After passing the required test to get a scholarship, he came to Austin, Texas, to attend an English course at Texas Intensive English Program in November 1993.

In August 1994 he entered the doctoral program in the Department of Physics and Astronomy at Louisiana State University in Baton Rouge, Louisiana. In May 1999, he received a second master’s degree in physics from Louisiana State University. He is married and has two children, Rifki and Erdem. He will receive the degree of Doctor of Philosophy in December, 2000.
DOCTORAL EXAMINATION AND DISSERTATION REPORT

Candidate: Cabir Terzioglu

Major Field: Physics

Title of Dissertation: Electron Paramagnetic Resonance and High Temperature Susceptibility Measurements in CeB6

Approved:

[Signatures]

Major Professor and Chairman

Dean of the Graduate School

EXAMINING COMMITTEE:

[Signatures]

Date of Examination:

July 19, 2000