Magnetic polarons and magnetoresistance in EuB$_6$

M.J. Calderón$^1$, L.G.L. Wegener$^1$, and P.B. Littlewood$^{1,2}$

(1) Cavendish Laboratory, Cambridge University, Madingley Road, Cambridge CB3 0HE, UK
(2) National High Magnetic Field Laboratory, Pulsed Field Facility, LANL, Los Alamos NM 87545, USA

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EuB$_6$ is a low carrier density ferromagnet which exhibits large magnetoresistance, positive or negative depending on temperature. The formation of magnetic polarons just above the magnetic critical temperature has been suggested by spin-flip Raman scattering experiments. We find that the fact that EuB$_6$ is a semimetal has to be taken into account to explain its electronic properties, including magnetic polarons and magnetoresistance.

I. INTRODUCTION

Europium hexaboride is part of the large and heterogeneous class of materials that exhibit Colossal Magnetoresistance (CMR). The ferromagnetic transition in EuB$_6$ is accompanied by a dramatic change in resistivity. There is a large body of experimental data available on the magnetic and electric properties, but a thorough understanding is lacking.

EuB$_6$ has a cubic unit cell with Eu-ions at its vertices and a Boron octahedron at its center. The material is ferromagnetic and shows two magnetic transitions: at $T_M = 15.3$K and at $T_C = 12.5$K. These have been associated with a spin reorientation and a ferromagnetic transition, respectively. Neutron diffraction experiments have given a magnetic moment $\mu = 7.3 + 0.5 \mu_B$. This is exclusively due to the localized half-filled $f$-shell in the Eu$^{+2}$ ions.

Electronic structure calculations, Shubnikov-de Haas and de Haas-van Alphen measurements show that EuB$_6$ is a semimetal. The Fermi surface consists of two ellipsoidal pockets, one electron-like and one hole-like, centered on the X point in the Brillouin zone. The pockets contain very few carriers: Hall effect measurements yield $n_{tot} \sim 10^{-2}$ carriers per formula unit at low temperatures. Small dilations of the boron octahedra cause overlap of the conduction and valence bands at the X points rendering EuB$_6$ semimetallic. The carrier concentration decreases smoothly as temperature increases.

The electrical resistivity is metallic in the ferromagnetic regime. It shows a sharp peak near $T_C$. Above this temperature, the resistivity decreases with an almost activated temperature dependence until it reaches a minimum at about 30K. At higher temperatures it increases and eventually starts to saturate at about room temperature.

The application of a magnetic field produces sharp changes in the resistivity. Close to the magnetic transition, negative magnetoresistance (MR) values of up to 100% have been observed. This decrease in resistivity is accompanied by a large decrease in the (negative) Hall coefficient and an increase in the plasma frequency. The change in the plasma frequency is more gradual than the changes in resistivity and Hall coefficient.

In the ferromagnetic regime, on the other hand, the MR is large and positive: at 1.7 K resistivity changes of up to 700% have been observed in a transversal applied field of 7T. The MR depends quadratically on the applied field strength at low temperatures.

Just above $T_C$ and up to $\sim 30$K, the existence of magnetic polarons has been proposed as the cause of the dominant energy scale turns out to be considerably lower - by a factor of thirty - than expected based on reliable estimates of the exchange interaction.

Wigger et al. showed how the crossover between large positive and large negative MR from well below to well above the ferromagnetic transition can be explained by the dominance of orbital scattering at $T \ll T_C$ to spin scattering at $T \gg T_C$. The model we shall use for the carrier transport in these regimes is similar to that of ref. and we shall thus suppress most of the details. The key feature of the model is its multiband nature - there are two types of carrier.

In this paper we concentrate principally on the regime close to $T_C$ and analyze the evidence for the existence of magnetic polarons in Europium Hexaboride. We show how the SFRS results can be explained using a multiband model, resolving the conundrum of the anomalously small energy associated with the carrier spin flip.

II. MODEL AND PARAMETERS

We model EuB$_6$ as a ferromagnetic semimetal with a low carrier density. Both electrons and holes are itinerant and are coupled to the local moments $S = 7/2$. This can be described by the following general Hamiltonian:

\[
H = -t \sum_{i,j,\sigma} c^+_{i\sigma} c_{j\sigma} - J \sum_{\langle i,j \rangle} \vec{S}_i \cdot \vec{S}_j - J'_e \sum_{i} c^+_{i\sigma} \sigma \tau_{\sigma,\sigma'} c_{i\sigma'} \vec{S}_i - J'_h \sum_{i} c^+_{i\sigma} \sigma \tau_{\sigma,\sigma'} c_{i\sigma'} \vec{S}_i (1)
\]

Here, the hopping parameter is roughly $t = 0.1$ eV. $c^+_{i\sigma,\sigma'} \tau_{\sigma,\sigma'} c_{i\sigma'}(e,h)$ is the itinerant carrier spin operator and the subindices $e$ and $h$ stand for electrons and holes.
respectively. $J'_{\sigma}$ ($J''_{\sigma}$) is the on-site coupling between the spins of the electrons (holes) and the local moments. $J$ is the magnetic exchange between local moments.

First of all we need to discuss what is the origin of the ferromagnetism and the order of magnitude of the magnetic couplings. Ferro- and antiferro-magnetism of the insulating Eu-chalcogenides (EuX, X= O, S, Se, Te) has been explained as due to superexchange interaction between neighbor Eu ions through the anion between them. The density of carriers in the undoped chalcogenides is too low to expect any indirect RKKY (Ruderman-Kittel-Kasuya-Yosida) interaction. The ferromagnetic interaction arises instead from the overlap between the 4f- and 5d-orbitals at different cations. This overlap leads to an effective exchange interaction in third order in perturbation theory. This does not apply directly to EuB$_6$ due to the different crystalline structure, but nevertheless one expects that the superexchange coupling $J$ is small. Moreover, the increase of magnetic critical temperature and concomitant decrease of resistivity under high pressures has revealed that the magnetic exchange in EuB$_6$ is mainly due to the RKKY interaction. Therefore, $J$ in Eq. is negligible.

The RKKY magnetic exchange is mediated by the itinerant carriers via their coupling with the lattice magnetic moments. An effective Heisenberg-like magnetic exchange can be written in terms of the local Hund’s like exchange coupling $J'$ ($J'_\sigma$ or $J''_\sigma$)

$$J_{\text{eff}} = -9\pi J'^2 E_F n^2 \sum_i F(2k_F r_i)$$

where $F(x) = \frac{-x \cos x + \sin x}{x^3}$, $n$ is the density of carriers, and $E_F$ is the Fermi energy. $J_{\text{eff}}$ is an oscillating function of $x$ but is ferromagnetic for small $x$. This is the relevant limit for Europium Hexaboride, as its low carrier density implies $k_F r \rightarrow 0$.

To estimate the value of $J'$ we use the mean field relation between $T_C$ and $J_{\text{eff}}$, $T_C \sim z S^2 J_{\text{eff}}$, where $z$ is the coordination number for Eu, and $S$ is the $z$-component of the local moments. Using a critical temperature $T_C \sim 12 K$ and a parabolic approximation to the bands, $J' \sim 0.1 eV$ is found, consistent with reported data for isolated Eu-ions. In this estimation we are considering that only one kind of carrier is responsible for the magnetism.

III. MAGNETIC POLARONS

When the local exchange coupling $J'$ is large enough, carriers can be localized by ferromagnetic clusters and form composite objects called magnetic polarons. Ferromagnetic polarons can exist in the low temperature phases of antiferromagnets but here we are interested in those formed in the paramagnetic phase. A necessary condition for the existence of magnetic polarons is that the density of carriers is very low compared to the inverse of the correlation volume, namely $n \xi^3 << 1$. When this condition is fulfilled, polarons are well-defined non-overlapping entities.

There are two kinds of magnetic polarons: free and bound. A free magnetic polaron is a carrier localized in a ferromagnetic cluster embedded in a paramagnetic background. A carrier that is coupled strongly to local moments via a Hund’s like coupling tends to align the moments that are within a Bohr radius. This causes a trapping potential that localizes the carrier. The potential can be enhanced by random fluctuations of the magnetization that produce an alignment of local moments in the carrier’s vicinity.

The carrier thus traps itself by the magnetization it causes. It could increase the alignment of the local moments and hence decrease its energy by localizing itself in a smaller volume. However, this would lead to an increase in kinetic energy. The quantity that determines the stability and size of these objects is therefore $J'/t$ where $J'$ is the coupling of the carrier spin to the local moments and $t$ is the hopping parameter. The ratio $J'/t$ needs to be typically larger than one to guarantee stability of the free magnetic polaron.

On the other hand, in bound magnetic polarons the main driving force trapping the carrier is not the local magnetic interaction but the electrostatic potential created by impurities. The formation of the ferromagnetic cluster described above does occur. However, it is a second order process, as the magnitude of Hund’s coupling is much smaller than the Coulomb interaction. Mean field and Monte-Carlo calculations have shown that magnetic polarons can exist within a temperature window above $T_C$ whose width depends on the ratio $J'/t$. At higher temperatures, magnetic fluctuations are strong enough to destroy the magnetic polarons. Below $T_C$, the condition $n \xi^3 << 1$ is not fulfilled and the polarons overlap. If a magnetic field is applied within the existence temperature window, the size of a polaron increases until eventually the polarons overlap and produce a ferromagnetic transition.

Free and bound magnetic polarons can be differentiated by their dynamics and the resistivity they cause. Bound magnetic polarons are bound to an impurity in the system so the only way of transport is via an activated process: when the trapped carrier is “ionized” it is free to move until it is trapped by another impurity. Therefore they produce a resistivity $\rho$ such that $\partial \rho/\partial T < 0$. In contrast, free magnetic polarons are able to move to adjacent areas when random fluctuations of the nearby spins produce an aligned region. There is not a barrier to overcome in this process. This transport mechanism has been called “fluctuation-induced hopping” and produces a metallic resistivity $\partial \rho/\partial T > 0$.

Magnetic polarons have been largely studied in connection with Eu-chalcogenides (EuO, EuS, EuSe, EuTe) and diluted magnetic semiconductors such as Cd$_{1-x}$Mn$_x$Te and Pb$_{1-x}$Mn$_x$Te with $x$, the concentration of magnetic ions, small. Experimental evidence included photoluminescence spectra and magneto-
optical experiments as Spin Flip Raman Scattering \cite{25,26}. The Raman scattering spectrum shows an inelastic peak at low frequencies (Stokes’ shift) which, for the dilute magnetic semiconductors, depends as follows on polaronic properties. \cite{16}

$$\Delta E = \tilde{x} J^I \langle S_z \rangle,$$

where $\tilde{x}$ is the density of magnetic ions participating in the formation of polarons \cite{27}, and $J^I$ is the local exchange interaction between the $s$ itinerant electrons and the $d$ electrons localized in the Mn ions. The low density of local moments makes for a small Stokes’ shift, which - for Cd$_{1-x}$Mn$_x$Se - is consistent with experiment. \cite{14}

SFRS measurements done in EuB$_6$ have similarly revealed a zero-field peak in scattered intensity of the order of $\sim 12\text{meV}$ \cite{3,10} at 18K, just above the magnetic critical temperature. The behavior of this peak with temperature and external magnetic field is consistent with the stability conditions theoretically established for magnetic polarons. Free magnetic polarons are not expected to be stable in EuB$_6$ as $J^I$ and $\tilde{t}$ are comparable. Moreover, we have argued above that the activated behavior of the resistivity is better explained by means of bound magnetic polarons. Eu-site vacancies would produce the binding Coulomb potential for electrons.

We expect the energy of the Stokes’ shift to be given by Eq. 3 but now $\tilde{x} \sim 1$ as EuB$_6$ has a local moment on every Eu site in the cubic lattice. Few very site vacancies are expected in this fairly clean material. Mean-field theory predicts that bound magnetic polarons are fully spin polarised so $\langle S_z \rangle = 7/2$. Using this value and the energy of the Stokes’ shift we obtain $J^I \sim 3\text{meV}$. This is far too low compared to the values reported in the literature for $J^I$ in isolated Eu ions $\sim 100\text{meV}$ \cite{14,15}.

We are therefore left with a conundrum: the peak in the light scattering intensity follows all the trends calculated for an object with magnetic origin but the energy of that peak is almost two orders of magnitude smaller than expected. The solution to this problem lies in the fact that both polarised electrons and holes are found at the Fermi Energy.

Electrons and holes come from different B and Eu orbitals and therefore their magnetic couplings to the localized spin in the Eu $4f$ orbitals, $J'_x$ and $J'_y$ respectively, can be very different. Electronic structure calculations \cite{8} reveal that the hole pocket comes from the highest intraoctahedron B $2p$ band. On the other hand, the electron pocket comes from bonding combinations of the cation $d$ orbitals pointing along the cartesian directions with some hybridization with the B atoms and some free-electron-like character on the (110) axes between the cations. In other words, the electron charge density distribution is mainly found around the Eu ions while the holes are found around the B. Therefore, the coupling of the electrons is expected to be much larger than that of the holes. Consistently, Fig. 10 in Ref. \cite{8} shows a much larger majority-minority spin band splitting for electrons than for holes.

In conclusion, we propose that the ferromagnetic ordering is produced by the itinerant electrons coupled to the localized spin in Eu with $J'_z \sim 100\text{meV}$, while the itinerant holes, much more weakly coupled ($J'_z \sim 5\text{meV}$), account for the SFRS Stokes’ shift. A corollary of this identification is that there is likely a much higher energy feature in the SFRS, so far unobserved, that correspond to spin-flip of the electron state.

In the following section we will see how the existence of both electrons and holes is necessary to explain other electronic properties of EuB$_6$.

IV. MAGNETORESISTANCE

A. Positive MR at $T < T_c$

At low temperatures the magnetoresistance is due to the presence of two types of carriers and we will call it “orbital” MR. There are two effects involved. The same physics that causes the Hall effect is the most important cause of the MR. In addition to this, there is also a small shift of the bands with applied magnetic field that causes a small change in the carrier density.

In a simple metal with one type of carrier and a simple Fermi surface, there is no MR. A current that flows perpendicular to a magnetic field is initially deflected due to the transverse Lorentz force. This causes an electric field, the Hall field $E_H$, to build up:

$$E_H = \frac{e\tau}{4\pi n} \vec{H} \times \vec{J}. \quad (4)$$

The carriers that are deflected hit the edge of the sample and accumulate. The field that is thus built up counteracts the Lorentz force. When it cancels the Lorentz force, the current is undeflected. This is well known; it means that there is no MR in a normal metal. The component of the current density that is parallel to the applied electric field is not affected by the magnetic field. Therefore the resistivity remains unaffected as well.

In a semiconductor, on the other hand, there are by definition two kinds of carriers. These two kinds will almost invariably have different scattering times and different masses. Eq. 4 shows that the Hall voltage depends on the scattering time and the mass of the carrier. Therefore, the Hall voltages of the different kinds of carriers are also different. There is thus no voltage at which the two carriers will travel through the sample without deflection.

The difference in the Hall voltages is proportional to the applied magnetic field, so that the component of the current parallel to the applied electric field decreases with increasing field. The resistivity increases therefore when a magnetic field is applied, and the MR is therefore positive. We call this orbital MR, since it is due to the difference of the masses and scattering times of the two types of carriers. These properties derive from particularities of the atomic orbitals in the material.
The MR can be calculated from a linearized Boltzmann equation that includes a magnetic field under the assumption of a spherical Fermi surface. This is a standard calculation, which can be found in [28] and [29]. We quote the result for the magnetoresistance:

$$\Delta \rho(H) \rho_0 = \frac{\sigma_e \sigma_h (\mu_e - \mu_h)^2 H^2}{(\sigma_e + \sigma_h)^2 + H^2(\mu_e \sigma_e + \mu_h \sigma_h)^2},$$

(5)

where $\sigma_e$ and $\sigma_h$ are the electron and hole conductivity respectively, and $\mu_e$ and $\mu_h$ are their mobilities, both in the absence of any magnetic field. The right hand side of the above formula is easily seen to vanish if both types of carriers have the same mass and scattering time: the difference of the mobilities in the numerator vanishes in that case.

At low temperatures the orbital MR is largest: the scattering time is largest, so that the deflection is largest as well. As the scattering time decreases the effect becomes less important. For sufficiently small scattering times orbital MR becomes negligible.

The second effect that causes MR in EuB$_6$ is the shifting of the bands when a magnetic field is applied. The shift is caused by the coupling $J'$ of the carriers to the Eu local moments. Let us write the local moments as the sum of their average and the deviations therefrom: $\vec{S}_i = \langle \vec{S} \rangle + \delta \vec{S}_i$. We now use this expression in the Hamiltonian in Eq. [1] and obtain a term that couples the carrier’s energy to the magnetization. As the magnetization grows, the electron-like band is shifted to lower energies, and the hole-like band to higher energies. This causes an increase in the number of carriers as carriers spill over from one band into the other.

The change in carrier density can be obtained from the following two requirements. Firstly, the band-shift introduced by the change in magnetization $M$ is $\delta E = J'_e M/2$ for electrons and $\delta E = J'_h M/2$ for holes. Secondly, the increase in the number of carriers of both kinds is equal: as the hole like band is shifted up, new holes are created as negatively charged particles spill into the electron-like band and vice versa. Overall charge balance is maintained. We also assume a spherical Fermi surface, an accurate assumption in the case of EuB$_6$ [1]. We can use the requirement that charge neutrality be conserved to calculate the shift in the Fermi level. The shift is then used to obtain the number of carriers by integrating the density of states up to the Fermi level. The increase resulting from the shift of the bands is small, even at full saturation of the magnetization. Its effect on the MR at low temperatures is then negligible. The magnetization as a function of applied field is obtained from a Curie-Weiss model.

We included this change in carrier density due to the bands shifting in our model for the orbital MR. The contribution to the MR due to band shifting is opposite to that of the orbital effects. An external magnetic field increases the carrier density, so that it decreases the resistivity. Since the magnetization is almost saturated at low temperatures, the carrier density does not change much with applied field, and the MR is affected only slightly. The orbital contribution to the MR dominates.

We plot the MR obtained for the combined effect of the band shifts and the orbital effects in Fig. [1]. The temperature dependent scattering times at zero field are obtained from experimental data in [2]. The electron and hole mobilities are obtained from the conductivity at zero field, the masses of the carriers [4] and the carrier densities. The latter were obtained from the plasma frequency in [5]. We introduced a small imbalance between the carrier densities of 6.10$^{-4}$ per unit cell, in accordance with [2]. This imbalance is thought to arise from impurities. These numbers provide input to the model.

Our simple model, which depends only on parameters measured at zero field, can reproduce the large positive MR at low temperatures accurately. Fig. [1] shows that it reproduces the magnitude of the MR well. It also predicts the (nearly) quadratic dependence in applied field. From Fig. [1] it is clear that the orbital contribution to the MR dwindles at higher temperatures. The model proposed will lose its validity near the magnetic transition and in the paramagnetic phase, when other effects dominate.

**B. Negative MR at $T \approx T_c$ and above**

The mechanisms that govern the low-temperature MR become insignificant near the ferromagnetic transition. Close to $T_c$ the scattering time is so short that the positive orbital contribution to the MR is negligible. On the other hand, the shift of the bands caused by an applied magnetic field becomes substantial. We estimate that the carrier density changes by about 7% as the applied field saturates the magnetization. This could explain only part of the negative MR in the critical regime.

Additionally, near the critical point, spin fluctuations may provide a large contribution to the electrical resis-
tance. The dominant modes near a ferromagnetic transition are those with small $q$. They only produce substantial backscattering if $2k_F$ is itself small. This is the case of EuB$_6$ as its carrier density is very small. The suppression of the spin fluctuations when a magnetic field is applied is largely responsible for the MR found in the critical regime. Moreover, as shown in Ref. [13] (see Fig. 3), the localization of the carriers in magnetic polarons further increases the magnetoresistance.

In the temperature regime - just above $T_c$ - where the SFRS data gives evidence for bound magnetic polarons, the magnetoresistivity is large, and strongly negative, as expected since an applied magnetic field suppressed the local spins while electrons are responsible for the magnetic ordering through the RKKY interaction. This resolves the puzzle that the RKKY transition temperature implies an exchange coupling of the carriers to the local moment of about 0.1 eV, about 30 times larger than the measured spin-flip energy of a carrier trapped in a bound polaron. The existence of bound magnetic polarons is also consistent with a large negative magnetoresistance above $T_c$. The positive magnetoresistance in the ferromagnetic phase is also produced by the interplay of two kinds of carriers with different masses and scattering times.

V. SUMMARY

EuB$_6$ is a low carrier density ferromagnet with unusual properties: the resistance changes from metallic to activated and then to metallic as the temperature increases and the magnetoresistance changes sign close to $T_c$. The activated region has been ascribed to the existence of bound magnetic polarons. We discuss their existence in the light of Spin Flip Raman Scattering measurements reported in Refs. [12] and [14]. We conclude that the signature seen by those experiments is due to the Hund’s like coupling of holes with the local spins while electrons are responsible for the magnetic ordering through the RKKY interaction.

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In the diluted magnetic semiconductors of the type \( \text{Cd}_{1-x}\text{Mn}_x\text{Se} \), the Mn are antiferromagnetically coupled via superexchange. This is a shortrange interaction. At very low \( x \), the probability of having Mn clusters is very low so \( \bar{x} \simeq x \). For larger \( x \), antiferromagnetically coupled clusters of Mn form, so not all the Mn ions will participate in the magnetization of the system. See, for instance [27].

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