Evaluation of evidence for magnetic polarons in EuB_6

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Spin flip Raman scattering measurements on the semi-metal EuB_6 show the appearance of a Stokes' shift above the ferromagnetic critical temperature. This has been interpreted as arising from the formation of magnetic polarons. However, this data contains a previously unremarked puzzle, in that the energy scale turns out to be considerable lower than expected based on reliable estimates of the exchange interaction mediated by electrons. We propose the Stokes' shift is due to the much smaller on-site coupling of holes with the local spins.

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INTRODUCTION

Europium hexaboride is part of the large and heterogeneous class of materials that exhibit colossal magnetoresistance. 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.[1] T_M has been associated to a charge delocalization transition resulting from the overlap of magnetic polarons while T_C is the proper ferromagnetic transition.[2] This is consistent with recent muon-spin rotation measurements[3] that have shown magnetic phase separation below T_M. Neutron diffraction experiments[4] have given a magnetic moment $\mu=6.9\pm0.2\mu_B$. This is exclusively due to the localized half-filled f-shell in the Eu^{+2} ions.[5]

Electronic structure calculations,[5] Shubnikov-de Haas and de Haas-van Alphen measurements[6] 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 $n_{\text{eff}}\sim10^{-2}$ carriers per formula unit[7] at low temperatures. The carrier concentration decreases smoothly as temperature increases.

The electrical resistivity is metallic in the ferromagnetic regime. It shows a sharp peak near T_M. Above this temperature, the resistivity decreases until it reaches a minimum at about 30 K. 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.[2,7] This decrease in resistivity is accompanied by a large decrease in the (negative) Hall coefficient[7] and an increase in the plasma frequency.[8] 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 7 T.[6,7] The MR depends quadratically on the applied field strength at low temperatures.[9]

Just above T_M and up to ~30 K, the existence of magnetic polarons has been proposed as the cause of the Stokes' shift measured with spin flip Raman scattering (SFRS).[10] The resistivity decreases as temperature increases within the temperature range in which magnetic polarons exist. This is consistent with the existence of bound magnetic polarons, as they move via an activated process. However, the Stokes' shift energy is much smaller than expected from estimates of the exchange interaction, as we will show below.

Wigger *et al.*[9] 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. 9 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 emphasize 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.

MODEL AND PARAMETERS

We model EuB_6 as a ferromagnetic semimetal with 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:

$$H=-t\sum_{i,j,\sigma}c^{+}_{i\sigma}c_{j\sigma}-J\sum_{i,j}\vec{S}_i\vec{S}_j-J'_e\sum_i c^{+}_{i\sigma e}\vec{\tau}_{\sigma,\sigma'}c_{i\sigma e}\vec{S}_i-J'_h\sum_i c^{+}_{i\sigma h}\vec{\tau}_{\sigma,\sigma'}c_{i\sigma h}\vec{S}_i. \quad (1)$$

The hopping parameter is estimated to be $t=0.1$ eV.[5] $c^{+}_{i\sigma(e,h)}\tau_{\sigma,\sigma'}c_{i\sigma(e,h)}$ is the itinerant carrier spin operator and the subindices e and h stand for electrons and holes, respectively. J'_e (J'_h) is the on-site coupling between the spins of the electrons (holes) and the local moments. J is the magnetic exchange between local moments.

The origin of ferromagnetism in EuB_6 was discussed by Cooley *et al.*[11] They argued that the increase of magnetic critical temperature and concomitant decrease of resistivity

under high pressures implies that the magnetic exchange in EuB_6 is mainly due to the RKKY interaction. Therefore, J in Eq. (1) is negligible. This is in contrast to Eu-chalcogenides where superexchange coupling mediated by the anion is the dominating mechanism leading to magnetic order.[12,13]

The Ruderman–Kittel–(Kasuya)-Yosida (RKKY) magnetic exchange is mediated by the itinerant carriers via their coupling with the lattice magnetic moments. An effective Heisenberg-type magnetic exchange can be written in terms of the on-site exchange coupling J' (J'_e or J'_h)[14]

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

where $F(x)=(-x\cos x+\sin x)/x^4$, n is the density of carriers, and E_F is the Fermi energy. J_{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 $k_F r \to 0$.

To estimate the value of J' we use the mean field relation between T_C and J_{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 the value found in the literature,[20,21] assuming the carriers have d-character. Such an estimate presupposes that a single carrier species is responsible for the magnetism.

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 and in the paramagnetic phase of ferromagnets. A necessary condition for the existence of magnetic polarons is that the density of carriers is very low compared to the inverse of the magnetically correlated volume, namely $n\xi^3 \ll 1$. When this condition is fulfilled, polarons are well-defined nonoverlapping 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 ferromagnetic exchange 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.[15,16]

The carrier thus traps itself by the magnetization it causes. Its size is determined by the kinetic energy increase of localizing the carrier balanced against the reduction of exchange energy by aligning the local moments. 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[17,18] to guarantee stability of the free magnetic polaron.

On the other hand, in bound magnetic polarons the main driving force trapping the carrier is 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 the on-site coupling is much smaller than the Coulomb interaction.

Mean field[17] and Monte Carlo[18] 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 $n\xi^3 \ll 1$ is not fulfilled and the polarons overlap. If a magnetic field is applied, the size of the polarons increases until eventually they overlap and produce a ferromagnetic transition.

Free and bound magnetic polarons may 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 ρ 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"[19] 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)[20,22,23] 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[24] and especially the magneto-optical experiment of spin flip Raman scattering.[16,25,26] The SFRS spectrum shows an inelastic peak (Stokes' shift) at low frecuencies due to the onsite coupling J'. The zero-field Stokes' shift for EuB_6 just above T_M ($T=18$ K) is $\Delta E \sim 12$ meV.[10] Thermodynamic fluctuations at larger temperatures destroy the peak that reemerges and shifts its energy as a magnetic field is applied. This corresponds to an increase of the magnetization inside the polarons $\langle S_z \rangle$ that follows a Brillouin function. Saturation of this shift—corresponding to saturation of the polaron's magnetization—is achieved for lower fields than the one required to saturate the bulk magnetization.

Free magnetic polarons are not expected to be stable in EuB_6 as J' and t are comparable. Moreover, we have argued above that the negative temperature-coefficient of the resistivity is better explained by means of bound magnetic polarons.

We expect the energy of the Stokes' shift to be given by the spin-flip energy[25,27]

$$\Delta E = J' \langle S_z \rangle, \tag{3}$$

where $\langle S_z \rangle = 7/2$ when the magnetic polarons are fully polarized. Note that the spin-flip energy does not depend on the size of the polarons, but only on their magnetic moment. The magnetic polarons close to T_M are fully polarized so Eq. (3) gives $J' \sim 3$ meV. This is far too low compared to the values reported in the literature $J' \sim 100$ meV[20] and estimated above.

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 polarized 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'_e and J'_h, respectively, can be very different. Electronic structure calculations[5] 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. 5 shows a much larger majority-minority spin band splitting for electrons than for holes.

This leads us to propose that the ferromagnetic ordering is produced by the itinerant electrons coupled to the localized spin in Eu with $J'_e \sim 100$ meV, while the holes, much more weakly coupled ($J'_h \sim 5$ 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 corresponds to spin-flip of the electron state.

It remains to show that our picture of SFRS is consistent with magnetotransport data below and above T_c.

POSITIVE MAGNETORESISTANCE AT $T < T_c$

In the ferromagnetic state polarons evaporate and the contribution of spin fluctuation scattering to the resistance is small. Here the MR is due to the presence of two types of carriers and we will call it "orbital" MR. The physical mechanism involved is the same as in the Hall effect but, as there are two types of carriers with different masses and scattering times, there is not a unique Hall voltage. In other words, different carriers are deflected differently in an applied field, so there is no voltage at which both components of the current are kept going in the same direction. Therefore, we expect the resistance to increase with the applied magnetic field—positive MR. This MR has been calculated[9,28,29] to be

$$\frac{\Delta\rho(H)}{\rho_0} = \frac{\sigma_e\sigma_h(\mu_e - \mu_h)^2H^2}{(\sigma_e + \sigma_h)^2 + H^2(\mu_e\sigma_e + \mu_h\sigma_h)^2}, \qquad (4)$$

where σ_e and σ_h are the electron and hole conductivity, respectively, and μ_e and μ_h are their mobilities, both in the absence of any magnetic field. The MR vanishes if both types of carriers have the same mass and scattering time. This effect is largest at low temperatures, when scattering times are largest.

An applied magnetic field can also cause shifting of the bands due to the coupling of the carriers to the Eu local moments J'. The electron and hole bands overlap leading to an increase in the number of carriers as they spill over from one band into the other. Therefore, this effect leads to negative MR. At low temperatures, this effect is very small as the magnetization is almost saturated.

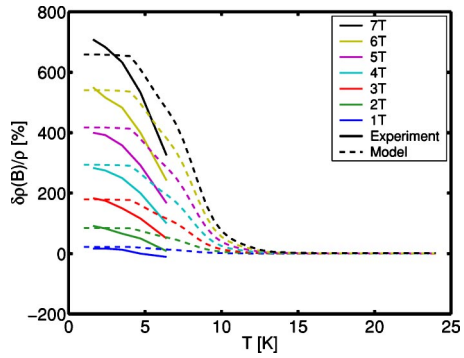

FIG. 1. (Color online) Orbital MR at low temperatures for different applied magnetic fields. The data is taken from Ref. 7. The plateau seen in the model below 5 K is an artifact of data digitization.

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 and the carrier densities are obtained from Ref. 7. The electron and hole mobilities are obtained from the conductivity at zero field, the masses of the carriers[6] and the carrier densities. We introduced a small imbalance between the carrier densities of $6.10^{-4}q_e$ per unit cell, in accordance with Ref. 6. This imbalance is thought to arise from impurities.

Our simple model, which depends only on parameters measured at zero field, reproduces the large positive MR at low temperatures and its (nearly) quadratic dependence in applied field. Near the magnetic transition and in the paramagnetic phase other effects dominate.

NEGATIVE MR AT $T \approx T_c$ AND ABOVE

Close to T_c 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 can explain only part of the negative MR in the critical regime.

Additionally, near the critical point, spin fluctuations are expected to provide a large contribution to the electrical resistance when the carrier density is small.[17,30] The suppression of the spin fluctuations when a magnetic field is applied would produce a large MR in the critical regime. Moreover, as shown in Ref. 17 (see Fig. 3), the localization of the carriers in magnetic polarons further increases the MR. In the temperature regime—just above T_c—where the SFRS data gives evidence for bound magnetic polarons, the MR is large, and strongly negative, as expected since an applied magnetic field suppressed the magnetic polarons. At temperatures greater than about 30 K where the polarons are destabilized, we have a smaller (but still negative) MR dominated by local spin fluctuation scattering.

As mentioned above, the negative MR is accompanied by a shift in the plasma frequency.[8] We find that the carrier density change produced by the band shifting alone is too small to account for the change in plasma frequency. In contrast Wigger *et al.*[9] get the right magnitude for this effect, essentially because they include the emptying of trap states by magnetic field, an effect absent entirely in our simple model.

SUMMARY

EuB_6 is a low carrier density ferromagnet with unusual properties: The temperature coefficient of resistance changes from positive (metallic) below T_c to negative just above, and then to positive again at higher temperature. The MR changes sign close to T_c but is always large. The regime of activated (though not Arrhenius) transport 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 Ref. 10. We conclude that the signature seen by those experiments is due to the on-site coupling of holes with 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* MR above T_c. The *positive* MR in the ferromagnetic phase is also produced by an interplay of two kinds of carriers with different masses and scattering times.

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