# Spectroscopic study of bound magnetic polaron formation and the metal-semiconductor transition in $EuB_6$

P. Nyhus, S. Yoon, M. Kauffman, and S. L. Cooper
*Department of Physics and Frederick Seitz Materials Research Laboratory, University of Illinois, Urbana-Champaign, Urbana, Illinois 61801*

Z. Fisk and J. Sarrao
*Department of Physics and National High Magnetic Field Laboratory, Florida State University, Tallahassee, Florida 32306*
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We present a Raman-scattering study of the metal-semiconductor transition in $EuB_6$. The metal-semiconductor (MS) transition in this compound manifests itself as a change from a diffusive electronic scattering response in the high-temperature paramagnetic phase, to a flat continuum scattering response in the low-temperature ferromagnetic metal phase which is characteristic of a strongly correlated metal. Most interesting is evidence that the MS transition in $EuB_6$ is precipitated by the formation of bound magnetic polarons involving carriers bound to defects. [S0163-1829(97)02930-5]

Recently there has been a resurgence of interest in ''colossal magnetoresistance'' behavior exhibited by magnetic semiconductors such as $La_{1-x}(Ca,Sr,Ba)_xMnO_3$ (Ref. 1) and Eu-based compounds EuO (Ref. 2) and $EuB_6$ (Refs. 3,4). A number of remarkable features are exhibited by these materials. At high temperatures, they are paramagnetic (PM) semiconductors with activation energies of $E_A \sim 0.1$ eV in $EuB_6$ (Ref. 3), $E_A \sim 0.3$ eV in EuO (Ref. 2), and $E_A \sim 0.1$ eV in $La_{1-x}(Ca,Sr,Ba)_xMnO_3$ (Ref. 1), while at low temperatures they develop short-range magnetic correlations before becoming ferromagnetic metals at $T_c \sim 12$ K in $EuB_6$, $T_c \sim 69$ K in EuO, and $T_c \sim 200-350$ K in $La_{1-x}(Ca,Sr,Ba)_xMnO_3$. Unfortunately, many details regarding the phase diagram of these magnetic semiconductors remain unresolved, including the nature of the short-range magnetic correlations near the Curie temperature, and the specific mechanism(s) causing the metal-semiconductor (MS) transition. For example, it is generally believed that the diverse properties exhibited by the Eu-based magnetic semiconductors derive primarily from the interaction between the itinerant $d$ electrons and the $Eu^{2+}$ $4f$ local moments, which leads to a complex interplay between the direct $d$-$f$ exchange interaction [$J_{df} \sim 0.1$ eV (Refs. 2,5)] and the direct $f$-$f$ exchange coupling between the moments. However, the nature of the MS transition in these materials is controversial, and has been variously attributed to (i) a trap level that crosses the conduction band,[6] (ii) exchange-induced splitting of an impurity level in a He-like model,[7] and (iii) an exchange-induced Mott transition involving the development of ferromagnetic spin clusters (magnetic polarons).[2,5,8] Uncertainty regarding the MS transition in the magnetic oxides is even more profound, in part due to the complex structural phases present in these materials.

In this paper we present temperature- and magnetic-field-dependent Raman-scattering measurements of $EuB_6$ with which we have been able to study the different regimes of behavior in this system, and in particular, those regimes just above and below the Curie temperature $T_c$. Our aim in this study is not only to clarify the nature of the MS transition in $EuB_6$, but also to use this structurally simple material to study ''colossal magnetoresistance'' behavior absent the diverse structural phases that complicate analysis of the magnetic oxides. Among other results, our data provide direct spectroscopic evidence that the metal-semiconductor transition in $EuB_6$ is precipitated by the formation of bound magnetic polarons, i.e., ferromagnetic clusters of $Eu^{2+}$ ions within the Bohr orbits of defect-bound carriers. This observation provides insight into the origin of the MS transition in $EuB_6$, and perhaps affords clues as to the nature of ''colossal magnetoresistance'' in higher $T_c$ magnetic semiconductors such as EuO and $La_{1-x}(Ca,Sr,Ba)_xMnO_3$.

Raman-scattering measurements were performed on the (100) surfaces of cubic ($O_h^1$-$Pm3m$), single-crystalline $EuB_6$ prepared from an aluminum flux. Some zero-field measurements were performed using a Spex Triplemate spectrometer equipped with a nitrogen-cooled charge-coupled device (CCD) array detector. The magnetic-field measurements were performed in a true backscattering geometry using a modified subtractive triple spectrometer with a Photometrics liquid nitrogen-cooled CCD, while the sample was cooled to temperatures as low as 1.5 K in a pumped Oxford flow cryostat which was mounted in the bore of an Oxford superconducting magnet. Spectra were obtained with the incident and scattered light polarized in the following configurations in order to identify the symmetries of the excitations studied: $(\mathbf{E}_i,\mathbf{E}_s)=(\mathbf{x},\mathbf{x}):A_{1g}+E_g$; $(\mathbf{E}_i,\mathbf{E}_s)=(\mathbf{x},\mathbf{y}):T_{2g}+T_{1g}$; $(\mathbf{E}_i,\mathbf{E}_s)=(\mathbf{x}+\mathbf{y},\mathbf{x}+\mathbf{y}):A_{1g}+\frac{1}{4}E_g+T_{2g}$; $(\mathbf{E}_i,\mathbf{E}_s)=(\mathbf{x}+\mathbf{y},\mathbf{x}-\mathbf{y}):\frac{3}{4}E_g+T_{1g}$; where $\mathbf{E}_i$ and $\mathbf{E}_s$ are the incident and scattered electric-field polarizations, respectively, $\mathbf{x}$ and $\mathbf{y}$ are the [100] and [010] crystal directions, respectively, and where $A_{1g}(\Gamma_1^+)$, $E_g(\Gamma_3^+)$, and $T_{2g}/T_{1g}$ $(\Gamma_5^+/\Gamma_4^+)$ are the singly, doubly, and triply degenerate irreducible representations of the $EuB_6$ space group ($O_h^1$-$Pm3m$), respectively. The magnetic-field spectra were obtained in (LCP,LCP) and

 

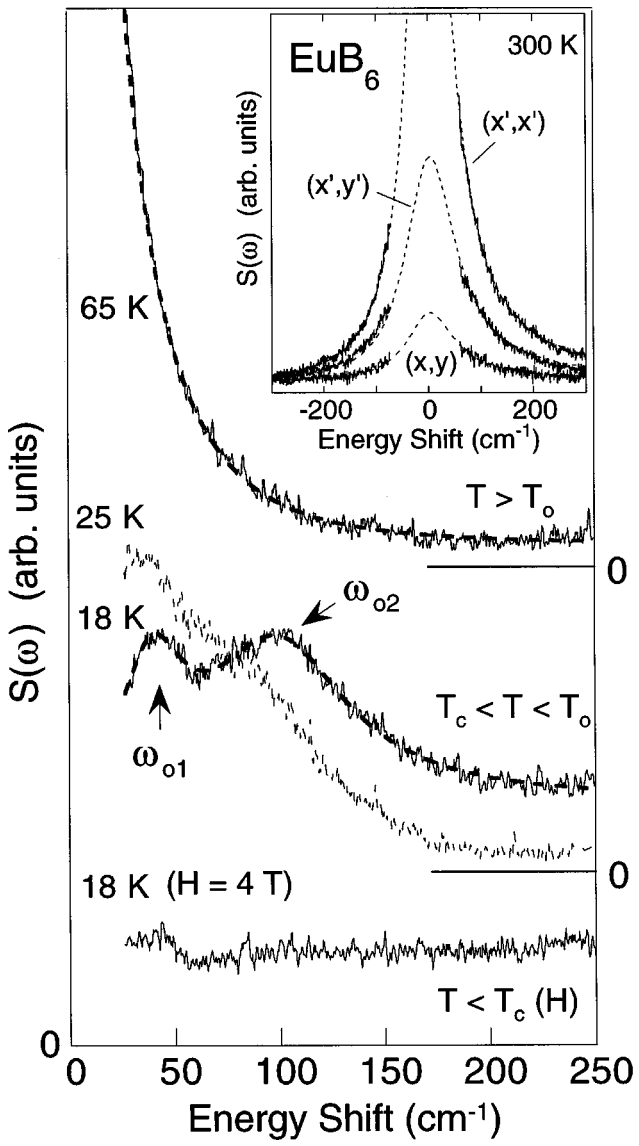


FIG. 1. Raman spectra of $EuB_6$ in the (RCP,RCP) polarization geometry for various temperature regimes, showing: (top) a diffusive response [Eq. (1)] in the high-temperature, paramagnetic (PM) regime, (middle) two inelastic peaks, $\omega_{01}$ and $\omega_{02}$, in the intermediate temperature, short-range magnetic order (SRMO) regime, and (bottom) a flat continuum response in the low-temperature, ferromagnetic (FM) regime. The dashed line in the top spectrum is a fit to a simple relaxational response function [Eq. (1)], while the dashed line in the middle spectrum is a fit to two simple Lorentzians. Inset: Polarization dependence of the room-temperature diffusional scattering response.

(LCP,RCP) geometries, where RCP and LCP are right and left circularly polarized, respectively.

Figure 1 illustrates the low-frequency ($0<\omega<250\ \mathrm{cm}^{-1}$) Raman-scattering spectrum of $EuB_6$ as a function of temperature and symmetry (inset). The high-temperature scattering response ($T>60$ K) associated with the paramagnetic semiconductor phase (top spectrum and inset of Fig. 1) is typical of that observed for single-particle excitations in degenerate or doped semiconductors (e.g., $n$-type Si),[9] and is well described by a simple relaxational scattering response (top dashed line),

$$S(\omega)=[1-\exp(-\hbar\omega/k_BT)]^{-1}\frac{A\omega\Gamma}{\omega^2+\Gamma^2}, \qquad (1)$$

where $[1-\exp(-\hbar\omega/k_BT)]^{-1}=[1+n(\omega)]$ is the Bose-Einstein thermal factor, and $\Gamma$ is the carrier scattering rate. The strong, polarization-dependent scattering response in the PM phase of $EuB_6$ (inset of Fig. 1) can be best appreciated by first noting that the scattering intensity of single-particle excitations is expected to be unobservably small in metals and degenerate semiconductors with spherical Fermi surfaces, since in such systems the associated density fluctuations are screened by the long-range Coulomb interaction. On the other hand, systems with anisotropic Fermi surfaces exhibit neutral charge density fluctuations which are not screened by the Coulomb interaction; consequently, scattering from such fluctuations can be substantial. The electronic Raman-scattering intensities associated with neutral charge density fluctuations are given by,[9]

$$I\propto\left\langle\left[\mathbf{e}_S\cdot\left(\frac{1}{\mathbf{m}^*}-\left\langle\frac{1}{\mathbf{m}^*}\right\rangle\right)\cdot\mathbf{e}_I\right]^2\right\rangle,$$

where $\mathbf{e}_S$ and $\mathbf{e}_I$ are the polarization vectors of the scattered and incident electric fields, respectively, and $\mathbf{m}^*$ is the effective-mass tensor. In the case of cubic $EuB_6$, the neutral charge-density fluctuation model, applied to a simple tight-binding description that incorporates only the transfer integrals of Eu $d$ orbitals between nearest-neighbor sites, predicts the strongest scattering intensity in the $E_g$ geometry, a small scattering intensity in the $A_{1g}$ geometry, and zero intensity in the $T_{2g}$ geometry. By contrast, the observed diffusive electronic scattering in the PM phase of $EuB_6$ has comparable $E_g$ and $A_{1g}$ scattering intensities and a small $T_{2g}$ intensity. We believe this symmetry dependence reflects the substantial hybridization present between the $Eu^{2+}$ $5d$ and the $sp$ bands from the boron octahedra;[10] a more detailed discussion of this is beyond the scope of this paper and will be presented in a future publication. Figure 2 shows that the scattering rate $\Gamma$ associated with the simple-relaxational scattering response decreases precipitously with temperature in the high-temperature PM phase, but levels off, and then rises again, upon entering the short-range magnetic order (SRMO) regime. Additionally, Fig. 3 shows that the simple-relaxational scattering response exhibits a slight magnetic-field dependence near $T_0$, presumably reflecting the development of a small field-dependent scattering rate [Eq. (1)] due to the increasing importance of spin scattering at these temperatures.

The transition to the ferromagnetic metal (FM) regime in $EuB_6$ is rather dramatically revealed in the Raman-scattering spectra of Figs. 1 and 3 with the development of a flat electronic Raman continuum below $T_c(H)$ (bottom spectra). Unlike the PM and SRMO regimes, this flat continuum is totally field independent, consistent with the complete saturation of the spins in the FM regime. Interestingly, the flat spectral response in the FM phase of $EuB_6$ is typical of spectra observed in a number of strongly correlated metals, including the high-$T_c$ cuprates and the doped titanates such as $La_{1-x}Sr_xTiO_3$.[11] While the microscopic origin of this response in strongly correlated metals is still the subject of debate, it is generally believed to reflect the presence of a

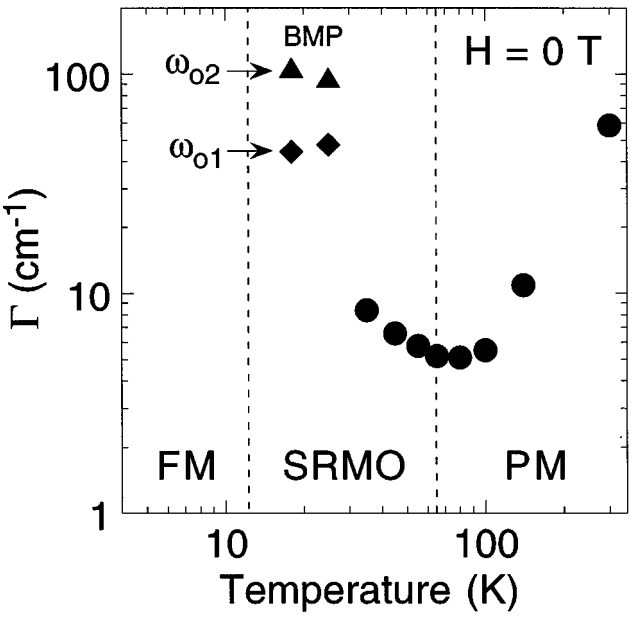


FIG. 2. (filled circles) Carrier scattering rate, $\Gamma$, as a function of temperature (zero field) deduced from fits of Eq. (1) to the $E_g$ symmetry diffusional response in the PM and SRMO regimes. Also plotted is the zero-field temperature dependence of the inelastic peaks, $\omega_{01}$ (filled diamonds) and $\omega_{02}$ (filled triangles), observed just above $T_c$.

strongly correlated metallic phase which is dominated by inelastic scattering from some spectrum of excitations. Indeed, the flat continua observed in strongly correlated metals are commonly described phenomenologically using the simple relaxational form in Eq. (1) with a frequency- and temperature-dependent scattering rate.[11] Therefore, while specific details concerning the ferromagnetic metal state are difficult to extract from the featureless continuum in $EuB_6$, these Raman data suggest that the metal-insulator transition in this compound is associated with a crossover from a high-temperature regime characterized by diffusive scattering of the carriers, to a strongly correlated metal regime in which inelastic (spin) scattering of the carriers predominates.

Perhaps the most interesting behavior is exhibited in the SRMO regime of $EuB_6$, which is characterized in the Raman spectra by (i) an increase in the diffusive scattering rate with decreasing temperature (see Fig. 2), and (ii) by the development just above $T_c(H)$ of two inelastic peaks which appear exclusively in the $\mathbf{E}_i \perp \mathbf{E}_s$ scattering geometry ($T_1$ symmetry): (a) a field-independent peak at $\omega_{01}$ which persists to some extent even into the FM phase, and (b) a strongly field-dependent peak at $\omega_{02}$ (middle spectra, Figs. 1 and 3) which disappears completely in the FM phase. Based upon their symmetry, temperature, and field dependences, we can identify these excitations as spin-flip processes arising from the development of bound magnetic polarons, i.e., spin-polarized clusters of $Eu^{2+}$ ions formed within the Bohr orbits of carriers bound to local ''defects.'' In particular, the strongly field-dependent peak at $\omega_{02}$ is consistent with spin-flip transitions of the bound carriers, while the peak at $\omega_{01}$ can be attributed to spin-flip transitions between adjacent levels of the $Eu^{2+}$ ground-state Zeeman multiplet.[12] Importantly, the large energy and field dependence of the spin-flip Raman-scattering (SFRS) peak at $\omega_{02}$ reflects the substantial ferro-

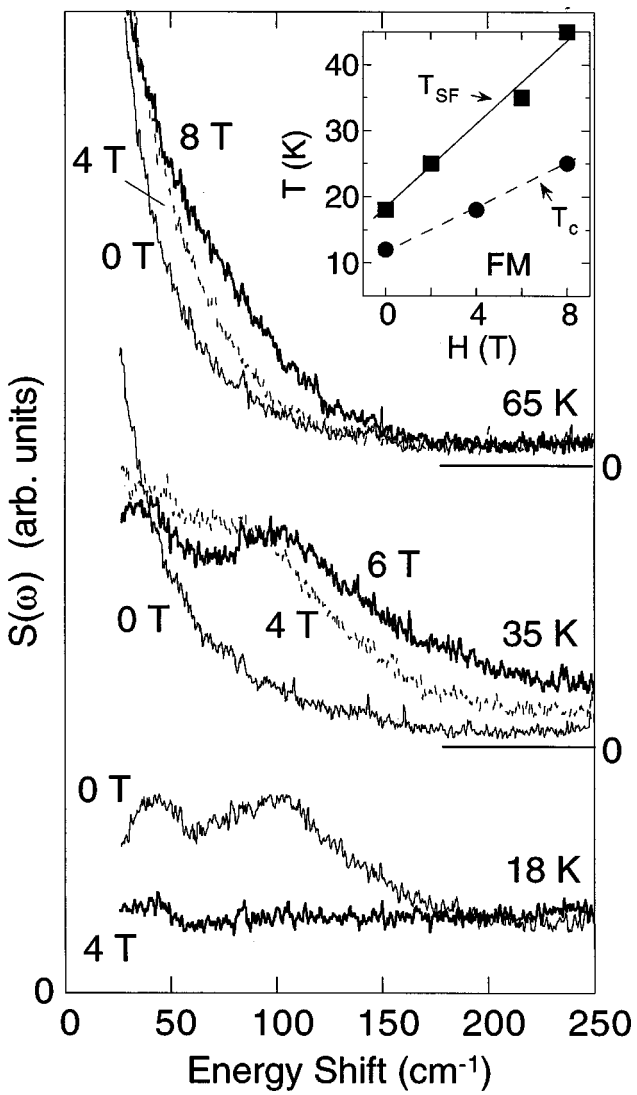


FIG. 3. Field dependences of the Raman spectra in the (top) PM regime, (middle) SRMO regime, and (bottom) across the FM transition. Inset: The field dependences of the temperature $T_{SF}$ at which the spin-flip Raman-scattering peaks at $\omega_{01}$ and $\omega_{02}$ are observed, and of the Curie temperature $T_c$ at which the flat continuum response is observed.

magnetic exchange interaction $J_{df}$ between the bound carriers and the $Eu^{2+}$ spins in $EuB_6$.

The field dependence of the Raman spectra provide the most compelling evidence that the inelastic peaks which appear just above $T_c$ are associated with SFRS due to the formation of magnetic polarons. In the presence of strong $d$-$f$ exchange, the energy shift associated with SFRS from the bound carriers is expected to be dominated by the $Eu^{2+}$ magnetization according to[12,13]

$$\hbar\omega_0 = \overline{x}\alpha N_0 \langle S_z \rangle, \tag{2}$$

where $\overline{x}$ is the concentration of ''defects'' contributing to the magnetization, $\alpha N_0$ is the exchange constant, $\langle S_z \rangle = (7/2)B_{7/2}[g m_B H/k_B(T-T_c)]$ is the thermal average of the $Eu^{2+}$ spin, and $B_{7/2}$ is the Brillouin function $B_J$ for $J=7/2$. Equation (2) ignores the Zeeman contribution to the spin-flip energy, since the exchange field associated with the $Eu^{2+}$

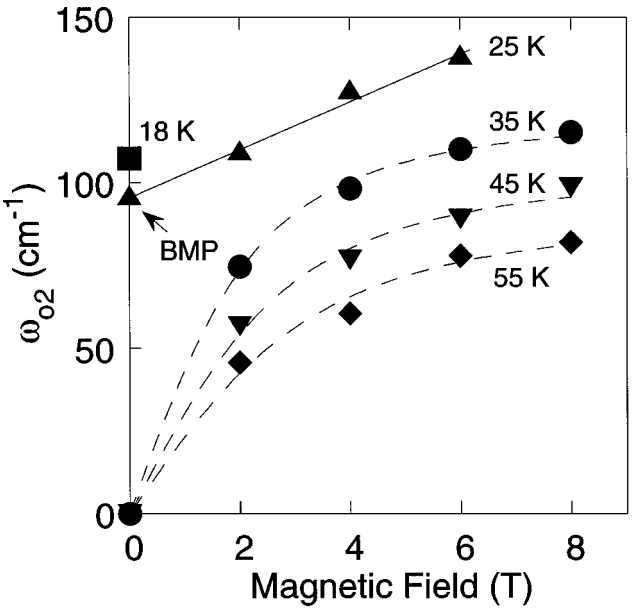


FIG. 4. Field dependence of the spin-flip Raman-scattering energy of the bound carrier $\omega_{02}$ at various temperatures. The dashed lines for $T \geqslant 35$ K are fits to Eq. (2), illustrating the functional dependence of a Brillouin function $B_J$ for $J=7/2$. The solid line for $T=25$ K is a linear fit. Note the finite zero-field splitting for 18 and 25 K, revealing the presence of bound magnetic polarons at these temperatures.

ions is substantially larger than the applied field ($H_{\text{exch}} > 50$ T) in $EuB_6$. Figure 4 clearly shows that the field dependence of the SFRS peak at $\omega_{02}$ follows a Brillouinlike functional form $B_{7/2}$ for $T > 25$ K (dashed lines), confirming that the SFRS energy associated with the bound carriers is governed by the $Eu^{2+}$ magnetization. Assuming that $\omega_{02}$ is associated with a single spin flip, $\Delta m_S = 1$, fits of the 35 K data in Fig. 3 (dashed lines) give very reasonable values of $g_{\text{eff}} \sim 10$ and $\overline{x}\alpha N_0 = 3.65$ meV. The latter corresponds to an exchange constant of $\alpha N_0 \sim 0.1$ eV for defect concentrations of $x \sim 3\%$. Significantly, the nature of the defects which help stabilize the BMP state by binding the carriers is uncertain. However, two possibilities are worth noting: (i) $Eu^{2+}$ vacancies, which may exist in concentrations as high as 10% in $EuB_6$ (see Refs. 4 and 7); (ii) ''dynamical defects'' such as local polaronic distortions. Two additional features of the fits to the data in Fig. 4 are also worth noting. First, the effective $g$ factor deduced from these data is quite large, reflecting the enhanced field-dependent splitting of the carrier spin states due to the magnetization of the $Eu^{2+}$ ions. Second, Fig. 4 shows that the size of the splitting at high fields ($\sim \langle S_z \rangle$) increases with decreasing temperature, suggesting that the average size of the magnetic clusters (polarons) increases as $T$ approaches $T_c$. This is consistent with theoretical calculations of magnetic polaron formation in magnetic semiconductors.[14,15]

Most significantly, Figs. 2–4 illustrate that *zero-field* SFRS excitations at $\omega_{01}$ and $\omega_{02}$ develop just above the MS transition [$T_c(H=0) < T \leqslant 25$ K] in $EuB_6$, revealing the spontaneous formation of bound magnetic polarons. Bound magnetic polarons are energetically favored at sufficiently low temperatures in magnetic semiconductors because the impurity-bound carriers gain magnetic exchange energy ($J_{df}S \sim 0.35$ eV in $EuB_6$ and EuO) by spontaneously aligning their spins parallel to the spins within their Bohr radii.[2,6,13] Indeed, the linear field dependence of $\omega_{02}$ at 25 K indicates that the net magnetization of $Eu^{2+}$ spins within the bound carrier's Bohr radius is already fully saturated at $H=0$, and that the average size of the polarons increases with increasing magnetic field, in agreement with theoretical predictions.[14,15]

These results provide direct spectroscopic evidence for magnetic polaron formation at the MS transition of a magnetic semiconductor, corroborating a possibility which has been suggested previously for several ''colossal magnetoresistance'' compounds including $EuB_6$ and EuO.[2,6] Indeed, our results strongly favor interpreting the MS transition in $EuB_6$ as an ''exchange-induced Mott transition'' similar to that described previously for EuO.[2,8] In this description, carriers become bound by the defect potential of the $Eu^{2+}$ vacancies, or some other defect, at temperatures below $T_0$, nucleating small ferromagnetic clusters of $Eu^{2+}$ spins via the strong (ferromagnetic) $d$-$f$ exchange interaction between the bound carriers and the defects. The formation of these ferromagnetic clusters results in a spin splitting of the valence and conduction bands, and a concomitant large increase in the carrier density which induces a Mott-type transition at $T_c(H)$. Notably, zero-field Hall effect measurements of $EuB_6$ confirm that there is a fivefold increase in the carrier density between 77 and 4.2 K.[3,5] Furthermore, in this description, transport in the SRMO regime involves activated hopping of bound carriers between polaron sites, and the dramatic increase in conductivity with increasing field near $T_c$ reflects the increased size, and consequent increased overlap, of the polarons with field. Our observation that $T_c(H)$ in $EuB_6$ increases roughly linearly with field (inset, Fig. 3) supports this interpretation.

To summarize, we find that the MS transition in $EuB_6$ is characterized by a transition from a diffusive regime at high temperatures to a frequency-dependent scattering regime below $T_c$ which is likely associated with strong inelastic spin scattering of the carriers. Most importantly, we observe strong evidence that the ferromagnetic transition in $EuB_6$ is precipitated by the formation of bound magnetic polarons arising from the mutual ferromagnetic alignment of bound carries and $Eu^{2+}$ spins within their orbits. These results provide additional impetus to search for similar evidence for magnetic polarons near the MS transition of magnetic semiconductors such as EuO and $La_{1-x}(Ca,Sr,Ba)_xMnO_3$.

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