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Charge transport and pressure dependence of Tc of single crystal, ferromagnetic EuB6

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We present Hall Effect and resistivity data which demonstrate that EuB$_6$ is a degenerate semiconductor transforming into a metal or semimetal below the ferromagnetic ordering temperature, $T_c = 13.7$ K. We also report an anomalously large, positive pressure dependence of $T_c$, $(1/T_c)(dT_c/dP) = 4 \times 10^{-2}$ kbar$^{-1}$. EuB$_6$ is a cubic material having B$_6$ octahedra at the corners of a simple cubic lattice and Eu at the body center. It orders ferromagnetically with a transition temperature sensitive to sample purity and stoichiometry. Early band structure calculations predicted that pure EuB$_6$ is a semiconductor, whereas more recent calculations show that, at least in the ordered state, EuB$_6$ is expected to be a semimetal. Experimental support for both points of view have been given. A decrease in resistivity above room temperature argues for a small semiconductor energy gap of $\sim 0.1$ eV, whereas the metallic conductivity below 200 K, which has been observed in all samples regardless of preparation, favors a semimetal rather than a degenerate semiconductor description.

In this letter we present Hall effect and resistivity data which demonstrate that EuB$_6$ is a degenerate semiconductor transforming into a metal or semimetal below the ferromagnetic ordering temperature ($T_c = 13.7$ K). Where comparisons are possible, our experimental results on Al flux grown single crystals are in good agreement with polycrystalline data by Ishikawa which have recently been summarized by Kasuya, et al. We also report a very large, positive pressure dependence of the magnetic ordering temperature.

All transport measurements were performed in the Van der Pauw geometry on single crystals of the same batch described in ref. 4. Although microprobe analysis disclosed the presence of Al in the crystals, these spots were well separated by areas of stoichiometric EuB$_6$ (Eu = 70 ± 2 wt.%). Various samples from the batch showed similar transport properties as a function of temperature, indicating that no complete Al paths exist through the sample. The temperature dependence of the resistivity in 0 and 15 kOe applied magnetic field is shown in Fig. 1. In this letter we concentrate only on two features of the data: a) The magnetoresistance is large and negative, even for $T >> T_c$ (13.7 K); b) The resistance ratio $\rho_{300}$ K/$\rho_{4.2}$ K = 61.6/1.45 = 42.5. Other features, such as the peak in resistivity near $T_c$ and the saturation near 300 K depend on details of the scattering mechanisms. Here we simply wish to determine whether the resistivity variation is in part due to changes in carrier number.

![Fig. 1: Resistivity of single crystal EuB$_6$ at $H_A=0$ and 15 kOe as a function of temperature.](image-url)
Ordinarily the Hall effect in magnetic materials is complicated by a large anomalous term, $R_s$, as can be seen from the following equation for the Hall resistivity, $\rho_H$:

$$\rho_H = R_o B + R_s 4\pi M.$$  \hspace{1cm} (1)

Here $R_o$ is the normal Hall coefficient related to the number of carriers, $B$ is the magnetic induction and $M$ is the magnetization of the sample. We have consequently plotted in Fig. 2 $\rho_H$ as a function of $B$ at 4.2 K, and find an almost linear relationship between $\rho_H$ and $B$. Such deviations as do exist can be explained by a small contribution from $R_s$ or a 10% decrease in $R_o$ with increasing $B$. 

In the paramagnetic region Eq. 1 may be written as

$$\frac{\rho_H}{H_A} = R_o + [(1-N)R_o + R_s]4\pi x^\ast.$$  \hspace{1cm} (2)

where $H_A$ is the applied field, $N = 0.633$ is the demagnetizing factor, and $x^\ast = x/(1+4\pi N x)$ the measured susceptibility. Fig. 3 displays $\rho_H/H_A$ as a function of $x^\ast$. The high temperature, ($small x^\ast$) region appears linear. However, the slope and the intercept extrapolated to $x^\ast = 0$ do not yield a consistent value for $R_o$ for any reasonable $R_s$. We are, therefore, forced to conclude that $R_o$ is changing throughout the temperature range shown in Fig. 3. In particular, if a one band model is assumed, we may interpret the curve as follows: Between 297 and ~150 K, electrons excited across an intrinsic semiconductor gap are gradually frozen out. The plateau between ~150 and ~100 K represents the exhaustion range with $n = 10^{-8} + (1\rho_H/H_A x) = 3.5\times10^{15}$ cm$^{-3}$ due to defects and impurities. Here the calculated mobilities are inordinately high at ~300 cm$^2$/v sec. The subsequent decrease in $|\rho_H/H_A|$ as the temperature is lowered further signals the onset of an electronic phase transition. It should also be mentioned that, below 70 K, $\rho_H$ is not linear in applied magnetic field, $H_A$, which might be interpreted as a field dependence of the carrier number. The major result of the Hall measurements, however, is that the EuB$_6$ is not a simple degenerate semiconductor. If that were the case, no change in $R_o$ would be expected at low temperature, whereas a factor 5 decrease is observed between 110 K and 4.2 K. We conclude, therefore, that EuB$_6$ has a magnetically driven phase transition to a low temperature semimetal or metal with a sizeable change in carrier number.

Sofar we have discussed the effect of magnetic order on the electronic structure and transport properties of EuB$_6$. The inverse effect, i.e. the variation of magnetic order with changes in carrier concentration is another natural consequence of the strong coupling between band electrons and localized Eu$^{2+}$ 4f spins. Large depressions in $T_c$ with increasing carrier concentrations and decreasing lattice constant have already been reported in EuB$_{6-x}$C$_x$[1-3]. In contrast, recent resistivity measurements as a function of pressure and temperature suggest an increase in $T_c$ with increasing carrier concentration and decreasing lattice constant[13]. Here we present data on
the pressure dependence of $T_c$ as measured with a low field SQUID magnetometer\[[14]\]. The results are summarized in Fig. 4, the insert giving an operational definition of $T_c$. There is a large positive shift in $T_c$, with \(\frac{1}{T_c} \frac{0T_c}{0P} \approx 4 \times 10^{-2} \text{ kbar}^{-1}\), roughly twice the value derived from the pressure dependence of the resistivity peak\[[13]\]. Pressure was measured by monitoring the change in superconducting transition temperature of Pb. For most of the runs the error in estimating pressure was \pm 0.5 kbar with two notable exceptions.

It is tempting to compare these results with the well known indirect exchange effects in the Eu chalcogenides. The exchange constant between neighboring Eu\(^{2+}\) ions can be written as

\[ J = 2t^2 \frac{J_{cf}}{S_f U^2}, \]

where $t$ is the transfer matrix element between the Eu 4f orbitals and the 5d orbitals on adjacent sites, $J_{cf}$ is an intra-atomic exchange constant, $S_f = 7/2$ for Eu\(^{2+}\) and $U$ is the energy difference between the 4f and d orbitals\[[15]\]. If it is assumed that nearest neighbor exchange dominates, $T_c$ is proportional to $J$, and \(\frac{0T_c}{0P}\) may be derived as follows:

\[ \frac{0T_c}{0P} = \frac{0J}{0P} \frac{0J}{0a} \frac{0a}{0P} = \frac{0J}{0a} \frac{0a}{0P} K \]

where $a_o$ is the lattice constant at STP and $K$ is the compressibility. But $t^2 = \exp(-8a/a_0)\[[15]\]$ and, as a first approximation, $U$ may be expressed as

\[ U = E_o - Ca^{-1}, \]

where $E_o$ is the energy difference between the 4f and d orbitals without crystal field effects and the second term represents the crystal field splitting of the rare earth d states. Therefore, combining Eqs. 3, 4 and 5, one obtains

\[ \frac{1}{T_c} \frac{0T_c}{0P} = \frac{K}{3} \left[ 8 + 2\zeta \left( \frac{E_o}{U} - 1 \right) \right]. \]

For EuO, \(\frac{1}{T_c} \frac{0T_c}{0P} = 5 \times 10^{-3} \text{kbar}^{-1}\)[16], $K_{RT} = 0.94 \times 10^{-3} \text{kbar}^{-1}\)[17] and $E_o/U = 2.66\[[18]\]$. Eq. 6 gives $\zeta = 2.4$, in reasonable agreement with 3.5, the value derived from a comparison of optical properties in the rare-earth chalcogenide series\[[19]\]. Neither number is close to the predictions of a point charge model, $\zeta = 5$.

Performing the same calculation for EuB\(_6\), with \(\frac{1}{T_c} \frac{0T_c}{0P} = 4 \times 10^{-2} \text{kbar}^{-1}\)[20], $K_{RT} = 0.83 \times 10^{-3} \text{kbar}^{-1}\)[21] and $E_o/U \approx 1.7\[[22]\] one obtains $\zeta \geq 45$, an utterly unreasonable result. The calculation is obviously a very rough approximation and serves only to demonstrate that the model for exchange valid in the insulating Eu chalcogenides is inadequate to explain the very large fractional shift of $T_c$ with pressure in EuB\(_6\). A more complex model, possibly involving local polarization as well as conduction band effects, is necessary.

Both the transport and pressure measurements lead to the conclusion that EuB\(_6\) cannot be described as a simple degenerate semiconductor. Furthermore, the unusually high mobilities (at 4.2K, $\mu \approx 2.4 \times 10^3 \text{cm}^2/\text{v sec}$) derived by assuming a one band model suggest that a semimetal involving several bands at $E_F$ is more appropriate at low temperatures. This conclusion is supported by the band structure calculations of Hasegawa and Yanase\[[7]\]. It also forms the basis of the description of the magnetic and transport properties by Kasuya, et al\[[9]\]. These authors, however, ignore the contribution of the valence band to the conduction process, thereby reducing the calculations to a one band model. It seems that this approach can only be justified if it can also explain the large mobilities in the presence of $3.5 \times 10^{19} \text{cm}^{-3}$ defects or impurities. Finally, the large positive logarithmic pressure derivative of the magnetic transition temperature, which contrasts sharply with the results of doping experiments\[[1]\], is not understood quantitatively. Similar experiments on EuB\(_6-x\)C\(_x\) are underway.

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References

[11] The suggestion in ref. 4 that these samples might contain 10% Eu vacancies is apparently incorrect.
[14] The magnetometer incorporates a SHE point contact SQUID. Pressure was produced in a clamp similar to that described by D. Wohlleben and B. Maple, Rev. Sci. Instrum. 42, 1573 (1971).
[21] $E_0$ and U are estimated from the known splitting in EuTe, ref.[18], (with Eu-Te $\approx$ 3.3Å compared to EuB$_6$ with Eu-B $\approx$ 3.6Å) and recent UPS and XPS measurements by Takakuwa, S. Suzuki, and T. Sagawa, Jap. J. Appl. Phys. 17, Suppl. 17-2, 284 (1978).