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CHARGE TRANSPORT AND PRESSURE DEPENDENCE OF T_c OF SINGLE CRYSTAL, FERROMAGNETIC EuB_6.

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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=13.7K. We also report an anomalously large, positive pressure dependence of T_c, $(1/T_c)(\Delta T_c/\Delta P) \simeq 4 \times 10^{-2}$ 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[1-5]. Early band structure calculation[6] 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[7]. Experimental support for both points of view have been given. A decrease in resistivity above room temperature[5] argues for a small semiconductor energy gap of ~0.1 eV, whereas the metallic conductivity below 200 K[1,3,4], 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[8] which have recently been summarized by Kasuya, et al.[9]. 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[10] 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.%)[11]. 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.

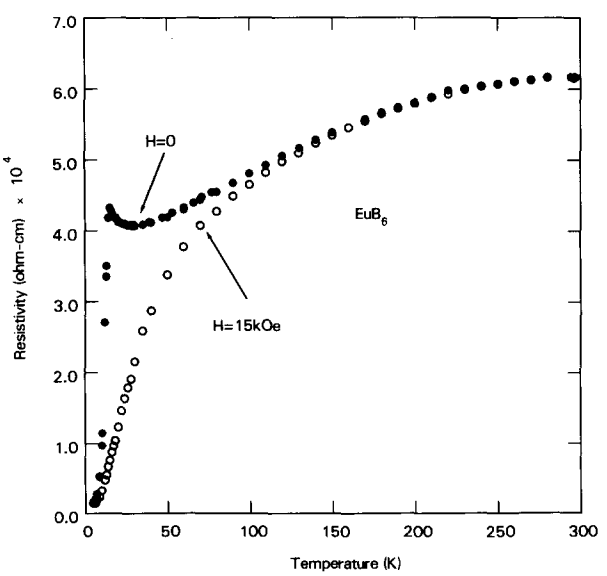

Fig. 1: Resistivity of single crystal EuB_6 at H_A=0 and 15 kOe as a function of temperature.

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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, e_H,

$$e_H = R_0 B + R_s 4\pi M. \quad (1)$$

Here R_0 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 e_H as a function of B at 4.2 K, and find

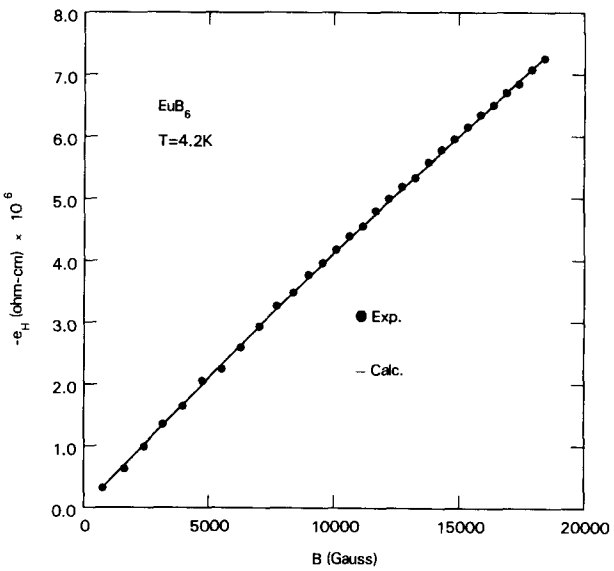

Fig. 2: The dependence of Hall resistivity, e_H, on magnetic induction, B, for EuB_6 at 4.2 K. The solid line is the calculated curve with $R_0 = -3.7 \times 10^{-10}$ Ω-cm/G and $R_S = -4.8 \times 10^{-11}$ Ω-cm/G.

an almost linear relationship between e_H and B. Such deviations as do exist can be explained by a small contribution from R_S[12]or a 10% decrease in R_0 with increasing B. A fit to the data, with $R_0 = -3.71 \times 10^{-10}$ Ω-cm/G and $R_S = -4.8 \times 10^{-11}$ Ω-cm/G, is also plotted in Fig. 2. On the assumption of a simple one band model, with $R_0 = 10^{-8}$/ne (practical units), one finds n(4.2 K) = 1.7×10^{20} cm^{-3} and the mobility μ (4.2 K) = 2560 cm^2/v sec.

In the paramagnetic region Eq. 1 may be written as

$$\frac{e_H}{H_A} = R_0 + \{(1 - N)R_0 + R_s\}4\pi\chi^*, \quad (2)$$

where H_A is the applied field, N = 0.633 is the demagnetizing factor, and $\chi^* = \chi/(1+4\pi N\chi)$ the measured susceptibility. Fig. 3 displays e_H/H_A as a function of χ^*. The high temperature, (small χ^*) region appears linear. However, the slope and the intercept extrapolated to $\chi^* = 0$ do not yield a consistent value for R_0 for any reasonable

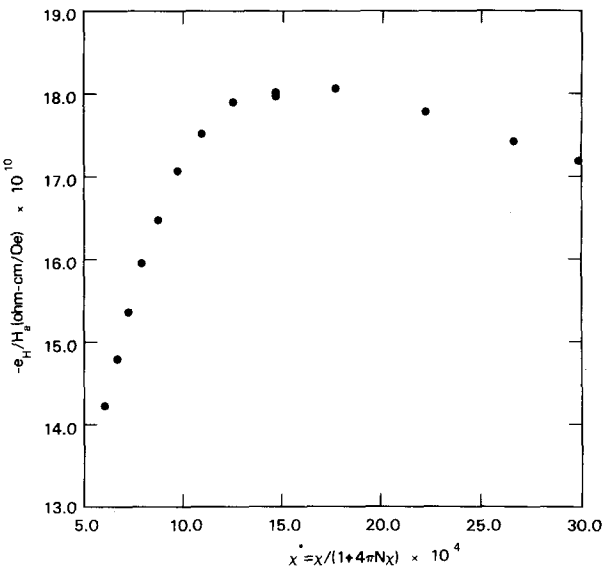

Fig. 3: Slope of curves of Hall resistivity, e_H, versus applied field H_A in the paramagnetic region, plotted against the effective susceptibility χ^*.

R_S. We are, therefore, forced to conclude that R_0 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 accross an intrinsic semiconductor gap are gradually frozen out. The plateau between ~150 and ~100 K represents the exhaustion range with $n = 10^{-8} \div (|e_H/H_A| \times e) = 3.5 \times 10^{19} cm^{-3}$ due to defects and impurities. Here the calculated mobilities are inordinately high at ~300 cm^2/v sec. The subsequent decrease in $|e_H/H_A|$ as the temperature is lowered further signals the onset of an electronic phase transition. It should also be mentioned that, below 70 K, e_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_0 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

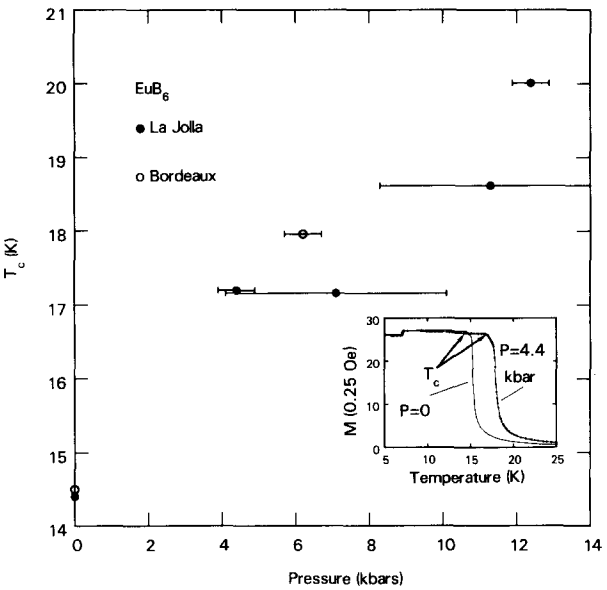

Fig. 4: Pressure dependence of the magnetic transition temperature, T_c, of EuB_6. Solid and open circles designate samples prepared at La Jolla and Bordeaux, respectively. The insert shows the actual signal and gives an operational definition of T_c.

of T_c. There is a large positive shift in T_c, with $(1/T_c)(\Delta T_c/\Delta P) \simeq 4 \times 10^{-2}$ 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 noteable 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

$$J = 2t^2 J_{cf}/S_f U^2, \tag{3}$$

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 $\partial T_c/\partial P$ may be derived as follows:

$$\frac{\partial T_c}{\partial P} \propto \frac{\partial J}{\partial P} = \frac{\partial J}{\partial a}\frac{\partial a}{\partial P} = \frac{\partial J}{\partial a}\frac{a_o}{3}K \tag{4}$$

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

$$U = E_o - Ca^{-\zeta}, \tag{5}$$

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

$$\frac{1}{T_c}\frac{\partial T_c}{\partial P} = \frac{K}{3}\left[8 + 2\zeta\left(\frac{E_o}{U} - 1\right)\right]. \tag{6}$$

For EuO, $(1/T_c)(\partial T_c/\partial P) = 5 \times 10^{-3}$kbar^{-1} [16], $K_{R.T.} = 0.94 \times 10^{-3}$ kbar^{-1}[17] and $E_o/U \simeq 2.66$[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 $(1/T_c)(\partial T_c/\partial P) = 4 \times 10^{-2}$ kbar^{-1}, $K_{RT} = .83 \times 10^{-3}$ kbar^{-1} [20] and $E_o/U \simeq 1.7$,[21] 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, $\mu \simeq 2.4 \times 10^3$cm^2/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 3.5×10^{19}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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