Magnetic, transport, and thermal properties of ferromagnetic EuB$_6$

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Magnetic measurements on Al-flux grown EuB$_6$ crystals show that this material orders ferromagnetically with a transition temperature $T_c = 13.7$ K. The effective moment derived from paramagnetic susceptibility measurements gives $\mu_{\text{eff}} = 7.76 \mu_B$ and the saturation magnetization extrapolated to 0 K is within 10% of the theoretical value of $7 \mu_B$ expected for Eu$^{2+}$. The magnetic order, however, cannot be that of a simple collinear ferromagnet because the magnetic specific heat in zero applied magnetic field shows a broad maximum centered about 9 K rather than the expected $\lambda$-like anomaly at 13.7 K. Finally, transport measurements suggest that EuB$_6$ is an intrinsic semiconductor.

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INTRODUCTION

EuB$_6$ is a cubic material crystallizing in a structure which may be regarded as a CsCl-type array of Eu atoms and $B_6$ octahedra. Recently, Isikawa et al. [1] have reported measurements on EuB$_6$ single crystals prepared by float-zoning. These measurements indicated that EuB$_6$ is semi-metallic, contains some Eu$^{3+}$ and becomes antiferromagnetic with $T_N = 5.6$ K. A recent investigation of carbon substituted EuB$_6$ indicates, however, that both the lattice constant and the paramagnetic Curie temperature diminish smoothly with increasing carbon content [2], that the order changes from ferro to antiferromagnetic [3], and that the Eu is divalent throughout the series; Kasya, et al. [2] suggest that the earlier finding of antiferromagnetism [1] may be due to carbon contamination. Since it has long been believed that EuB$_6$ is a semiconductor which orders ferromagnetically [4] ($T_c = 8$ K) and contains only Eu$^{2+}$ [5,6], we felt it worthwhile to check these results on crystals prepared by growth from molten Al. We present our findings below, along with a few comparative measurements on crystals grown from molten Eu metal.

CRYSTAL GROWTH AND LATTICE PARAMETER

Most of our measurements were made on crystals precipitated from molten Al [7]. 1.49 g of 99.9% Research Chemical Eu (this is excess Eu) and 0.282 g of 99.9995% Eagle-Picher B were placed in a recrystallized covered alumina crucible along with 71.1 g of 99.999% Al bar. This crucible was placed in a vertical tube furnace through which an argon flow was maintained. The load was soaked at 1450°C for 12 hrs., followed by a cool-down at 6°C/hr to 670°C. The crystals were then separated by dissolving the Al in hot NaOH solution.

Smaller crystals were also grown by heating boron in excess Eu sealed in a Ta tube at 1550°C for 10 minutes in an induction coil. The crystals were then separated by leaching in HCl.

The lattice parameter of our Al-grown material was found to be $a_0 = 4.188 \pm .0003$ Å; for an Eu-grown crystal, $a_0 = 4.1838 \pm .0003$ Å. The detailed study of Etourneau, et al. [8] showed that ThB$_6$ has a considerable range of stoichiometry corresponding to variable Th vacancies, and that the vacancies are larger than the occupied Th sites. We therefore infer from our lattice parameter measurements that the Al-grown material is Eu-deficient. This conclusion is based on the assumption that our Eu-grown material is stoichiometric, as its method of preparation would seem to favor. A rough interpolation from the results of Ref. 8 suggests as much as 10% Eu vacancies in the Al-grown material, a value which is consistent with estimates presented below.

HALL EFFECT AND ELECTRICAL RESISTIVITY

Hall effect measurements at both room temperature and 77 K gave the same negative Hall constant for the Al-grown crystals, which corresponded to between 3-7 $\times 10^{19}$ el/cm$^3$, depending on the sample. The float zoned crystal of Ref. 1 had a somewhat larger concentration, 4.2 $\times 10^{20}$ el/cm$^3$.

![Fig. 1](image_url) Temperature dependence of the electrical resistivity of Al-grown Eu$_{1-x}$B$_6$ single crystal, with $x = .13$ as estimated from the results shown in Fig. 2.
Figure 1 shows the electrical resistivity for a typical Al-grown crystal in the temperature range below 220 K. The average room temperature resistivity for some 10 samples is approximately 700 $\mu$-ohm-cm. A minimum at $\sim 30$ K suggests the onset of short range magnetic order, followed by long range ordering at 14 K. The spin disorder term is approximately 300 $\mu$-ohm-cm [9].

The fact that our room temperature electrical resistivity is some 7 times the value given in Ref. 1 is consistent with our carrier concentration being smaller by about this same factor of 7. However, there is no large spin disorder term below the ordering temperature for the float-zoned crystal, and its high residual resistivity ($\sim 100$ $\mu$-ohm-cm) is hard to understand.

The size of the lattice term at room temperature for our crystal is some 300 $\mu$-ohm-cm. This lattice term for LaB$_6$ is approximately 7 $\mu$-ohm-cm. This suggests about 2% carriers, which corresponds to $\sim 3 \times 10^{20}$ carriers/cm$^3$.

A further estimate for the carrier concentration of Al-grown EuB$_6$ can be obtained from the magnitude of the spin disorder resistivity. This resistivity, on a free electron model, should vary as $\mu^2$ (g-1)/$2Z^2$, where $Z$ is the number of conduction electrons per atom [10]. Utilizing our measured value for EuB$_6$ and the known magnitude of the spin disorder term in NdB$_6$ [11] leads to $Z = 0.08$ for our Al-grown sample.

MAGNETIC SUSCEPTIBILITY AND HEAT CAPACITY

Figures 2 and 3 show our susceptibility results for Al-grown crystals of EuB$_6$. The high temperature data (Fig. 2) can be fitted with a Curie-Weiss law, yielding an effective moment of 7.76 $\mu_B$ per Eu ion, assuming an exact EuB$_6$ composition; this value is 2.3% lower than expected for stoichiometric EuB$_6$ containing only Eu$^{2+}$. Assuming that the concentration of Eu$^{3+}$ is negligible (see below), the low effective moment corresponds to a formula Eu$_{1.87}$Ho$_{0.13}$B$_6$. This 13% Eu vacancy concentration for the Al-grown material is consistent with, albeit higher than, our other estimates. However, the puzzle remains that the negative Hall constant suggests electrons as the carriers, whereas band structure considerations [12,13] all point to vacancies as leading to hole carriers. The $\chi$($T$) data below 70 K are plotted in Fig. 3; these data as well as saturation magnetization data obtained from Arrott plots (see insert, Fig. 3) indicate that the Al-grown material orders ferromagnetically at 13.7 K.

![Fig. 2](image1)

**Fig. 2** Temperature dependence of the low field magnetic susceptibility for an Al-grown Eu$_{1.87}$Ho$_{0.13}$B$_6$ single crystal of mass 5.7 mg. The units of $\chi$ assume an exact EuB$_6$ composition.

![Fig. 3](image2)

**Fig. 3** Expansion of the low temperature region of Figure 2. Shown in the inset are saturation magnetization versus temperature data derived from Arrott plots on a separate 0.05 $\pm$ 0.01 mg crystal of Eu$_{1.87}$Ho$_{0.13}$B$_6$; the accuracy of the latter measurements is limited by the 20% accuracy of the sample mass measurement.

The total heat capacity between 1.4 and 26 K for the same 5.7 mg sample used in the low field susceptibility measurements is plotted in Fig. 4. The dashed line indicates our estimate of the lattice specific heat ($\theta_D$ = 293 K). It is immediately apparent that the magnetic specific heat anomaly (the difference between the dashed line and the data) does not correspond to the usual second-order transition. In fact, a broad maximum occurs at about 9 K, whereas $T_D = 13.7$ K. The magnetic order, therefore, cannot be that of a simple cusp ferromagnet. The magnetic entropy given below 20 K is 17.1 $\pm$ 1.1 J/mK, nearly the full value expected for Eu$^{2+}$ and consistent with our estimates of the vacancy concentration.

![Fig. 4](image3)

**Fig. 4** Low temperature specific heat of the same Eu$_{1.87}$B$_6$ crystal used in measurements shown in Figures 2 and 3; the dashed line is a least squares fit to the high temperature data points and represents our estimate of the lattice contribution with $\theta_D = 293$ K. The y-axis scale and $\theta_D$ assume an exact EuB$_6$ composition.

We have not as yet performed a complete set of measurements on the Eu-grown EuB$_6$. However, from ac-susceptibility measurements we find that the material orders ferromagnetically at 7 K.
DISCUSSION

R. L. Cohen [14] has performed Mössbauer measurements on our Al-grown EuB$_6$ crystals and found an extremely clean Eu$^{2+}$ spectrum, with less than 0.5% Eu$^{3+}$ possible. Therefore, the Eu$^{3+}$ concentration appears to be much smaller than our various estimates of the Eu vacancy concentration and will not be considered further in our discussion.

The important experimental points to be explained are the following: (i) the Hall effect indicates electron conduction while the band structure considerations point to hole conduction for Eu vacancies; (ii) the specific heat anomaly is not that of a simple ferromagnet; and (iii) the magnetization does not saturate in 20 kOe at 4.2 K.

In regards to point (i), it seems likely to us that EuB$_6$ is a semi-metal in which a slight band overlap produces the small carrier concentration observed; an electron mobility higher than the hole mobility would account for the negative sign of the Hall constant. The fact that our Al-grown material is off-stoichiometry does not alter this qualitative conclusion. In spite of the fact that the magnetic properties indicate well behaved ferromagnetic order, our thermal data shows that the order is more complicated. This observation is consistent with earlier data obtained on polycrystalline samples [15]. The exchange mechanism and therefore the type of magnetic order are obviously very sensitive to carrier concentration [2,16,17] and perhaps to the ratio of electron to hole conduction. Nonetheless, the detailed nature of these mechanisms is not presently understood.

In conclusion, we have found for single crystal EuB$_6$, the occurrence of ferromagnetism in contrast to the results of Ref. 1, although the thermal properties suggest that the order is not collinear. We further conclude from our measurements that EuB$_6$ is an intrinsic semi-metal, in agreement with the hypothesis of Isikawa, et al. [1].

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