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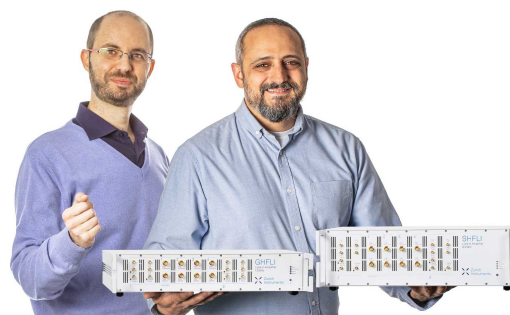
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Magnetic and transport properties of pure and carbon-doped divalent RE hexaboride single crystals

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Single crystals of pure and carbon-substituted divalent hexaborides EuB_6 and YbB_6 have been prepared by the Al flux method. Lattice parameters, density measurements, and microprobe analysis show that the single crystals are very close to stoichiometry, EuB_6 is ferromagnetic ($T_C = 12.5$ K and $\theta_p = 15$ K) while YbB_6 is diamagnetic. Resistivity and Hall effect measurements carried out over a wide temperature range show that both pure hexaborides are semiconductors with a small intrinsic gap. The carbon-substituted hexaborides $\text{REB}_{6-x}\text{C}_x$ (RE = Eu, Yb) have a metallic behavior due to the donation of electrons to the conduction band by carbon atoms. Metallic conduction, at low temperature, in the "pure" hexaborides is attributed to the formation of an impurity band containing more than 10^{18} electrons per cm^3 .

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I. INTRODUCTION

The rare-earth hexaborides REB_6 crystallize with a cubic structure which may be considered as a CsCl arrangement of RE atoms and B_6 octahedra. Among these compounds, EuB_6 and YbB_6 are characterized by a purely +II oxidation state of europium and ytterbium.¹⁻⁴ According to the results so far reported, EuB_6 is claimed to be either a semiconductor or a semimetal, whereas YbB_6 seems to have semiconducting behavior.⁴⁻⁷

Our recent investigations of carbon-substituted EuB_6 indicated that both lattice constant and paramagnetic Curie temperature diminish smoothly with increasing carbon content. Furthermore, magnetic ordering changes from ferromagnetic to antiferromagnetic and metallic behavior is appearing. The europium remains divalent throughout the series.⁸⁻¹⁰

Because of the previous disagreement on the intrinsic electronic structure, it seemed to be worthwhile to look again into the electrical and magnetic properties of EuB_6 crystals and compare them with those of YbB_6 crystals. Measurements of the magnetic susceptibility, electrical resistivity, and Hall constant have been made over a wide range of temperature on pure and carbon-substituted single crystals of both EuB_6 and — for the first time — YbB_6 .

II. CRYSTAL GROWTH

Single crystals of REB_6 and carbon-substituted $\text{REB}_{6-x}\text{C}_x$ (RE = Eu, Yb) have been grown from molten Al in covered alumina crucibles placed inside a tantalum tube. The starting mixture of REB_6 or $\text{REB}_{6-x}\text{C}_x$ and of Al powder corresponds to a weight ratio $\text{REB}_6/\text{Al} \approx 1/20$. The load was heated, under a purified argon flow in a high-frequency furnace, following the conditions given in Table I.

The REB_6 and $\text{REB}_{6-x}\text{C}_x$ powder samples used for the crystal growth have been prepared by borothermic reduction of RE oxides.⁸ One should point out that is impossible to obtain crystals by the Al flux technique with $x \gtrsim 0.05$ for Eu and $x \gtrsim 0.03$ for Yb since a considerable amount of carbon is dissolved in molten aluminum. A quantitative microprobe analysis has confirmed that the single crystals studied are very close to stoichiometry (Table II).

III. MAGNETIC PROPERTIES

A. EuB_6 and $\text{EuB}_{5.95}\text{C}_{0.05}$

The magnetic susceptibilities for EuB_6 and $\text{EuB}_{5.95}\text{C}_{0.05}$ single crystals have been measured from 4.2 K up to room temperature. The high-temperature data which can be fitted with a Curie-Weiss law indicate an effective moment of $7.92 \mu_B/\text{Eu}^{2+}$ for EuB_6 (Fig. 1) and of 7.96

TABLE I. Single-crystal growth conditions from Al flux for REB_6 and $\text{REB}_{6-x}\text{C}_x$.

Compounds	Temp. (°C)	Time (h)	Cooling rate (°C/h)
EuB_6 (No. 1)	1200	4	150 down to 600 °C
EuB_6 (No. 2)	1400	4	170 down to 600 °C
$\text{EuB}_{5.95}\text{C}_{0.05}$	1350	2	150 down to 500 °C
YbB_6	1450	2	150 down to 600 °C
$\text{YbB}_{5.97}\text{C}_{0.03}$	1450	1	150 down to 500 °C

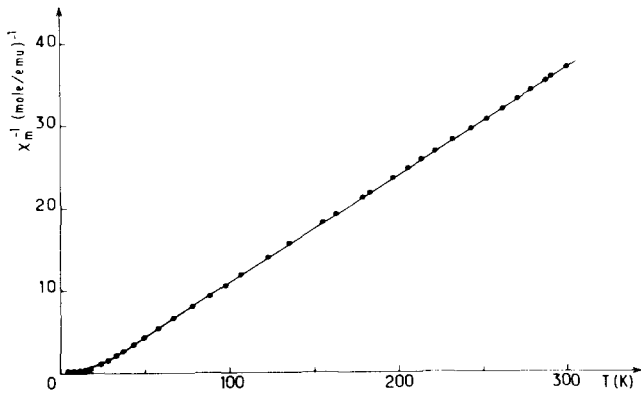


FIG. 1. Reciprocal magnetic susceptibility as a function of temperature for a EuB_6 single crystal.

μ_B/Eu^{2+} for $\text{EuB}_{5.95}\text{C}_{0.05}$. Both values are very close to the theoretical value of $7.93 \mu_B$ for $\text{Eu}^{2+} : 4f^7$.⁸ Our previous results on single crystals have shown that pure EuB_6 is ferromagnetic ($T_C = 12.5 \text{ K}$ and $\theta_p = 15 \text{ K}$). Mössbauer experiments and temperature dependence of the magnetization at different magnetic field have suggested that in $\text{EuB}_{5.95}\text{C}_{0.05}$, the exchange interactions are inhomogeneous as in a micro-magnetic phase ($T_{\text{order}} = 5.2 \text{ K}$ and $\theta_p = 7 \text{ K}$).^{9,10} In samples with greater carbon content ($x \geq 0.18$) the exchange interactions are again homogeneous and the magnetic order is helical.¹¹

B. YbB_6

It is well established that ytterbium is divalent in YbB_6 . The paramagnetic behavior found previously for this compound suggested the presence of RE impurities in the boron lattice.¹² We studied therefore the magnetic susceptibility of YbB_6 (1) on powder samples prepared by a borothermic method using Yb_2O_3 with two different purity levels (99.9% and 99.999%) (Table III); (2) on single crystals obtained by an Al flux method starting from YbB_6 powders of both purities.

The susceptibility χ_m has been measured between 4.2 and 300 K (Fig. 2). The YbB_6 single crystals are diamagnetic over most of the temperature range, but their behavior with temperature is directly related to their impurity content. The single crystals prepared with powder made from Yb_2O_3 (99.999%) have the smallest susceptibility and the sharp rise observed in the $\chi_m = f(T)$ curve below 20 K is characteris-

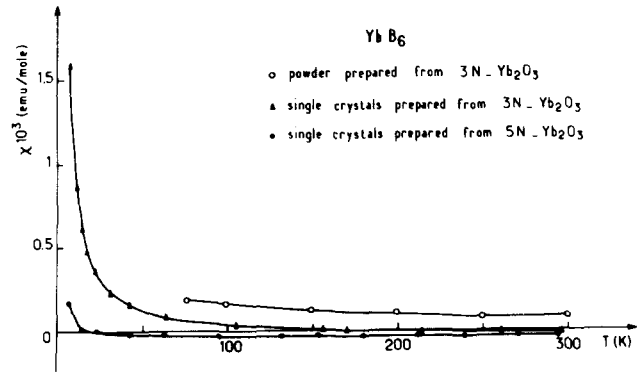


FIG. 2. Magnetic susceptibility as a function of temperature for YbB_6 single crystals prepared from two different impurity levels of Yb_2O_3 .

tic of the presence of magnetic impurities estimated at 100 ppm at least.

IV. ELECTRICAL RESISTIVITY AND HALL EFFECT

The electrical resistivity has been measured by the four-probe dc and ac techniques between 4.2 and 1000 K and the Hall constant has been determined at both 77 and 300 K for EuB_6 , $\text{EuB}_{5.95}\text{C}_{0.05}$, YbB_6 , $\text{YbB}_{5.97}\text{C}_{0.03}$ (for each sample the current has been applied along the [100] direction of the cubic single crystals).

A. EuB_6 and $\text{EuB}_{5.95}\text{C}_{0.05}$

The transport properties have been studied on two series of EuB_6 single crystals prepared at 1200 and at 1400 °C. The room-temperature resistivity of EuB_6 is about $800 \mu\Omega \text{ cm}$ for five samples of each series. The variation of the resistivity ρ between 4.2 and 300 K does not depend on the growth condition of the single crystals (Fig. 3). The resistivity decreases sharply below T_C ; the small minimum observed at $T > T_C$ suggests the onset of a short-range magnetic order and the maximum may be attributed to critical fluctuations.

In the high-temperature range above 300 K, the electrical conductivity increases with rising temperature (Fig. 4). This variation is more pronounced for EuB_6 single crystals prepared at 1400 °C than at 1200 °C and is consistent with a semiconducting behavior.

The resistivity of $\text{EuB}_{5.95}\text{C}_{0.05}$ at 300 K is lower than that of EuB_6 (Fig. 3). As temperature decreases, ρ goes through a shallow minimum and then increases rapidly be-

TABLE II. Lattice parameter microprobe analysis data and density measurements of some REB_6 and $\text{REB}_{6-x}\text{C}_x$ (RE = Eu, Yb) single crystals.

Crystals	Parameter ($a \pm 5 \times 10^{-4} \text{ \AA}$)	RE%		Density Theoret.	(g/cm ³) Expt.
		Theoret.	Expt.		
EuB_6 (No. 1)	4.1856	70.08	70 ± 0.35	4.91	4.83 ± 0.05
EuB_6 (No. 2)	4.1856	70.08	70 ± 0.35		
$\text{EuB}_{5.95}\text{C}_{0.05}$	4.1818	70.06	70 ± 0.35		
YbB_6	4.1486	72.73	72.4 ± 0.8	5.53	5.46 ± 0.05
$\text{YbB}_{5.97}\text{C}_{0.03}$	4.1476	72.72	72.5 ± 0.8		

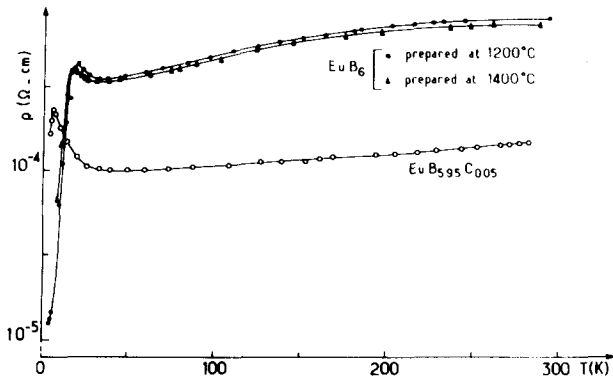


FIG. 3. Variation of the electrical resistivity below 300 K for EuB_6 and $\text{EuB}_{5.95}\text{C}_{0.05}$ single crystals.

low 20 K, showing a maximum at 5 K and decreases down to 4.2 K. The decreasing of the conductivity above 300 K indicates a metallic behavior (Fig. 4).

The Hall constant is negative for all single crystals studied. As it could be expected, the measured carrier concentration with rising temperature (77–300 K) increases for EuB_6 , whereas it remains constant for $\text{EuB}_{5.95}\text{C}_{0.05}$ (Table IV).

B. YbB_6 and $\text{YbB}_{5.97}\text{C}_{0.03}$

The temperature dependence of the electrical conductivity of a YbB_6 crystal is characteristic of a semiconductor above 300 K (Fig. 5). The activation energy deduced from the high-temperature data is $\Delta E = 0.11$ eV. Below 300 K the presence of impurities could be responsible of the shape of the $\rho = f(T)$ curve (Fig. 6).

$\text{YbB}_{5.97}\text{C}_{0.03}$ is metallic between 4.2 and 800 K (Figs. 5 and 6). As for EuB_6 and $\text{EuB}_{5.95}\text{C}_{0.05}$, the Hall constant is small and negative for YbB_6 and $\text{YbB}_{5.97}\text{C}_{0.03}$. The carrier

TABLE III. Impurities contained in two samples of Yb_2O_3 used for the preparation of YbB_6 .

	3N	5N	Yb_2O_3
La_2O_3	100	...	
CeO_2	37	...	
Pr_6O_{11}	<20	...	
Nd_2O_3	200	...	
Sm_2O_3	25	...	
Eu_2O_3	<10	...	
Gd_2O_3	<10	...	
Tb_4O_7	200	...	
Dy_2O_3	10	...	
Ho_2O_3	<20	...	
Er_2O_3	10	...	
Tm_2O_3	30	<5	
Lu_2O_3	50	<5	
Y_2O_3	<10	...	
Na_2O	11	...	
BaO	<50	...	
CaO	53	...	
Al_2O_3	<10	...	
Fe_2O_3	4	...	
SiO_2	10	...	

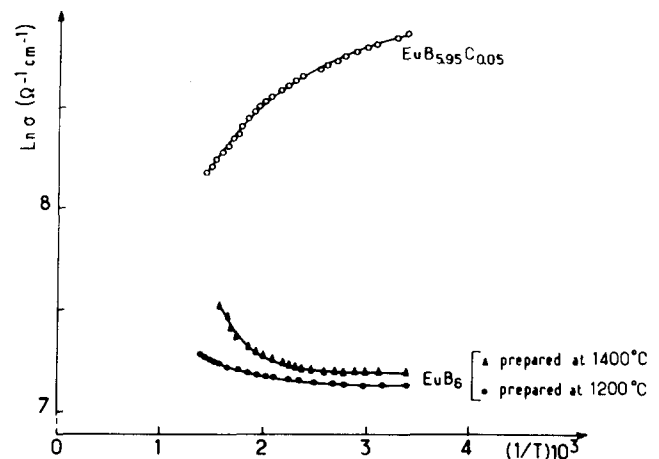


FIG. 4. Variation of the electrical conductivity above 300 K for EuB_6 and $\text{EuB}_{5.95}\text{C}_{0.05}$ single crystals.

concentration is higher at 300 K than at 77 K for YbB_6 , but does not change with temperature for $\text{YbB}_{5.97}\text{C}_{0.03}$ (Table IV).

V. DISCUSSION AND CONCLUSION

Magnetic and density measurements and chemical and microprobe analysis performed on pure and carbon-substituted EuB_6 and YbB_6 single crystals reveal that these compounds should not contain more than 1% of europium vacancies. Unlike ThB_6 no conclusion can be drawn about stoichiometry in EuB_6 from the lattice parameter, for which no variation within $\pm 0.0005 \text{ \AA}$ has been found for a series of samples prepared with initial Eu/B atomic ratios between 6 and 8.5.¹³

Considering now the question of whether pure EuB_6 and YbB_6 are intrinsic semiconductors or semimetals, the problem is to reconcile the low value of the resistivity at low temperature with the small negative value of the Hall constant R_H . According to Fisk and co-workers EuB_6 is an intrinsic semimetal; these authors base their conclusions on

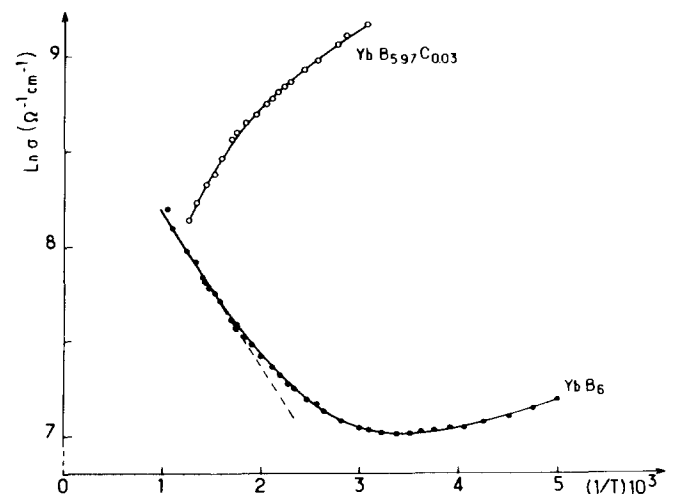


FIG. 5. Variation of the electrical conductivity above 300 K for YbB_6 and $\text{YbB}_{5.97}\text{C}_{0.03}$ single crystals.

TABLE IV. Hall constant R_H and carrier concentration n for a formula unit at 77 and 300 K for pure and carbon-doped EuB_6 and YbB_6 single crystals.

Compounds	77 K		300 K	
	R_H (V cm/A G)	n	R_H (V cm/A G)	n
EuB_6 (No. 1)	-2.98×10^{-9}	0.0015	-2.1×10^{-9}	0.0022
EuB_6 (No. 2)	-2.40×10^{-9}	0.0019	-1.78×10^{-9}	0.0026
$\text{EuB}_{5.95}\text{C}_{0.05}$	-2.01×10^{-10}	0.023	-1.95×10^{-10}	0.023
YbB_6	-7.91×10^{-9}	0.00056	-6.94×10^{-9}	0.00064
$\text{YbB}_{5.97}\text{C}_{0.03}$	-2.15×10^{-10}	0.021	-2.08×10^{-10}	0.021

the temperature variation of the resistivity below room temperature, which is actually in substantial agreement with our own data.⁸ However, we may note that the magnitude of the Hall constant corresponds roughly in a one band model to the amount of carbon doping in the mixed crystals and to 570–1900 ppm impurities in the “pure” crystals. If we were to explain the Hall effect measurements supposing EuB_6 to be a semimetal, we would have to assume practically equal mobility for electrons and holes, with that of the former being slightly greater. As a real coincidence, perfect cancellation would be necessary to account for the very small value measured for R_H in YbB_6 . Furthermore, in this model the increase in n with carbon doping (n being the number of carriers deduced from the Hall constant) should be exactly $2x$, whereas in fact it is rather less than x . For these reasons the pure hexaborides may be considered as semiconductors with a small gap (≈ 0.1 eV) separating the bottom of the $5d-6s$ conduction band from the top of the valence band formed essentially by the $2s$ and $2p$ states of the boron atoms. High-susceptibility data for EuB_6 up to 800 K gave a temperature-independent Curie constant corresponding to that expected for $\text{Eu}^{2+} : 4f^7$. It follows then that the $4f^7$ levels are at least 0.2 eV below the bottom of the conduction band.¹⁰ This energy scheme is consistent with recent XPS determinations on EuB_6 .¹⁴

The high negative value of the Seebeck coefficients of EuB_6 and YbB_6 at 300 K ($\alpha = -85 \mu\text{V/K}$ for EuB_6 and $\alpha = -215 \mu\text{V/K}$ for YbB_6) corroborates such a semiconducting behavior.

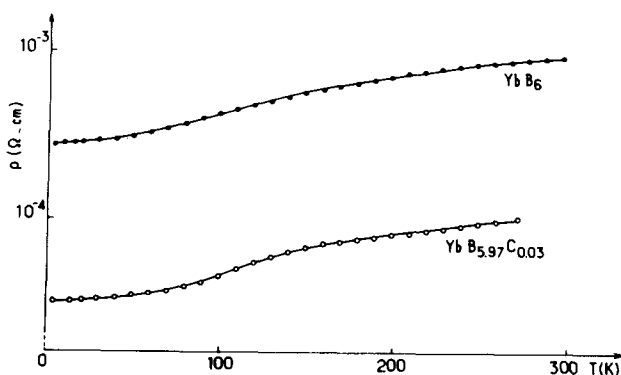


FIG. 6. Variation of the electrical resistivity below 300 K for YbB_6 and $\text{YbB}_{5.97}\text{C}_{0.03}$ single crystals.

The small resistivity and its metallic temperature dependence at low temperature in both EuB_6 and YbB_6 must be ascribed in a semiconductor model to an impurity band. We have seen from the susceptibility of YbB_6 that the impurity concentration in the best crystals correspond to more than 10^{18} carriers per cm^3 . At comparable impurity levels in silicon a metallic impurity band would form, it is likely to appear at rather lower concentration in the divalent rare earth hexaborides because of their small intrinsic gap, deduced from the high-temperature variation of the resistivity.

The carrier concentration determined from the Hall effect measurements indicates that in the mixed hexaborides the carbon atoms behave as electron donors and are at the origin of the metallic behavior at high temperatures.

To realize from the EuB_6 data a more precise model for a ferromagnetic semiconductor, it will be necessary to use much purer starting materials.

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