



Study of carbon-substituted EuB₆

Mitsuo Kasaya, Jean-Marie Tarascon, Jean Etourneau, Paul Hagenmuller

► To cite this version:

Mitsuo Kasaya, Jean-Marie Tarascon, Jean Etourneau, Paul Hagenmuller. Study of carbon-substituted EuB₆. Materials Research Bulletin, 1978, 13 (8), pp.751-756. <10.1016/0025-5408(78)90036-3>. <hal-03765673>

HAL Id: hal-03765673

<https://hal.science/hal-03765673v1>

Submitted on 31 Aug 2022

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.



HAL Authorization

STUDY OF CARBON-SUBSTITUTED EuB_6

M. Kasaya*, J.M. Tarascon, J. Etourneau and P. Hagemuller
Laboratoire de Chimie du Solide du C.N.R.S.

Université de Bordeaux I

351 cours de la Libération, 33405 Talence, Cedex, France.

ABSTRACT :

Carbon-substituted europium hexaborides $\text{EuB}_{6-x}\text{C}_x$ have been prepared by borothermal reduction. The homogeneity range is $0 \leq x \leq 0.21$. The lattice parameter decreases progressively from 4.1855 \AA to 4.1703 \AA with rising x . The paramagnetic Curie temperature diminishes from 15 to -6.5 K . Electrical properties have been studied for $x = 0$ and $x = 0.05$ on single crystals prepared by an Al-flux technique. Between 30 and 300 K both single crystals have metallic behavior and their resistivity at 300 K is of the order of $10^{-4} \Omega \cdot \text{cm}$. However each single crystal shows a rather different temperature-dependence of resistivity at low temperature.

Introduction

The physical properties of EuB_6 are of obvious interest because of their dependence on the number of conduction electrons (1, 2). The electron density in the conduction band depends upon the method of preparation, varying from about 0.09 el./Eu ion in polycrystalline material (3), through 0.03 el./Eu ion in a single crystal prepared by a floating-zone method (2), to roughly 10^{-3} el./Eu ion for thin films grown on a boron substrate (4). The origin of this variation may be due to impurity atoms and/or Eu defects. Actually the number of conduction electrons can be modified widely by intentional doping with Gd^{3+} or La^{3+} ions in the cationic sublattice of EuB_6 (1). However, no attempts have been made to control the number of conduction electrons by introducing foreign atoms in the B_6 skeleton itself.

To study the contribution of the conduction electrons to the physical properties, it seemed to be interesting to carry out a systematic study of the influence of carbon on the physical properties of EuB_6 , since carbon is expected to behave as an electron donor in the hexaborides. The purpose of the present paper is to report the method of synthesis and some physical characterizations of the phases of composition $\text{EuB}_{6-x}\text{C}_x$ ($0 \leq x \leq 0.21$). We also wish to draw attention to the possibility that some of the physi-

*Permanent address : Department of Physics, Faculty of Science, Tohoku University, Sendai, Japan.

cal properties reported earlier for "EuB₆" are in fact the result of carbon impurities.

Preparation

EuB_{6-x}C_x phases have been prepared for the first time by borothermal reduction under vacuum (10^{-5} torr) at 1700°C :
 $\text{Eu}_2\text{O}_3 + (15-y)\text{B} + y\text{C} \rightarrow 2\text{EuB}_{6-x}\text{C}_x + (3+2x-y)\text{BO} + (y-2x)\text{CO}$, where y is the amount of carbon mixed intentionally with B and Eu₂O₃, and x the carbon content determined by chemical analysis. The specially-prepared boron used in the synthesis contained less than 200 ppm carbon (5). X-ray diffraction reveals that a single phase of composition EuB_{6-x}C_x may be obtained for $0 \leq x \leq 0.21$. The lattice parameter of the unit cell decreases with rising x from $a = 4.1855 \text{ \AA}$ ($x = 0$) to $a = 4.1703 \text{ \AA}$ ($x_0 = 0.21$). The lower value found for the parameter is $a = 4.1695 \text{ \AA}$, but unfortunately the corresponding phase already coexists with a slight amount of free carbon. The variation of the lattice parameters as a function of x is given in Fig. 1.

For the study of the electrical properties, single crystals were used, prepared from sintered samples by Al-flux technique (6). In this process, considerable amounts of carbon are dissolved into the Al-flux and single crystals of EuB_{6-x}C_x with lattice parameter 4.1855 \AA and 4.1813 \AA , corresponding to $x = 0^{**}$ and 0.05

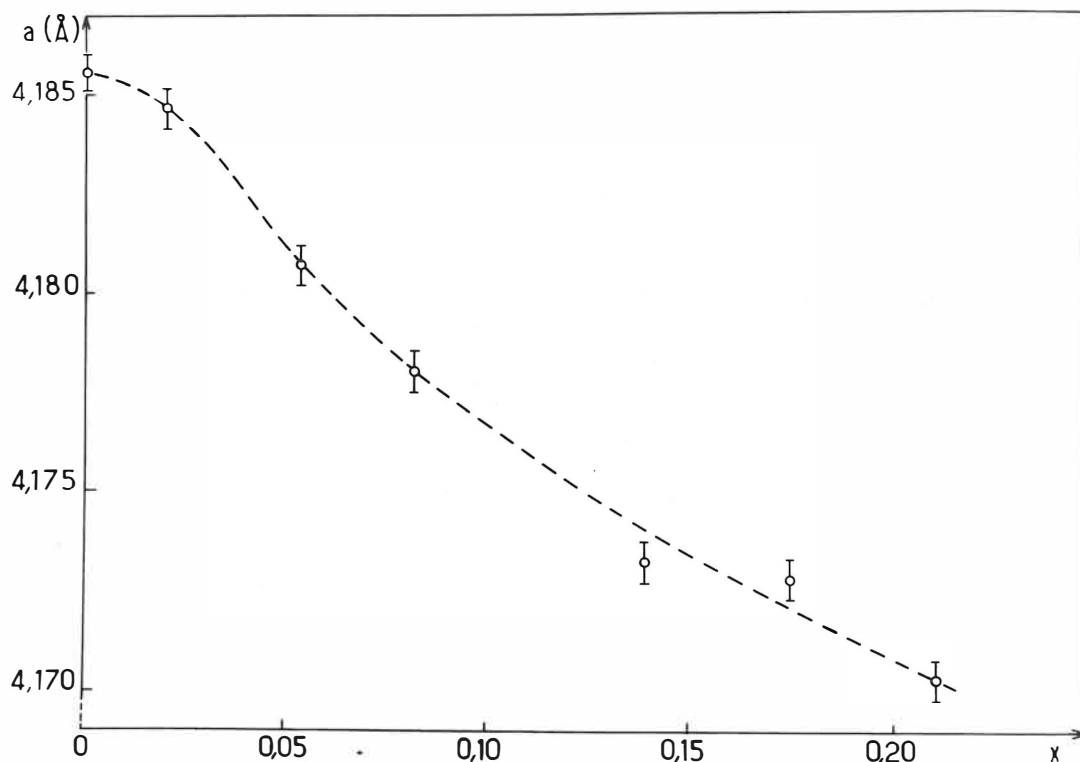


FIG. 1
Lattice parameter variation for EuB_{6-x}C_x

** Rigorously speaking, x is less than $1.8 \cdot 10^{-4}$.

respectively have been obtained. Electron probe microanalysis showed that the single crystals do not contain free boron or free europium.

Physical Properties

Magnetic Properties

Magnetic susceptibilities for single crystals ($x = 0$ and 0.05) and sintered samples ($x = 0.082$, 0.139 , 0.175 and 0.21) have been measured from 4.2 K up to room temperature. The variation of the paramagnetic Curie temperature θ_p vs x is given in Fig. 2. θ_p decreases progressively from 15 K to -6.5 K as x increases from 0 to 0.21 .

This result suggests that pure EuB_6 is ferromagnetic and that antiferromagnetic

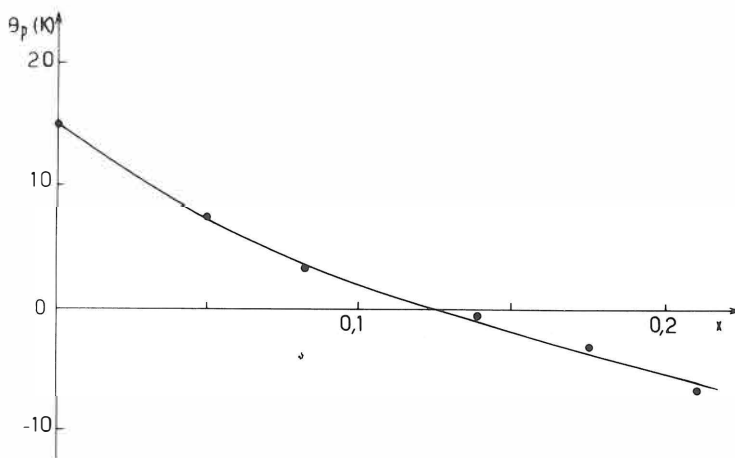


FIG. 2
Paramagnetic Curie temperature vs x for
 $\text{EuB}_{6-x}\text{C}_x$

exchange interactions are introduced by introducing carbon in EuB_6 . In fact a magnetization curve characteristic of a ferromagnet was observed for $x = 0$ at 4.2 K, whereas for $x = 0.21$ at 4.2 K the magnetization increases gradually with the external field: it was found to be $1.7 \mu_B/\text{Eu ion}$ at 10 kOe. The effective magnetic moments for $x = 0$, 0.05 , 0.082 , 0.139 , 0.175 and 0.21 are 7.90 , 7.96 , 7.94 , 7.85 , 7.89 and $7.92 \mu_B$ respectively, values which are very close to the theoretical value of $7.93 \mu_B$ for $\text{Eu}^{2+} : 4f^7$. The ordering temperature derived from Mössbauer resonance measurements is $T_C = 12.5$ K for $x = 0$ and $T_N = 5.5$ K for $x = 0.21$ (7).

Electrical properties

The resistivity measurements on single crystals were carried out by the four-probe dc method. The results are summarized in Fig. 3. The electrical resistivity ρ for $x = 0$ is about 4 times larger than that observed for $x = 0.05$ at room temperature. The $d\rho/dT$ for $x = 0.05$ is larger than that for $x = 0$ above 30 K. As temperature decreases, ρ for $x = 0$ shows a small peak at 18 K and then decreases down to $25 \mu\Omega\cdot\text{cm}$ at 4.2 K. For $x = 0.05$ ρ goes through a minimum and then increases rapidly below 20 K, showing a sharp maximum at 7 K and decreasing again down to 4.2 K. The resistivity anomaly observed for $x = 0.05$ at low temperatures is similar to that shown on a single crystal prepared by a floating-zone method (2).

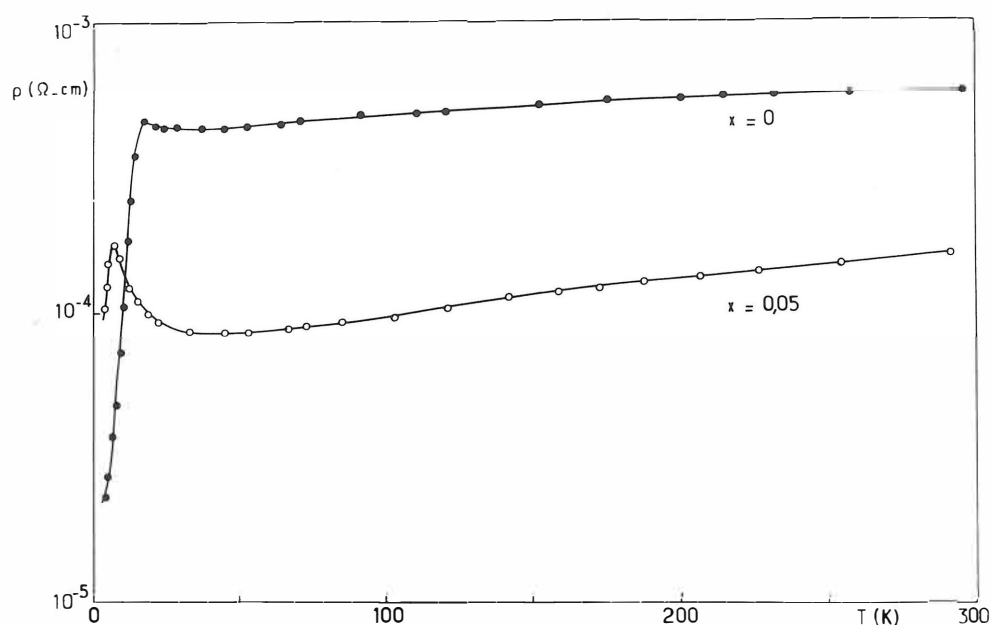


FIG. 3
Temperature dependence of the electrical resistivity of
 $\text{EuB}_{6-x}\text{C}_x$ for $x = 0$ and $x = 0.05$

Discussion

Firstly we shall discuss the changes of the lattice parameter with carbon content. In the crystal structure of EuB_6 , each boron atom have five neighbors, four in its own octahedron and one belonging to the adjacent octahedron, all five at a distance of approximately 1.73 \AA which is close to the covalent diameter of boron (1.76 \AA). Therefore it is reasonable to consider that the lattice parameter is determined predominately by the B_6 skeleton. The lattice parameter a is determined in such a case by the covalent diameter d : $a = d(1 + \sqrt{2})$. Using the covalent diameter 1.54 \AA for carbon and extrapolating to $\text{EuB}_{6-x}\text{C}_x$ with $x = 0.21$ leads to a lattice parameter of 4.169 \AA , which is reasonable compared to the experimental value of 4.1703 \AA . However it should be noted that a can be reduced also by the increase of metallic bonding, since carbon is expected to behave as an electron donor. In fact the lattice parameter of GdB_6 is 4.110 \AA and the difference of the lattice parameters between EuB_6 and GdB_6 should be explained not only in terms of atomic sizes of the rare earth elements but also by metallic bonding. If we assume that the difference comes from metallic bonding, the reduction of a due to one conduction electron per formula unit could be about 0.08 \AA . In $\text{EuB}_{6-x}\text{C}_x$ with $x = 0.21$, there may be 0.21 conduction electron per formula unit, so that the reduction of a due to metallic bonding could be 0.017 \AA , which is reasonable compared to the experimental value of 0.015 \AA . Therefore either of these two mechanisms is able to account for the observed reduction of the lattice parameter. At this stage it appears worthwhile to consider the influence of carbon on the lattice parameter of SmB_6 . A sintered sample of $\text{SmB}_{6-x}\text{C}_x$ with $x = 0.055$ was prepared by the same method, but no change of lattice parameter was observed. This result seems to

suggest that the reduction of a due to smaller size of the C atoms is not decisive. In $\text{SmB}_{6-x}\text{C}_x$ the extra electrons enter a narrow 4f band and so will not contribute to metallic bonding which may explain also the constancy of the unit cell (8). In fact the decrease of a in $\text{EuB}_{6-x}\text{C}_x$ is not exceptional. Preliminary experiments on $\text{YbB}_{6-x}\text{C}_x$ show that the lattice parameter also diminishes with increasing x . It is well known that YbB_6 and EuB_6 have the same electronic structure except for the number of 4f electrons. It appears that the reduction of the lattice parameter in $\text{YbB}_{6-x}\text{C}_x$ may be also due to an increase of metallic bonding.

Our experiments show that the single crystals of pure EuB_6 is ferromagnetic, which is consistent with the previous result on a sintered sample (1), but seems to contradict the recent work on a single crystal prepared by a floating-zone method (2). As x increases, the predominant magnetic interactions in $\text{EuB}_{6-x}\text{C}_x$ change from ferromagnetic to antiferromagnetic. The paramagnetic Curie temperature is 0 at $x = 0.125$. We shall discuss here the magnetic properties of $\text{EuB}_{6-x}\text{C}_x$ in the molecular field approximation. The total exchange energy E of the system is given by

$$E = -NJ(Q) \langle S \rangle^2 \quad (1)$$

where $J(Q)$ is defined by

$$J(Q) = \sum_{\vec{R}_i} J(\vec{R}_i - \vec{R}_j) \exp iQ(\vec{R}_i - \vec{R}_j). \quad (2)$$

If we take into account the exchange interactions up to the second nearest neighbors, the exchange integral $J(0)$ for ferromagnetic EuB_6 is given by :

$$J(0) = 6J_1 + 12J_2. \quad (3)$$

On the other hand, for a simple cubic lattice of magnetic atoms, three types of collinear antiferromagnets are possible ; $(\pi 00)$, $(\pi \pi 0)$ and $(\pi \pi \pi)$, with ferromagnetic layers parallel to the (100) , (110) and (111) planes respectively. The direction of the magnetic moment in each ferromagnetic layer alternates with that of the neighboring ones. The exchange constants are given in the three hypotheses by :

$$J(Q) = 2J_1 - 4J_2 \quad (4)$$

$$J(Q) = -2J_1 - 4J_2 \quad (5)$$

$$J(Q) = -6J_1 + 12J_2. \quad (6)$$

The stability range of each magnetic structure in the $J_1 - J_2$ plane is given in Fig. 4. The fact that EuB_6 is ferromagnetic suggests that $J_1 > 0$ and $J_1 > -4J_2$ for $x = 0$. As x increases, θ_p decreases. For a ferromagnet as well as an antiferromagnet, θ_p is given in the molecular field approximation by :

$$\theta_p = \frac{2S(S+1)J(0)}{3k} \quad (7)$$

Therefore $6J_1 + 12J_2$ decreases progressively as x increases from 0 to 0.21. For $x = 0$, the experimental value of $6J_1 + 12J_2$ is 1.43 K, while for $x = 0.21$, $6J_1 + 12J_2$ is - 0.62 K. For $x > 0.125$, one of the three antiferromagnetic spin arrangements may be stabilized. It is interesting to note that J_1 is negative for the $(\pi \pi 0)$ and $(\pi \pi \pi)$ arrangements, while J_1 is positive for $(\pi 00)$ (Fig. 4). To determine J_1 and J_2 separately and hence to decide the contribution of the conduction electrons to the exchange interactions,

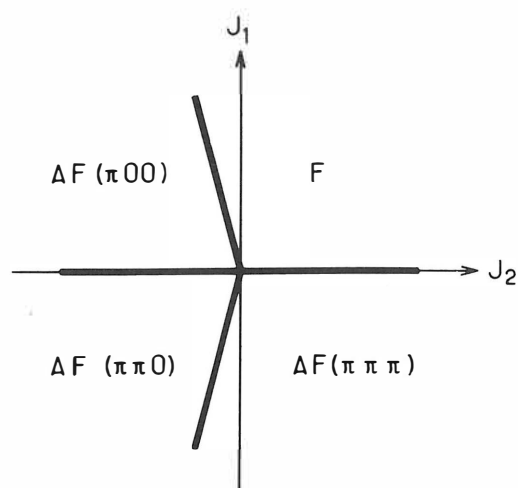


FIG. 4
Magnetic phase stability diagram
for EuB_6 in the J_1 - J_2 plane.

it will be necessary to determine the magnetic structure of antiferromagnetic $\text{EuB}_{6-x}\text{C}_x$ by neutron diffraction.

Finally, the electrical properties of $\text{EuB}_{6-x}\text{C}_x$ will be discussed briefly here. The resistivity of EuB_6 is two orders of magnitude smaller than that of sintered or fused samples reported previously (1, 2). However, the temperature dependence of ρ is similar here to that reported for fused samples (2). ρ decreases by one order of magnitude below T_C . This is an intrinsic property of EuB_6 due to magnetic ordering. At room temperature ρ is smaller for $x = 0.05$ than for $x = 0$, but $d\rho/dT$ is larger. This may be connected with the increase of the conduction electrons and higher phonon scattering. To determine the number of conduction electrons, hall effect measurements are now in progress. More detailed experimental results will be published and discussed later.

References

1. J. P. Mercurio, J. Etourneau, R. Naslain, P. Hagenmuller and J. B. Goodenough, J. Solid State Chem. 9, 37 (1974).
2. Y. Isikawa, M. M. Bajaj, M. Kasaya, T. Tanaka and E. Bannai, Solid State Commun. 22, 573 (1977).
3. G. V. Samsonov, High Temperature Compounds of Rare Earth Metals with Non-metals, 1-100. Consultants Bureau, New York (1965).
4. R. Bachmann, K. N. Lee, T. H. Geballe and A. Menth, J. Appl. Phys. 41, 1431 (1970).
5. R. Naslain, J. Etourneau and P. Hagenmuller, Boron, Vol. III, Preparation and Properties, 35-47. Pol. Sci. Publ., Warsaw (1970).
6. G. D. Sturgeon, J. P. Mercurio, J. Etourneau and P. Hagenmuller, Mat. Res. Bull. 9, 117 (1974).
7. O. Massenet, J. M. D. Coey, M. Kasaya and J. Etourneau, Proc.Int. Conf. on Mössbauer Effect, Kyoto (1978). To be published in J. Physique.
8. T. Kasuya, K. Kojima and M. Kasaya, in Valence Instabilities and Related Narrow Band Phenomena, 137-149. Plenum Press, New York (1977).