Features of Magnetic Phase Transitions in EuB$_{6-x}$C$_x$

T S Altshuler$^1$, Yu V Gorjunov$^1$, A V Levchenko$^2$ and V B Filippov$^2$

$^1$Zavoisky Physical-Technical Institute, Sibirsky trakt 10/7, 420029 Kazan, Russia
$^2$Institute for problems of Materials Science of NASU, 03680, Kiev, Ukraine

E-mail: tatiana@kfti.knc.ru

Abstract. The ESR measurements were performed on the single crystals EuB$_{6-x}$C$_x$ with x = 0, 0.02 and 0.07 at X band in the temperature range T = 10 - 300 K. It was observed the magnetic phase separation in spin system of Eu$^{2+}$ ions. The reason of the separation is accompanied by the self-localization of free charge carriers and the formation of magnetic polarons of two types. With decreasing temperatures the 2 phase transitions take place. The first transition is connected with the effect of magnetic ordering of the most intensive subsystem. The second transition is obliged to the delocalization of charge carriers and the system is converted from heterogeneous to homogeneous state.

1. Introduction

Europium hexaboride is part of the large and heterogeneous class of materials that exhibit colossal magnetoresistance (CMR). EuB$_6$ has a cubic unit cell with Eu-ions at its vertices and a boron octahedron at its center and because of its simple lattice it is very convenient for the researchers of CMR effect. However, despite numerous experimental and theoretical studies of the pure and doped EuB$_6$, understanding of the electronic properties and magnetic coupling still provides challenges. The substance shows two magnetic transitions: at $T_M = 15.3$K and at $T_C = 12.5$K. It orders ferromagnetically at 15.3K, which is accompanied by a huge decrease of resistivity and a significant blue shift of the reflectivity plasma edge. At 12.7 K another phase transition takes place, which is observed as a broad peak in the specific heat or an anomaly in the resistivity [1-3]. The origin of this transition was still unclear.

Until now the study of EuB$_6$ was carried out, in essence, by the methods, which reveal only physical properties of an entire sample. Meanwhile the electron paramagnetic resonance gives the possibility to observe such local phenomenon as magnetic phase separation [see, for example, 4-5], to investigate its temperature dependence, and hence also the features of the magnetic phase transitions.

2. Experimental

The electron spin resonance measurements were performed on the single crystals EuB$_{6-x}$C$_x$ with x = 0, 0.02 and 0.07 in X band in the temperature range T = 10 - 300 K. Carbon ion substitutes the boron ion and brings one electron into the conduction band of EuB$_6$. The single crystals of the pure and doped by carbon europium hexaboride were grown by inductive floating zone melting. The starting rods for melting were prepared by sintering of two types of the europium hexaboride powders with carbon and without it. EuB$_6$ crystals were synthesized by borothermal reduction of Eu$_2$O$_3$. Eu$_2$O$_3$...
purity was 4N, natural boron – 3N. The final compositions of three types of single crystals may be estimated as EuB_6, EuB_{5.98}C_{0.02} and EuB_{5.93}C_{0.07}, according to chemical analyses and hydrostatic density measurements. According to an optical spectral analysis the total content of the impurities apart from carbon was no more than 10^{-3} wt % for single crystals. The EuB_{5.93}C_{0.07} and EuB_6 lattice parameters are 4.176161±0.000036 Å and 4.184679±0.000015 Å correspondingly in agreement with published data [6]. The samples are the polished single crystal plates with 0.5 mm thickness cut from central part of the corresponding single crystals. One single crystal was grown by flux method also.

The ESR measurements were performed on frequency of 9.25 GHz in TE_{102} rectangular resonator with the flux helium cryostat, allowed to measure in the temperatures range from 7K to 300K. The measurements of the temperature dependences of the ESR spectra for thin single crystal plates were performed for perpendicular ($\theta = 90^\circ$) orientations of the plate with respect to the magnetic field in the carbon content europium hexaboribes and for both ($\theta = 0^\circ$ and $\theta = 90^\circ$) orientations in clean europium hexaboribie.

3. Results and Discussion
The single line from Eu^{2+} was observed at 300 K in all single crystals by ESR method. The lineshape is Lorentzian with Dyson distortion. The Eu^{2+} ion has the spin state with the electron spin $S = \frac{7}{2}$ and two stable isotopes with a nuclear spin of $\frac{5}{2}$; therefore 84 resonance lines should be observed. The absence of the fine and hyperfine structures is associated with the averaging of the lines due to strong exchange interactions (fig. 1). The Lorentzian lineshape can also indicate the strong exchange. The position and ESR lineshape are independent from the orientation of the sample plane to the static magnetic field.

3.1. ESR in EuB_6
Below 50K the ESR spectrum depends on the orientation of the sample plane to the static magnetic field. The position of the resonance field for the parallel and perpendicular orientation to EuB_6 plate is pointed in fig2 at T=22K. Such shift of the resonance lines is mainly determined by the demagnetizing fields. In our simplest case, where the external magnetic field is parallel or perpendicular to the sample plane, the position of the resonance line is calculated by the following well known formulas. The position of the magnetic resonance in parallel geometry at $\theta = 0$ is given by the expression

$$H_r(T) = \sqrt{H_{r0}^2 + 4\pi^2 M_{\text{eff}}^2(T)} - 2\pi M_{\text{eff}}(T)$$

(1)

where $H_{r0}$ is the resonance field at high temperatures (paramagnetic state) and $M_{\text{eff}}(T)$ is the effective magnetization. For a thin-plate sample in the magnetic field perpendicular to its plane ($\theta = 90^\circ$),

$$H_r(T) = H_{r0} + 4\pi M_{\text{eff}}(T).$$

(2)

Although these formulas are incompletely correct for a well-ordered ferromagnet near the Curie point, we use them for the rough description of the positions of the resonance lines.

Further we will examine the case, when external magnetic field is directed perpendicularly to the plane of the sample. At $T = 50K$ the ESR line is split into two lines with g factors of 1.95 and 2.06. (fig 1 and 2) and shifts of the g factors are $\Delta g = -0.05$ and $+0.06$, respectively, The intensity and temperature behaviour of the split lines are different. The ratio of the less intensive line (close circles in fig. 2) to the more intensive line (open squares) was 1:4. or 1.3.

The number of works [3, 7-9], directly points that magnetic and transport properties of EuB_6 can be explained by the existence of magnetic polarons. According to the magnetic phase diagram obtained in [7] for EuB_6, the region of polaron states begins at temperatures 40–30 K. Their appearance is accompanied by the self-localization of the charge carriers; this self-localization is a cause for the increase in the resistivity of europium hexaboride observed at 15 –40 K [11]. According to numerous investigations, no other features (e.g., structure changes, etc.) are observed in EuB_6 in this
temperature range. Therefore, the splitting of the EPR line into two lines is due to only the formation of the polaron. Since the temperature dependences of these two lines do not correlate with each other, we can conclude that there are two different regions of polaron states. Since \( g = 2.00 \), the more and less intense lines have the negative and positive shifts of the \( g \) factor, \( \Delta g = -0.05 \) and \( +0.06 \), respectively. We believe that the sign and value of the shift of the \( g \) factor from its value \( g = 2 \) for the free electron is obviously determined by the presence and character of the charge carriers interacting with a localized magnetic moment of the \( \text{Eu}^{2+} \) ion. In order for the shift \( \Delta g \) to be negative or positive, it is necessary to increase or decrease the local magnetic field acting on the \( \text{Eu}^{2+} \) ion, respectively. To this end, the magnetic moment of the localized spin must be parallel or antiparallel to the spins of the charge carriers, respectively. Kunes and Pickett [10] theoretically described the physical properties of \( \text{EuB}_6 \) in the model of the two-band: the antiferromagnetic (Kondo) coupling of the valence electrons with the local 4f magnetic moments and the ferromagnetic one (anti-Kondo) of the conduction electrons with the local 4f magnetic moments.

**Figure 1.** ESR spectra of europium hexaboride at different temperatures and the perpendicular orientation of the single crystal plane to the magnetic field. SM is the single crystal grown by flux melting, ZM1 and ZM2 are the single crystals grown by zone melting.

**Figure 2.** The temperature dependences of the resonance field \( H_r \) of the ESR-lines at the perpendicular orientation of the “zone melt” \( \text{EuB}_6 \) single crystal plate to the magnetic field. The magnetic resonance field \( H_r \) of the ESR signal for the parallel orientation at \( T = 22K \).
Thus, our data are experimental evidence that two types of coupling of free charge carriers—with Kondo and anti-Kondo couplings are formed in EuB₆. With a temperature decrease ferromagnetic ordering is observed in both (Kondo and anti-Kondo) phases, but ordering temperature $T_c$ and value of the magnetization $M$ of these phases are different. It is clear that Kondo phase has the lower values $T_c$ and $M$ than anti-Kondo phase. It is known that the value of the shift of ESR line into the high fields is proportional to the magnetization of the system.

At temperatures below 40 K the most intense line of EuB₆ shifts towards higher fields (see Figs. 1, 2), reaching 10 kG at a temperature of 15K. This is the first phase transition. It is connected with the ferromagnetic exchange of the magnetic polarons in the anti-Kondo phase. At $T = 13.5T$ this ESR line is shifted towards lower fields and the second line is shifted to the high field on towards the first. This is the region of the second phase transition. It is connected with exchange interaction between two spin subsystems (Kondo and anti-Kondo phases). The meeting of two ESR lines in the lower fields indicates that the exchange between two subsystems has an antiferromagnetic nature.

The sharp decrease in the resistivity observed in this temperature range [11] can be attributed to the delocalization of the charge carriers.

### 3.2. ESR in EuB₅.⁹₈C₀.⁰₂ and EuB₅.⁹₃C₀.⁰₇

In EuB₅.⁹₈C₀.⁰₂ we observed also the magnetic phase separation at $T = 45-50$K as in EuB₆. Then the more intensive ESR line is shifted into the large fields, reached only 4 kG, and the second line is shifted to the lower fields, i.e. the magnetization of this sample is lower then in EuB₆. Carbon ion substitutes the boron ion and brings one electron into the conduction band of EuB₆. The transport and magnetization investigations showed that carbon, doping in EuB₆, increases conductivity and decreases magnetization of the samples [11-13]. Even insignificant doping with carbon changes picture.

More stronger changes are observed into EuB₅.⁹₃C₀.⁰₇. At high temperatures the position and the shape of the ESR line in EuB₅.⁹₃C₀.⁰₇ were not differed practically from the position and the shape in EuB₆.

At $T = 135$K the ESR line is split into two lines as well as in the case of a pure EuB₆ (fig 3, 4). One of the lines has the negative g-shift and another one has the positive g-shift. We attribute this phenomenon to the formation of the magnetic polarons of two types: Kondo- and anti-Kondo coupling of europium localized magnetic moments with the charge carriers. However the formation of

![Figure 3. ESR spectra of the EuB₅.⁹₃C₀.⁰₇ at the different temperatures](image-url)
magnetic polaron occurs at the more higher temperature then in EuB₆ (T=40K). A tetravalent carbon substitutes a trivalent boron and acts as a single electron donor. The higher density of conduction electrons in EuB₅.₉₃C₀.₀₇ increases the RKKY exchange interaction between localize europium moments and therefore the magnetic structure is generating more rapidly. We observed another than in EuB₆ the temperature dependence of the two split lines. Now more intensive line belongs to Kondo-phase (with the antiparallel i.e.anti-ferromagnetic connection of valence electrons with the f- electrons of europium). It is shifted to the lower field. The less intensive line ( anti-Kondo-phase ) had a slight displacement to the high fields. It is clear that doping of the europium hexaboride by carbon reduces magnetization of the both phases. This means that the exchange interaction between additional conduction electrons carried by carbon and each of Kondo or anti-Kondo phases has antiferromagnetic nature. However, we see signal ESR i.e., the compensation for magnetic moments of both phases incomplete. It is possible that here as in EuB₅.₉₅C₀.₀₅ [13 -15] the magnetic structure can be presented as helimagnetic domain. Actually, Kondo phase, described by most intensive ESR line, consists of the complex ferro- and antiferromagnetic exchanges. EuB₅.₉₃C₀.₀₇ was investigated by ESR up to 74K. We saw a good ESR signals from Eu²⁺ at 76K, but already at 74K the ESR signals from both phases disappeared. This fact can be interpreted, in our opinion, by the antiferromagnetic exchange of two phases. System passed into the antiferromagnetic state with the complete compensation for magnetic moments. The reason of this process is probably a delocalization of the charge carriers, i.e. a destruction of the polaron of both phases.

![Figure 4.](image)

The temperature dependences of the resonance field of the ESR-lines at the perpendicular orientation of the EuB₅.₉₃C₀.₀₇ single crystal plate to the magnetic field. Lines are drawn for eye.

Our investigations showed that there are in EuB₅.₉₃C₀.₀₇ two phase transitions. The first transition is connected with the helimagnetic ordering of the most intensive Kondo- phase, the second transition is connected with the delocalization of the charge carriers of both phases and the passage of entire system in the uniform antiferromagnetic state.

One of the most interesting and requiring further studies is the fact of the very high temperatures of magnetic phase separation - 130K and the phase transition of 74K in EuB₅.₉₃C₀.₀₇.

Until now phase transitions in hexaboride of europium, clean and alloyed by different admixtures were observed only at low temperatures; in the carbonized samples, for example, at 7 -18 [11-13].

4. Conclusion
The EuB₆₋ₓCₓ , where x = 0, 0.02 and 0.07, have been investigated in the temperature range 10–300 K. A single ESR line from Eu²⁺ is observed in the room temperature. With a further decrease in the
temperature, it is split into two lines: at 40-50K in EuB$_6$ and EuB$_{5.98}$C$_{0.02}$ and at 130K in EuB$_{5.93}$C$_{0.07}$.
An analysis of the ESR spectra indicates that the magnetic phase separation of EuB$_{6-x}$C$_x$ are observed.
It is due to the formation of the bound states of the magnetic moments of Eu$^{2+}$ ions with the
conduction electrons and valence electrons (holes). We have observed two different types of coupling
between the localized europium spins and charge carriers: Kondo coupling with holes (or valent
electrons) and anti-Kondo coupling with conduction electrons. The interaction of the charge carriers
with localized magnetic moments in europium hexaboride is likely accompanied by the self-
localization of free charge carriers and the formation of magnetic polarons of two types. It was
observed 2 phase transitions in all single crystals. The first phase transition is connected with ferromagnetic ordering of the more intensive anti-Kondo phase in EuB$_6$ and EuB$_{5.98}$C$_{0.02}$ at 15-16K
and the helimagnetic ordering of the more intensive Kondo phase in EuB$_{5.93}$C$_{0.07}$ at 76K. The second
phase transition is connected with antiferromagnetic interaction between Kondo and anti-
Kondo phases. In this case the delocalization of the charge carriers occurs and the system passes on a
homogeneous state.

Acknowledgments
The work was supported by grants from RFBR and Presidium of RAS.

References
[1] Degiorgi L, Felder E, Ott H R, Sarrao J L and Fisk Z 1997 Phys. Rev. Lett. 79 5134
[2] Sulow S, Prasad I, Aronson M C, Sarrao J L, Fisk Z, Hristova D, Lacerda A H, Hundley M F,
Vigliante A and Gibbs D 1998 Phys. Rev. B 57 5860
[3] Sulow S, Prasad I, Aronson M C, Bogdanovich S, Sarrao J L and Fisk Z 2000 Phys. Rev. B 62
11626
[4] Deisenhofer J, Braak D, Krug von Nidda H-A and Eremina R M 2005 Phys.Rev. Lett. 95
257202
[5] Badrutdinov A O, Zarubezhnova E M, Talanov Yu. I. et al 2007 JETP, 105 79
[6] Kasaya M, Tarascon J M, Etourneau J and Hagenmuller P 1978 Mater. Res. Bull., 13 751
[7] Snow S, Cooper S L, Young D P, Fisk Z, Comment A and Ansermet J P 2001 Phys.Rev. B 64
174412
[8] Calderon M J, Wegener L.G.L and Littlewood P B 2004 Phys.Rev. B 70 092408
[9] Yu U and. Min B I 2006 Phys.Rev. B 74 094413
[10] Kunes J and Picket W E 2004 Phys.Rev. B 69 165111
[11] Tarascon J M, Etourneau J, Dordor P, Hagenmuller P, Kasaya M and Coey J M D 1980 J. Appl. Phys. 51(1) 574
[12] von Molnar S, Tarascon J.M and Etourneau J 1981 J. Appl. Phys. 52 2158