Effect of Anisotropy in Temperature Dynamics of Magnetic Phase Separation in Europium Hexaboride

T.S. Altshuler 1, Yu.V. Goryunov1, N.Yu. Shitsevalova2, A. Dukhnenko2
1 Zavoiskii Physical-Technical Institute, Russian Academy of Sciences, Sibirskii trakt 10/7, Kazan 29, 420029 Russia
2 Frantsevich Institute of Materials Science Problems, National Academy of Sciences of Ukraine, ul. Krzhizhanovskogo 3, Kiev, 03680 Ukraine

E-mail: gorjunov@kfti.knc.ru

Abstract. The ESR measurements of the EuB6 single crystal samples were executed on frequency 9.25 GHz in TE102 rectangular cavity in the temperature range from 15 to 300 K. We used samples of identical form and size, but different crystallographic orientation to estimate their magnetization. At T = 30 - 40K was observed the magnetic phase separation, which, most likely, is accompanied also by charging separation. The anisotropy magnetization of more intensive magnetic phase (with anti-Kondo interaction) along the different crystallographic directions was found above a temperature of the ferromagnetic transition. We conclude that this result connect with existence the ferronic states and charging separation in the EuB6 single crystal. Estimations of angular distribution of the magnetic moment of ferrons in EuB6 are made.

1. Introduction
The formation of inhomogeneous spin and charge states in compounds with colossal magneto-resistance, the magnetic phase separation has been actively discussed in recent years (see, e.g., [1]). Unfortunately, most such compounds have a sufficiently complex crystal structure, which complicates the interpretation of the experimental data. The exception is europium hexaboride EuB6 with a simple crystal structure similar to cesium chloride. Europium hexaboride EuB6 is a ferromagnet; the perfect samples of this ferromagnet undergo two magnetic phase transitions at 15–16 and 12–13 K. They are accompanied by the appearance of colossal negative magnetoresistance. However, despite numerous experimental and theoretical investigations (see, e.g., [2–5]), many problems concerning the nature of ferromagnetism, the phase transition, and the relation between the magnetic and electron properties remain unclear. The electron paramagnetic resonance (EPR) is one of the most efficient methods for investigating the magnetic systems. In this work, we investigate the anisotropy of magnetization in EuB6 single crystals in non-ferromagnetic state by ESR method.

2. Experiment
The EPR measurements were performed at a frequency of 9.25 GHz in a TE102 rectangular cavity at the temperatures 10 - 300 K. The europium hexaboride single crystals were grown using two methods: zone melting (ZM) and solution in melt (SM). The lattice parameters of the ZM and SM samples are 4.184679 ± 0.000015 Å and 4.182543 ± 0.000015 Å, respectively, in agreement with ref. [3]. The measurements of the temperature dependences of the ESR spectra for thin single crystal plates were
performed for the perpendicular and parallel orientations of the plate with respect to the magnetic field. A single ESR line from the bivalent europium Eu$^{2+}$ with a g factor of 1.96 and a width of $\Delta H \sim 800$ Oe is observed at room temperature for all samples (see Fig. 1). The lineshape is Lorentzian with Dyson distortions due to the skin layer [6].

Bivalent europium has ground state is purely spin $S = 7/2$ and g factor close to 2. The Eu$^{2+}$ ion has the electron spin $S = 7/2$ and two stable isotopes with a nuclear spin of 5/2; 84 resonance lines should be observed. The absence of the fine and hyperfine structures is associated with the averaging due to strong exchange interactions. The Lorentzian lineshape can also indicate the strong exchange. When the temperature decreases to 50 K, the position and EPR lineshape are independent of the orientation of the sample. With a further decrease in the temperature, the continuous splitting (first manifested as a shape distortion) of the single resonance line into two lines with g factors of 1.95 and 2.06 is observed. The behaviours of the angular and temperature dependences of the ESR spectra for samples prepared using different methods are qualitatively the same. For this reason, we present the experimental data for the ZM sample in figures. 2 and 3. The behaviours of the split lines are different. When the sample plane is perpendicular to the static magnetic field, the most intense line shifts towards higher fields. In case of the orientation of sample along sweep magnetic field ESR spectrum shifts towards lower fields. (see Figures. 1, 2).

3. Results and discussion

The resonance magnetic field for a strong magnet is determined by many factors such as the crystal magnetic anisotropy, Neel anisotropy, and demagnetizing and internal exchange fields. In our case, according to [3], where the magnetic properties of EuB$_6$ were investigated, its magnetic anisotropy is weak and can be disregarded, because the observed strong shift of the resonance line with a decrease in the temperature cannot be attributed to a change in the magnetic anisotropy constant. The Neel contribution behaving as demagnetizing fields [6] also cannot be large, because it is associated with the violation of the symmetry of the environment of the Eu$^{2+}$ ion only on the sample surface. Thus, only the demagnetizing fields remain. 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 (1)

$$H_r(T) = \sqrt{H_{r0}^2 + 4\pi^2M_{\text{eff}}^2(T)} - 2\pi M_{\text{eff}}(T)$$  \hspace{1cm} (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 ($\theta = 90^\circ$),

$$H_r(T) = H_{r0} + 4\pi M_{\text{eff}}(T)$$  \hspace{1cm} (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. From formulas (1) and (2) with the measured resonance fields for the perpendicular and parallel orientations of the sample plane with respect to the static magnetic field, the effective magnetization $4M_{\text{eff}}$ at 20 K is determined as 2020 and 2380 G, respectively. Since the difference is about 15%, the shift of the resonance lines is mainly determined by the demagnetizing fields.

Some reasons of the splitting of the EPR line at 40 K in EuB$_6$, has discussed in ref. [12-14]. In the present work we have found out that character of splitting depends on a direction of crystal axes relative a sweep magnetic field. This is an additional argument in favour of the main reason of splitting of a ESR line - formation in the sample of magnetic phase heterogeneity, and also the new interesting result, concerning properties of a polaron state.

Figure 3 shows the calculations of the effective magnetization with the use of the resonance fields of main resonance line for the EuB$_6$ sample in different crystal axis at $\theta = 90^\circ$. The maximum effective magnetization of the first phase is $4\pi M_{\text{eff}} = 6120$ G for sample with deviation 16° of [100] axis from normal. Taking into account that the spin subsystem includes about 80% of all spins (recall that the ratio of the intensities of the EPR lines for this sample is 1 : 4.5), we obtain a value of the average magnetic moment of the Eu$^{2+}$ ion about 5.2 $\mu_B$, whereas a value of 6.9 $\mu_B$ is known from the neutron experiments [7]. The estimation of average magnetic moment of the Eu$^{2+}$ ion for second phase gives about 5.6 $\mu_B$. Taking into account the errors in the initial approximations, not complete ordering of the magnetic moments such an agreement between the resulting values should be treated as good.

Thus, our estimates of the magnetization are evidence of a magnetic phase separation in the EuB$_6$ and dependence of its temperature dynamics on mutual orientation magnetic field and crystal axis.

In a number of works [5, 9–11], it was shown that the magnetic and transport properties of EuB$_6$ can be explained by the existence of magnetic polarons, which are bound states of conduction electrons and localized moments, in this compound. According to the magnetic phase diagram obtained in [10]
for EuB₆, the region of polaron states begins at temperatures 40–30 K. Their appearance is accompanied by the self-localization of the conducting charge carriers; this self-localization is a cause for the increase in the resistivity of europium hexaboride observed at 40–15 K. As mentioned above, the more and less intense lines have the negative and positive shifts of the g factor. 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 charge carriers interacting with a localized moment. 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 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. Using the local density approximation, Kunes and Pickett [11] theoretically described the physical properties of EuB₆ in the model of the two-band Kondo lattice with the parallel (ferromagnetic) coupling of the conduction electrons and antiparallel (antiferromagnetic) coupling of the valence electrons with local 4f moments. Thus, this work is experimental evidence that two types of coupling of free charge carriers—with Kondo and anti-Kondo couplings—are formed in EuB₆ at temperatures below 40 K.

In respect to the method applied to study of the EuB₆ it is necessary to mention [12]. The paper [12] is in essence methodical, it is reduced to the negation of the possibility of the data acquisition about the magnetic state of europium hexaboride (and obvious by of others magnetic non-uniform systems) in the ESR experiments and ignores the discussion [13, 14] about the experimental ESR data in [12] early published in [13]. The basic physical result of our present work, the detection of the magnetization anisotropy in europium hexaboride at the temperatures above the temperature of ferromagnetic ordering is doubtless. The observed effect is definitely connected with magnetization and with its anisotropy.

4. Conclusion
The EPR in EuB₆ has been investigated in the temperature range 10–300 K. An analysis of the EPR spectra and estimate of the magnetic moments of europium obtained from the magnetization curves of both lines indicate that the magnetic phase separation of EuB₆ is observed. Temperature dynamic of magnetic phase separation depends on orientation external magnetic field relative crystal axis. 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). 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 (ferrons) of two types. The polarization of polarons in magnetic field depends on its direction relative crystal axis.

This work was supported by the RFBR (project No. 09-02-00727a) and program of the RAS No.P-05.

References
1. M. Yu. Kagan, A. V. Klapcov, I. V. Brodskii, et al., Phys. Usp. 46, 851 (2003)
2. L. Degiorgi, E. Felder, H. R. Ott, et al., Phys. Rev. Lett. 79, 5134 (1997)
3. S. Sulow, I. Prasad, M. C. Aronson, et al., Phys. Rev. B 57, 5860 (1998); B 62, 11626 (2000).
4. R. R. Urbano, P. G. Pagliuso, C. Rettory, et al., Physica B 354, 326 (2004).
5. F. J. Dyson, Phys. Rev. 98, 349 (1955); M. Peter, D. Shaltiel, J., et al., Phys. Rev. 126, 1395 (1962).
6. Yu. V. Goryunov, N. N. Garif'yanov, G. G. Khaliullin, et al., Phys. Rev. B 52, 13450 (1995).
7. W. Heggeler, H.-R. Ott, D. P. Young, and Z. Fisk, Solid State Commun. 108, 929 (1998).
8. P. Nyhus, S. Yoon, M. Kaufman, et al., Phys. Rev. B 56, 2717 (1997).
9. C. S. Snow, S. L. Cooper, D. P. Young, et al., Phys. Rev. B 64, 174412 (2001).
10. V. V. Glushkov, A. V. Bogach, K. V. Gonkov, et al., Zh.Eksp. Teor. Fiz. 132, 150 (2007)
11. J. Kunes and W. E. Pickett, Phys. Rev. B 69, 165111(2004).
12. A. V. Semeno, V.V.Glushkov et al., Phys. Rev. B 79, 014423 (2009),
13. S.V. Demishev, A.V. Semeno et al. JETP Letters, 88,777(2008)
14. T.S. Altshuler, Yu.V. Goryunov, JETP Letters, 88,779(2008); JETP Letters, 88,224(2008)