Paramagnetic Curie Temperature of EuB$_{6-x}$C$_x$ from ESR data

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Abstract. The ESR measurements of the EuB$_{6-x}$C$_x$ (x<0.1) single crystal samples were performed on frequency 9.25 GHz in TE$_{102}$ rectangular cavity in the temperature range from 10 to 300 K. We found that the single-crystal europium hexaboride with substituting 2% of boron by carbon behaves in fields around 0.4 T along the [111] - direction as a ferromagnetic, while for field along the [100] - direction its behavior resembles the behavior of an antiferromagnetic.

1. Introduction

It is known, that complex forms of magnetic order are realized in rare-earth compounds. However, unusual behavior of these compounds may be also in paramagnetic region. Earlier, we have observed [1] in single crystal of europium hexaboride the anisotropy of the induced magnetization $M$, which associated with anisotropy magnetic susceptibility. Unusual behavior of magnetic susceptibility in paramagnetic state was observed by other researchers [2, 3]. A practice shows that the method of electron magnetic resonance (ESR) may be useful for the selective measurement of magnetic susceptibility. It is well known that the intensity of the ESR spectrum is proportional to the magnetic susceptibility of the sample. In general, the magnetic susceptibility $\chi$ is a tensor and components of vector of magnetization are associated with components of magnetic field vector as follows:

$$M_i = \sum_{j} \chi_{ij} \cdot H_j \quad (1)$$

In this approximation the magnetic susceptibility dependence on magnetic field and temperature can be presented as follows:

$$\chi = \frac{\mu_0 \mu_B g_e}{2 H_0} \left( (2S + 1) \coth \left( \frac{(2S + 1) \mu_B g_e H_0}{2kT^*} \right) - \coth \left( \frac{\mu_B g_e H_0}{2kT^*} \right) \right) \quad (2)$$

$$T^* = T + \Theta_p; \quad \Theta_p = \frac{1}{3} k S(S+1) \Sigma J_{ij},$$

where $H_0$ – magnetic field, $M$ – magnetization , $T$ – temperature, $\Theta_p$ - paramagnetic Curie temperature $J_{ij}$ – exchange integral of the $i$ - $j$- atom interactions.

In this regard, the components of magnetization can have not a proportional relation with the components of the external magnetic field and the Curie-Weiss's law can be different for different directions. Thus, paramagnetic Curie temperature can be anisotropic in case of anisotropic exchange interaction. Present work is devoted to experimental study of this question.
2. Results and Discussion

2.1. Experimental details
The ESR measurements of the EuB6 single crystal samples were performed on frequency 9.25 GHz in TE_{102} rectangular cavity in the temperature range from 10 to 300 K. We used samples of identical form and size but different orientation of crystal axis, to estimate the temperature dependences of the ESR spectra parameters, namely: resonance field, linewidth, intensity, lineshape. Paramagnetic Curie temperature was estimated by measuring the temperature dependences of inverse intensity of ESR signal. The induced by magnetic field magnetization of the sample was studied by measuring the shift of the resonance line under the influence of the demagnetizing field at perpendicular orientation of the sample plane to external magnetic field as [1, 4].

2.2. Influence of Carbon concentration on Magnetic order and Paramagnetic Curie temperature
As a rule, in temperature range 150 -300 K lineshape was lorentzian shape with dysonian distortion. Also as in [4], at T = 10 – 30 K was observed the magnetic phase separation in samples with small impurities of carbon. For sample with more content of carbon splitting of single ESR line was observed at higher temperature and the dependences of resonance field and linewidth are quite different. Figure 1 shows the temperature dependence of the inverse ESR intensity of the spectrum for the orientation of the plates [100] pure europium hexaboride and europium hexaboride, in which 7% of boron substituted carbon. Dependence in figure 1a is a classic example of the temperature dependence of the susceptibility of the ferromagnet. Dependence in figure 1b is a typical temperature dependence of susceptibility for not compensated antiferromagnet - ferrimagnet. These curves show quite high in comparison with the magnetic ordering temperature paramagnetic Curie temperature with opposite signs. A sample of europium hexaboride single crystal plate in the orientation [100] with a smaller (2%) admixture of carbon also showed negative a paramagnetic temperature. Thus, the substitution of boron with carbon leads to a monotonic amplification of antiferromagnetic properties of europium hexaboride.

![Graph](image1)

**Figure 1.** The temperature dependence on inverse intensity of the ESR spectrum of the EuB_{6-x}C_x single crystal.

2.3. Influence of Magnetic field direction on Paramagnetic Curie temperature
Earlier in [1], we found a strong anisotropy of the induced magnetization of pure europium hexaboride (see Fig. 2). For pure hexaboride this anisotropy was in considerable amplification of the magnetization along [111] direction. Also, there is an amplification of the ferromagnetic properties along this direction and to antiferromagnetic samples with impurity carbon. This is most clearly evident for the samples of the EuB_{6-x}C_x. We found that the single-crystal europium hexaboride with substituting 2% of boron by carbon behaves in fields around 0.4 T along the [111] - direction as a
ferromagnetic, while for field along the [100] direction its behavior resembles the behavior of an anti-ferromagnetic

![Magnetization](image)

**Figure 2.** Effective magnetization induced by resonance magnetic field along different crystal axes of the EuB₆ sample for various temperatures.

Paramagnetic Curie’s temperature was about +8 K in case an external magnetic field parallel to [111] axis and it is negative temperature about -7 K for the magnetic field along the [100] axis (see fig. 3).

![ESR](image)

**Figure 3.** Temperature dependences of the inverse intensity of the ESR spectra for two orientations of the EuB₆ single crystal in sweep magnetic field.

It should be noted that for the orientation [100] the deviation of inverse susceptibility from the linear dependence is similar to figure 2, but point Tₘ finds at lower temperatures.

2.4. Structure of EuB₆ and the role of boron in the indirect exchange interaction between Eu ions

From the viewpoint of possibility of implementing those or other interactions between ions europium it is useful to consider the structure of europium hexaboride more detail than is usually done. As is
known, the structure of europium hexaboride represents two inserted into each other the simple cubic lattices of europium ions and B$_6$ octahedra with size of the cube 4.18 Å. In general, the boron octahedra are also charged, negatively, and they have a deficiency of valence electrons.

Assuming equidistant (1.73 Å) of the boron-boron bonds we obtain that europium ion is surrounded by 24 boron atoms, placed on a sphere of radius 3.08 Å. The 24 atoms are organized in a triples of boron atom from 8 different octahedra B6. The spheres have a common boron atoms in the directions {100} and {110}, and in the direction of {111} there were none. In other words, the planes (111) of an europium ions are separated by two planes of boron atoms, the planes (100) of an europium ions are separated by a single layer of boron atoms and the planes (110) contain a boron atoms.

Direct exchange interaction between europium magnetic moments is practically excluded in such an environment of 24 boron atoms. Conventional RKKY interaction can not be effective due to the small number of electrons in the conduction band. From effective mechanisms of the indirect exchange interaction remain the mechanisms of indirect exchange via the valence electrons, namely superexchange Kramers-Anderson [8-10] and the modified RKKY-interaction [11] Bloembergen-Rowland [12]. These mechanisms are practically indistinguishable for such alternation of layers.

Indirect exchange interaction (superexchange Kramers-Anderson) via p-orbitals has a anisotropic character, it can be both antiferromagnetic and ferromagnetic, thus leading to the formation of helical magnetic structures [6, 7]. In our case, assuming a character of indirect exchange interaction via sp-orbitals of boron is antiferromagnetic, we automatically obtain the same for directions {100} and {110}, and the ferromagnetic exchange for the directions {111}. It should be also noted that the boron-boron bonds have the directions only {100} and {110}.

Because the sp-orbitals boron of the octahedra impede to the direct moving of the valence 4f electron from one europium ion to other ion, the localized 4f- electrons impede the free movement of sp-electrons, forming with them the bound states.

The appearance of free electrons leads to filling of sp-hybrid orbitals of the octahedra B$_6$, which should lead to their local compression, as by strengthening the real covalent bonds, and due to their compression by positive ions europium which are attracted to the excess negative charge of the B$_6$ octahedra. In fact, this is the formation of lattice polarons with the ferromagnetic axis along the {111} direction and symmetry breaking. In this case, the behavior of the B$_6$ octahedron is somewhat similar the behavior of the Jahn-Teller ion.

3. Conclusion

Thus, summing up the discussion, we conclude the following. The external magnetic field changes the distribution of spin density in electron shells by means polarization of the localized spins and these shells, thereby changing the character of the exchange interaction depending on the direction of the external magnetic field. Changing the exchange integrals leads to a change in the average energy of interaction between the localized moments, to the change of the magnetic structure in the ground state and, consequently, a change in the paramagnetic Curie temperature.

Acknowledgments

This work was supported by grants from RFBR and Presidium of the RAS.

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