Detection of the Influence of the Magnetic Field Direction on a Paramagnetic Curie Temperature of EuB$_{6-x}$C$_x$

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Abstract. For the first time found that the Curie-Weiss law depends on the crystallographic direction along which the measuring field is directed. The ESR measurements of the EuB$_{6-x}$C$_x$ ($x<0.1$) single crystal indicated that the sample with $x = 0.02$ behaves in fields along the [111] direction as a ferromagnetic, while for field along the [100] - the anti-ferromagnetic behavior.

1. Introduction

Complex forms of magnetic ordering, which are realized in the compounds of rare earth metals may be due to effects such as Jahn-Teller's effect occurring in the anionic complexes of these compounds under the influence of the magnetic field. There is suspicion of such behavior in respect europium hexaboride. Recently we have observed [1] in single crystal of europium hexaboride the anisotropy of magnetic susceptibility as anisotropy of induced magnetization $M$. Such behavior of magnetic susceptibility in paramagnetic state is observed by other researchers [2, 3]. In general, the magnetic susceptibility $\chi$ is a tensor and components of magnetization can have not a proportional relation with the components of the external magnetic field and the Curie-Weiss's temperature can be different for different directions. Curie-Weiss’s temperature can be anisotropic in case of anisotropic exchange interaction, it can depend on magnetic field direction and its value, it can indicate on magnetic quantum transition.

2. Results and Discussion

2.1. Experimental details

The ESR measurements were performed on frequency 9.25 GHz in TE$_{102}$ rectangular cavity at the temperature 10÷300 K. We used for measurements the EuB$_6$ single crystal 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. The crystals were grown by zone melting as [1,4]. Curie-Weiss’s temperatures were estimated by measuring the temperature dependences of inverse intensity of ESR signal. The induced by magnetic field magnetization of the sample was measured 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 [1, 4].

2.2. Influence of Magnetic field direction on Curie-Weiss’s temperature.

Observed ESR line had lorentzian shape with dysonian distortion in temperature range 150 -300 K. Also as before (see [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 the 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 dependences of resonance fields and linewidth of the ESR for the two orientation of the plates [100] and [111] EuB$_{5.98}$C$_{0.02}$ single crystal sample. Dependence in figure 1a is a classic example of the temperature dependences for the strong paramagnet. Dependence in figure 1b is a typical temperature dependences for case the strong paramagnet with strong magnetic fluctuation.

Recently in [1], we found a strong anisotropy of the induced magnetization of pure europium hexaboride. 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 for anti-ferromagnetic samples with impurity carbon. This is most clearly evident for the samples of the EuB$_{5.98}$C$_{0.02}$. We found (see Fig. 2) that the single-crystal europium hexaboride with substituting 2% of boron by carbon behaves in fields around 4 kOe along the [111] - direction as a ferromagnetic, while for field along the [100] - direction its behavior resembles the

Figure 1. The temperature dependences on resonance fields and linewidth of the ESR in the EuB$_{5.98}$C$_{0.02}$ single crystal sample.

Figure 2. Temperature dependences of the inverse intensity of the ESR spectra for two orientations of the EuB$_x$ single crystal in sweep magnetic field.

Figure 3. The ESR spectrum for the EuB$_{5.98}$C$_{0.02}$ [111] single crystal sample for perpendicular orientation of the sweep magnetic field to the sample plate. There is The low field features is not for [100] sample.
behavior of an anti-ferromagnetic. Namely, paramagnetic Curie-Weiss’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. It should be noted that for the orientation [100] the deviation of inverse susceptibility from the linear dependence (see Fig. 2) is similar to sample with content of carbon x = 0.07, but point T_c finds at lower temperatures. Difference in the behaviour of the EuB_6 samples for orientations of external magnetic field along the [111] and [100] at low temperatures is evident not only in the behavior of the linewidth, but also in views of the ESR spectra. Anomaly in dependence of the first derivation of absorption dP/dH on H, which is visible in the spectrum on Fig. 3 for the [111] orientation is absent for the same spectra in the orientation [100]. We attribute this spectral feature with the reorientation of the spins of europium ions along the [111] direction.

2.3. Influence of Carbon on Magnetic order and Curie-Weiss’s temperature.
A direct consequence the results of section 2.2 is a distinction between the dependences of the paramagnetic Curie temperature on carbon concentration for different crystallographic directions. Figure 4 shows the Curie – Weiss’s temperature dependences on the carbon impurities concentration obtained earlier [5] and by us in this work. The figure clearly shows that dependence for the [100]-direction is very different previously known results [5], obtained without taking into account the effects of anisotropy, and it is almost identical with them to the [111]. Indirect exchange interaction is more ferromagnetically in the [111] direction, whereas for other crystal direction it is significantly weakened or even can change sign. Thus, upon application of the measuring field along the [111]-direction with a total antiferromagnetic order arises ferromagnetic component, which manifests itself as a reorientational transition in low fields region of spectra (see Fig.3).

2.4. Structure of EuB_6 and the role of boron in the indirect exchange interaction between Eu ions.
As well known, the structure of europium hexaboride represents two inserted into each other the simple cubic lattices of europium ions Eu^{2+} and B_{6} octahedra with lattice constant 4.18 Å. (CaB_{6}-type structure, space group Pm3m). In general, the boron octahedra are charged negatively and they have a deficiency of valence electrons. Moving an electron from one octahedron to another should cause to expansion of one and compression another octahedron due to the strengthening of the covalent bonds.

Assuming equidistant of the B-B bonds we obtain that Eu^{2+} ion is surrounded by 24 boron atoms, placed on a sphere of radius 3.08 Å. The spheres have a common boron atoms in the directions \{100\} and \{110\}, and in the direction of \{111\} there are not a common boron atoms. In other words, the planes (111) of Eu^{2+} ions are separated by two planes of boron atoms (Eu-B-B-Eu, FM-supertexchange), the planes (100) of Eu^{2+} ions are separated by a single layer of boron atoms and the planes (110) contain a boron atoms (Eu-B-Eu AFM-supereexchange). Direct exchange interaction between Eu^{2+} magnetic moments is practically excluded. 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 [6,7] and the modified RKKY-interaction [8] Bloembergen-Rowland [9]. These mechanisms are practically indistinguishable for such alternation of layers.

Indirect exchange interaction (superexchange Kramers-Anderson) via p-orbitals has an anisotropic character, it can be both antiferromagnetic and ferromagnetic, thus leading to the formation of helical magnetic structures [10, 11]. 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 B6, 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 B6 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 B6 octahedron is somewhat similar the behavior of the Jahn-Teller ion. The decrease in lattice energy due to compression promotes self-localization of free electrons.

3. Conclusion
Thus, summing up the discussion, we conclude that we have detected the influence of magnetic field direction on view of the Curie-Weiss’s temperature dependence on the impurity concentration. 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 Curie-Weiss’s temperature. This means that not such simple behavior of the Curie-Weiss's temperature can point on the magnetic quantum transition associated with the restructuring of the electronic structure of compounds under the influence of a magnetic field and impurities.

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