Unusual Magnetism of the Eu Based Compounds – EuB$_{6-x}$C$_x$, EuZn$_2$As$_2$: the Low Temperature ESR Study

Yu V Goryunov $^1$, A V Levchenko $^2$, A N Nateprov $^3$

$^1$ Kazan Physical-Technical Institute of the RAS, 420029, Kazan, Russia
$^2$ Institute of Material Science Problems of the NASU, 03680, Kiev, Ukraine
$^3$ Institute of Applied Physics of the ASM, 2028, Kishinev, Moldova

e-mail: gorjunov@kfti.knc.ru

Abstract. The ESR study in EuZn$_2$As$_2$ powder and EuB$_{6-x}$C$_x$ (x<0.1) single crystal samples was performed at the frequency 9.3 GHz in the temperature range 4.2 - 300 K. The observed resonance line with the g-factors 1.96 of the Eu$^{2+}$ ions was symmetric and it was described very good by a Lorentzian lineshape at temperatures above 120 K. We found that the single-crystal EuB$_{6-x}$C$_x$ with x =0.02 behaves in fields around 0.4 T along the [111] - direction as a ferromagnetic, while along the [100] - direction its behavior is similar to anti-ferromagnetic. Also antiferromagnetic EuZn$_2$As$_2$ shows positive paramagnetic temperature Curie. Both compounds showed signs of the spin-flop transition in the ESR spectrum at low temperatures.

1. Introduction

Earlier, we have observed [1] in the EuB$_6$ single crystal the anisotropy of induced magnetization $M$, which associated with anisotropy magnetic susceptibility. Unusual behavior of magnetic susceptibility is observed by other researchers [3]. Rare-earth compounds are known those, that complex forms of magnetic order are realized in their. However, unusual magnetism of these compounds is seen also in paramagnetic region. As a practice shows the method of electron magnetic resonance is not replaced for the selective magnetic measurement. 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 vector of magnetization are associated with magnetic field $H$ as follows: $M_i = \sum \chi_{ij} H_j$.

In this approximation magnetic susceptibility depends on magnetic field and temperature by complex manner (see, for instance [5]). 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 and magnetic field.

2. Results and discussion

2.1. Experimental details

The ESR measurements of the EuB$_6$ single crystal samples were performed on frequency 9.3 GHz in TE$_{102}$ rectangular cavity in the temperature range from 4.2 to 300 K. We used single crystal EuB$_6$ 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.
Single crystals of the EuB_{6-x}C_{x} \ (x\leq0.1) were grown by zone melt method. EuZn_{2}As_{2} was prepared by direct reaction of the stoichiometric amounts of Zn, As, B (99.99 %) and Eu (99.99 %) in an Al_{2}O_{3} crucible enclosed in an evacuated quartz ampoule. The trigonal CaAl_{2}Si_{2}-type crystal structure (space group \textit{P3} \textit{m1}) and cubic CaB_{6}-type (space-group \textit{Pm3m}) were confirmed by X-ray diffraction. 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 measured by measuring the shift of the resonance line under the influence of the demagnetizing field [1,3].

2.2. Resonance fields, linewidth and g- factor
The observed single resonance lines of the Eu^{2+} ions were symmetric and they are described very good by a Lorentzian lineshape with linewidths 500 - 900 Oe at temperatures above 120 K. Position and width of the resonance lines were not changed and the g-factors was 1.96 in this temperature range. Eu^{2+} ion has the electron spin 7/2 and two isotopes with a nuclear spin of 5/2. Therefore 84 resonance lines should be observed. The absence of the fine and hyperfine structures is associated with the averaging due to strong exchange interactions. At the temperature decreasing we were observed an exponential-like increasing of linewidth and a decreasing of the resonance field, indicating the magnification of antiferromagnetic fluctuations and the molecular Weis's field. Large deviation of the g-factor (\Delta g \sim 0.03) from 2.0 (free electron, [4]) indicates on the strong hybridization of the f-electron states Eu with the sp-states of the band electrons. Since 4f\textsuperscript{7} configuration of the Eu\textsuperscript{2+} ions is pure spin state \textit{s}\textsuperscript{7/2}, the resultant orbital momentum equal to zero. The crystal field may split its ground state. In a crystalline field of cubic symmetry, the averaged energy of the spin-spin interaction between electrons of a single paramagnetic ion does not depend on their orientation and the ground state ion is completely degenerate in spin. The crystal field of lower symmetry deforms the ion electronic cloud and the spin degeneracy is lifted. However, these interactions leading to change in g-factor leaving its isotropic. Given that the ESR measurements of the EuZn_{2}As were made on the powder sample, the resonance line symmetry allows to conclude that we are dealing with a real resonance line with isotropic g-factor, but not with the convolution of the line with an anisotropic g- factor.

2.3. Intensity of the ESR line.
Intensity of the ESR spectrum is proportional to magnetic susceptibility of a spin systems. If there are not effects which influence on quantity of spins, we have selective susceptibility of spin sub-system. Peculiarities in the behavior of the spectrum baseline ESR is usually associated features of the dependence of microwave surface impedance of the sample on the magnetic field. These relationships can be caused by mutations occurring in the spin system under the influence of an external magnetic field, magnetoresistance, superconductivity. Features, associated with the magnetoresistance, have the following character with decreasing temperature. Originating in the high fields they move to low field. Features, associated with superconductivity, have the opposite character. Nucleating at low fields, they quickly move to the high fields. In addition, this features are significantly stronger than the intensity of the resonance lines. The most suitable explanation for our case of the low field ESR features of the spectrum is the restructuring of the spin system EuZn_{2}As_{2} in relatively small fields. If we turn to the previously investigated similar compounds EuZn_{2}Sb_{2} [2], we see that in fields less than 400 Oe is the spin-flop transition in the magnetic sub-lattices of the antiferromagnet. In our case, the region of features of the baseline, which we associate with the spin-flop transition, begins with a temperature slightly higher than the Neel temperature, determined by the maximum intensity of the ESR. This may be due to the induced external magnetic field induced ferromagnetic order on the background of strong antiferromagnetic fluctuations. The changing of intensity of the ESR line with temperature corresponds to a typical temperature dependence of the susceptibility of an antiferromagnet. However, it should be emphasized that, unlike the typical for antiferromagnet negative paramagnetic Curie-Weiss temperature \theta_{CW} we obtained positive \theta_{ESR} and significantly greater than the Neel’s temperature \textit{T}_{N}. This fact of positiveness paramagnetic Curie-Weiss tempereature for the antiferromagnet is
confirmed by direct measurements of the dc susceptibility. The obtained values of the paramagnetic temperatures were quite close. $\theta_{ESR} = +20.4$ K and $\theta_{CW} = +21.2$ K.

2.4. 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. 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. 1). The obtained by us positive values of paramagnetic Curie temperature for investigated antiferromagnets can be explained by the magnetic phase transition (spin-flop transition) under the influence of the magnetic field. This is confirmed by ESR spectra characteristics of both compounds at low fields (see Fig. 2). These observations raise the question of change of the magnetic structure (main state) of the compounds under the influence of the magnetic field at zero temperature.

2.5. Structure of compounds and the role of anion complex in the indirect 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.

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 [7] and the modified RKKY-interaction [8] Bloembergen-Rowland [9]. These mechanisms are practically indistinguishable for such cases. The localized 4f$^2$ electrons impede the free movement of sp - electrons, forming with them the bound states.

Quite similarly we can consider the indirect interaction of europium ions through the orbitals of anionic complexes Zn$_2$As$_2$, role of which in the structure of the EuZn$_2$As$_2$ pnictides are similar to the B$_6$ complexes. The appearance of free electrons leads to filling of sp-hybrid orbitals, which should
lead to their local compression by strengthening the real covalent bonds. In fact, this is the formation of a lattice polarons and symmetry breaking. In this case, the behavior of the anion complexes is somewhat similar the behavior of the Jahn-Teller ion.

3. Conclusion

Thus, we can conclude on the base of obtained data that EuZn$_2$As$_2$ is an antiferromagnet, in which there are strong ferromagnetic correlations in the fields above 1000 Oe. This is reflected in the positive sign of the paramagnetic Curie-Weiss temperature. We can explain the observed strong decreasing of the g-factor by the formation of bound states of the Eu$^{2+}$ magnetic moment with free charge carriers. Taking into account that the density of electrons in the conduction band is very low, we believe that this shift is due to hybridization and the formation of bound states of 4f-electrons Eu$^{2+}$ ions with the electrons of the valence band. As a consequence the indirect exchange interaction between the Eu$^{2+}$ ions through the electrons of the valence band, the so-called modified-RKKY Bloembergen-Rowland’s [8, 9], is responsibly behind anti-ferromagnetism of this Eu-compounds. Comparison of the behavior of the magnetization of the "ferromagnetic" EuB$_6$ and antiferromagnetic EuZn$_2$As$_2$ investigated by us allows to suggest that EuB$_6$ is an antiferromagnet (in the ground state), as all the other REM compounds of this type. Ferromagnetic fluctuations and anomalously high magnetic susceptibility of the antiferromagnet camouflages the antiferromagnetism in it.

4. Acknowledgments

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