Investigation of Eu Ternary Pnictide by ESR

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Abstract. The investigation of the ESR in EuZn2As2 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 Eu2+ ions was symmetric and it was described very good by a Lorentzian lineshape at temperatures above 120 K. At the temperature decreasing well before the magnetic ordering temperature (TN) we observed an exponential-like increasing of linewidth and a decreasing of the resonance field, indicating the magnification of antiferromagnetic fluctuations and the effective molecular Weis's field. The shape of the resonance line changes from Lorentzian to Gaussian at the temperature close to the TN. Below TN we observed a decrease of the lineswidth and the changing of the lineshape to the shape close Dysonian.

1. Introduction

Electron spin resonance (ESR) has proved its effectiveness in the investigation of magnetic phenomena in rare-earth compounds. F-electron compounds showed us an amazingly wide range of different ground states, including complex forms of magnetic order, heavy-fermion and Kondo-lattice. The large variety of ground states is generally attributed to the presence of strong electronic correlations. However, the nature of the electronic correlations in f-electron materials is as diverse as the row of different ground states which they assume. Europium has a half-filled 4f - shell. The electronic configuration of the f-shell in Eu - compounds is 4f6 (nonmagnetic) or 4f7 (magnetic) depending on whether the valence of the europium is either 3+ or 2+. The divalent 4f7 state is a purely spin state S= 7/2. The energetic proximity of these configurations may lead to valence fluctuations. This is the reason why the properties of the intermediate-valent systems have attract great scientific interest [1-3]. Relevance of researches of an electronic interactions in the "122" superconducting iron pnictides attaches great interest in studying similar pnictides of rare-earth metal.

2. Results and discussion

2.1. Experiment

Polycrystalline EuZn2As2 was prepared by direct reaction of the stoichiometric amounts of Zn, As (99,999 %) and Eu (99,99 %) in an Al2O3 crucible enclosed in an evacuated quartz ampoule. The trigonal CaAl2Si2-type crystal structure (space group P3 1m1, Int. tables No. 164) was confirmed by X-ray powder diffraction. The ESR (electron spin resonance) measurements of the EuZn2As2 powder samples (size of particles ~ 4 μm) were performed on frequency 9.3 GHz in TE102 rectangular cavity of EPR-spectrometer “Bruker” in the temperature range from 4.2 to 300 K. The dc susceptibility M/B was measured at 2 - 400 K with a commercial Vibrating Sample Magnetometer (Oxford Instruments).
2.2. Electron spin resonance in EuZn$_2$As$_2$

2.2.1. 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 $\Delta H = 530$ Oe at temperatures above 120 K (see fig. 1). Position and width of the resonance lines were not changed and the $g$-factors was 1.96(3) in this temperature range. Bivalent europium has the electron spin $7/2$ and two stable 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 well before the magnetic ordering temperature we was observed an exponential-like increasing of linewidth and a decreasing of the resonance field, indicating the magnification of antiferromagnetic fluctuations and the effective molecular Weiss's field. Also this is confirmed by changing the shape of the resonance line from Lorentzian to Gaussian. Large deviation of the $g$-factor ($\Delta g \sim 0.03$) from 2.0 ($g$-factor of free electron, see also [4]) indicates on the strong hybridization of the europium f-electron states with the p- s- states of the band electrons.

![Figure 1. Types of the ESR lines under changes of temperature for EuZn$_2$As$_2$ powder sample. Parameter of line asymmetry A/B for T=4.2 K is 2.31. It is equal to 1.2 for high temperature.](image)

Since $4f^7$ configuration of paramagnetic ions Eu$^{2+}$ is pure spin state $8S_7/2$, the resultant orbital angular momentum equal to zero. The crystal field may split its main levels (the 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 with respect to each other and the ground state ion is completely degenerate in spin. Under the influence of crystal field of tetragonal or trigonal symmetry of the ion electronic cloud deforms slightly and averaged over the electron cloud energy of the spin-spin interaction depends on the relative orientation of electron spins of magnetic ions - the spin degeneracy is lifted. However, these interactions leading to some change in $g$ - factor leave its isotropic. Given that the measurements were made on the powder sample, the isotropy of $g$ - factor allows us to conclude that we are dealing with a real resonance line, but not with the convolution of the line with an anisotropic g - factor in the directions.

2.2.2. Shape of ESR line
At the temperature decreasing from room temperature to about 120 K, we observed a nearly symmetric resonance line of Lorentzian shape. A small asymmetry is described by a small (few percent) admixture of the dispersion associated with the Dyson’s distortions caused by the presence of the skin layer. At temperatures around 100 K, the line asymmetry parameter $A / B$ was 1.2. (A and B are values of $dP/dH$, respectively, for the high field peak and the low field peak in the first derivative of the field absorption line ESR). At further decrease in temperature occurs the deviation from the Lorentzian lineshape which increased along with broadening of the resonance line. The shape of the ESR line is getting shape closer to a Gaussian. This is seen most dramatically in the temperature range
10 – 23 K, where it was required of additions of the 40% of the impurity of Gaussian shape line for an acceptable description of the shape (see fig. 2). Also in the spectra measured at temperatures below 21 K, appeared and became a prominent feature of the low field, similar in form to the high field wing of the resonance line width of about 300 Oe and a zero resonant field. Spectra of this band is best described by three resonance lines of Gaussian shape: a line called the zero-field, the main line with a low field peak near 2500 Oe and the line with a resonant field near 1800 Oe. The width of the last line was close to the width of the main line, and the intensity was about 10% of the intensity of the main line. How such a description reflects the actual spectra can be judged from the figure 2, where are shown two calculated spectra for the temperatures 17.6 K and 12.5 K. The measurements of ESR at 4.2 K showed that markedly decreased the intensity and the width of the ESR, and line was shifted even more to lower field. The lineshape at 4.2 K was once again the ideal Lorentzian shape. But the Dyson's distortion increased so much that it became consistent with the ESR lineshape of the bulk metallic sample: the asymmetry parameter A / B line ESR was 2.31 against 2.56 of its value for a bulk sample (see figure 1).

![Figure 2. Types of the ESR spectrum at low temperatures. The upper and lower spectra are the result of calculation. The initial part of the spectrum at temperatures near to $T_N$ is interpreted as due to the spin-flop transition.](image_url)

Another possible explanation for the distortion of the line shape of ESR, like Dyson’s distortion, may be anisotropy of the antiferromagnetic fluctuations. But this explanation does not currently seem likely. If we assume the resonant field that substantially exceeds the value of the field of spin-flop transition (as is evident from the behavior of the baseline in low fields on fig.2), the magnetic sub-lattices in such magnetic field are known to be able to slant, regardless of the orientation of the antiferromagnetic axis with respect to the external magnetic field. Therefore to believe there is a specific anisotropy of the resonance fields leading to such "Dyson's distortions" was not warranted. Need for additional line of small intensity in the field around 1800 Oe is consistent with the possibility of formation of bound states of magnetic ions with electrons and valence band and conduction band (magnetic polarons). If we assume that this additional line due to the interaction with conduction electrons, and its position affect the fluctuations of the exchange field in the same manner as they impact on the main line, the difference of resonance fields of this line and main line is ~ 1250 Oe. It gives origin g – factor of the small intensity line ~ 3, 0.

2.2.3. **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 moves 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 restructing 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. Low value of the Neel temperature obtained from measurements of the intensity of the ESR could be related to the peculiarities of these measurements are associated with the use of microwave radiation. As the figure shows the changing of intensity of the ESR line with temperature corresponds to a typical temperature dependence of the susceptibility of an antiferromagnet. Also the temperature dependence of inverse intensity is typical. 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 $T_N$. This fact of positiveness paramagnetic Curie-Weiss temperature 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.

2.3. DC – susceptibility

The magnetic properties of EuZn$_2$As$_2$ were studied on polycrystalline samples. In the temperature range 10 - 300 K the susceptibility $M/B$ follows a Curie-Weiss law (see Fig. 4). The effective paramagnetic moment $\mu = 7.1 \mu_B$/Eu and antiferromagnetic order with $T_N = 16.5$ K (Fig. 4). As the ESR date the inverse susceptibility shows a positive paramagnetic Curie-Weiss temperature $\theta_{CW} = 21.2$ K. The saturation moment of the magnetization is $5.7 \mu_B$/Eu. The reduced values point out the presence of some Eu$^{3+}$ ions in EuZn$_2$As$_2$.

![Figure 4. DC Susceptibility of the polycrystalline EuZn$_2$As$_2$.](image-url)
We found no evidence for ferromagnetic order, however the positive Weiss temperature points to the existence of ferromagnetic correlations in this material.

It is clear that the antiferromagnetic fluctuations are caused by fluctuations in the exchange field, which in turn is related to density fluctuations of the conduction band electrons and the valence band electrons. Fluctuations in the density of valence band electrons may well cause fluctuations in the valence state of europium between the magnetic state of Eu$^{2+}$ and nonmagnetic Eu$^{3+}$. This explains small value of the saturation magnetization obtained in the measurements of dc susceptibility.

3. Conclusion

Thus, we can conclude on the basis 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. Strong Dyson’s distortions of the ESR lineshape for powder sample are associated with a sharp decrease in 5-10 times of the skin layer and with a corresponding increase of the conductivity of the sample, i.e. its transition from a semiconducting to metallic character and the disappearance of the narrow gap between the valence and conduction bands. The observed strong decrease of the g-factor we can explain by the formation of bound states of the magnetic moment of europium 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$^{2+}$ ion with the electrons of the valence band. As a consequence the indirect exchange interaction between the divalent ions of europium through the electrons of the valence band, the so-called modified-RKKY Bloembergen-Rowland’s [5, 6], is responsibly behind anti-ferromagnetism of EuZn$_2$As$_2$.

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