The ESR Study of Eu Ternary Pnictides EuCd$_2$Sb$_2$, EuZn$_2$As$_2$

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Abstract. The magnetic properties of the Zintl compounds EuZn$_2$As$_2$ and EuCd$_2$Sb$_2$ have been studied. The measurements of resistance, magnetic susceptibility and the ESR (X band) was performed in the range 4 - 300 K. The symmetric Eu$^{2+}$ ESR lines had the g -factors 2.00 (EuZn$_2$As$_2$), 2.03 (EuCd$_2$Sb$_2$) and a Lorentzian shape above 120 K. The change of shape to Gaussian indicates on the magnetic fluctuations. EuZn$_2$As$_2$ and EuCd$_2$Sb$_2$ order antiferromagnetically with the $T_N$ 16.5 and 7.4 K, respectively; but with positive Curie-Weiss temperatures. The study revealed metallic conductivity for EuCd$_2$Sb$_2$ and semiconductor type for EuZn$_2$As$_2$.

1. Introduction
Recently some ternary Eu and Yb pnictides with CaAl$_2$Si$_2$-type structures have become the subject of particular interest, because they exhibit very promising thermoelectric properties [1]. The CaAl$_2$Si$_2$ structure is a trigonal form of the AB$_2$X$_2$ family, where, similar as in the better known tetragonal ThCr$_2$Si$_2$ structure the cations on the A-site form layers interspersed with B$_2$X$_2$-layers, where the B-ions sit in the center of an X$_4$ tetrahedron. The way of packing these layers distinguishes between the ThCr$_2$Si$_2$ and structure [2]. This indicates a possible structural instability B$_2$X$_2$-layers. Europium has a half-filled 4f - shell. The electronic configuration of the f-shell in Eu - compounds is 4f$^6$ (nonmagnetic) or 4f$^7$ (magnetic) depending on whether the valence of the europium is either 3+ or 2+. The energetic proximity of these configurations may lead to valence fluctuations. The magnetic properties and the type of magnetic ordering in EuCd$_2$Sb$_2$ and EuZn$_2$As$_2$ are still unclear.

2. Results and discussion

2.1. Experiment
EuCd$_2$Sb$_2$ and EuZn$_2$As$_2$ were prepared by direct reaction of the stoichiometric amounts of Zn, Sb, As (99,999 %) 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 $P$3$m_1$) was confirmed by X-ray powder diffraction. The ESR (electron spin resonance) was measured on the powders (size ~ 4 μm) in X-band (9.3 GHz) in TE$_{10}$ rectangular cavity of spectrometer “Bruker” at 4.2 - 300 K. The dc susceptibility was measured at 2 - 400 K with a commercial Vibrating Sample Magnetometer (Oxford Instruments).

2.2. Electron spin resonance

2.2.1. Resonance fields, g- factor, linewidth, and shape of the ESR lines
The observed single resonance lines of the Eu$^{2+}$ ions were symmetric and they are described very good by a Lorentzian lineshape with linewidths 530 Oe (EuZn$_2$As$_2$) and 1050 Oe (EuCd$_2$Sb$_2$) above 120 K.
Position and width of the resonance lines were not changed and the g-factors were 2.00 and 2.03, respectively, in this temperature range. Bivalent europium has the electron spin $\frac{7}{2}$ and two stable isotopes with a nuclear spin of $\frac{5}{2}$. 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 observed an increasing of linewidth and a decreasing of the resonance field, indicating the magnification of antiferromagnetic (AFM) fluctuations and the effective molecular Weiss’s field. 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 further decrease in temperature occurs the deviation from the Lorentzian lineshape and resonance line is mixture of Lorentzian and Gaussian shapes (Foidt’s lineshape). The most dramatic change in the lineshape occur in the temperature range $10 \rightarrow 23$ K (see Fig. 1), where it was required of additions of the 40% of admixture of Gaussian shape line for an acceptable description of the shape. In this temperature range, a sharp increase in the asymmetry of the spectral shape and a decrease in its intensity due to narrowing of the resonance lines. Thus we observed a change lineshape from symmetric Lorentzian to asymmetric Gaussian lineshape. The change of shape from Lorentzian to Gaussian indicates on the magnification of antiferromagnetic fluctuations in paramagnetic range. The increase in asymmetry of the spectral shape may be caused by a decrease of the skin layer and the changing nature of the spins motion at the transition in the AFM-state. The ESR line has pure Dyson’s shape at $T = 4.2$ K in deep AFM-state.

Large deviation of the g-factor ($\Delta g \sim 0.03$) from 2.0 (g-factor of free electron, see also [3]) indicates on the strong hybridization of the europium f-electron states with the p-s states of the band electrons.

Figure 1. The ESR spectrum at low temperatures. The upper and lower spectra are the result of calculation. These calculation spectra consist from three lines. The first line (initial part of the spectrum) arising at temperatures near to $T_N = 16.5$ K is interpreted as non-resonant absorption due to the spin-flop transition. The second and third indistinguishable resonance lines may be due to the phase separation of AFM in a magnetic field.

Since ground state of Eu$^{2+}$ ion is pure spin state $^8S_{\frac{7}{2}}$, the resultant orbital angular momentum equal to zero. 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. Symmetry and isotropy of ESR line for the powder samples allows us to conclude that we are dealing with a real resonance line, but not with the convolution of the line with anisotropic g-factor. We associate significant increase in the g factor and the ESR line width, the reducing $T_N$ and $\theta_{CW}$ on going from EuZn$_2$As$_2$ to EuCd$_2$Sb$_2$ with the change of the conductivity from the semiconductor-like to the metal.

2.2.2. Intensity of the ESR line.
Intensity of the ESR spectrum is proportional to magnetic susceptibility of a spin systems if there is no influence of the skin layer. 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. Such causes are not in our case (the skin layer is much larger than the size of the powder
particles). 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$_2$ [4], 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 ferromagnetic order on the background of strong AFM fluctuations. As the Fig.2 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 we obtained positive $\theta_{\text{ESR}}$. This fact of positiveness paramagnetic Curie-Weiss temperature for the antiferromagnet is confirmed by direct measurements of the dc susceptibility. The obtained values of paramagnetic temperatures were quite close. $\theta_{\text{ESR}} = +20.4$ K and $\theta_{\text{CW}} = +21.2$ K. Respectively for EuCd$_2$Sb$_2$, $\theta_{\text{ESR}} = +5.4$ K and $\theta_{\text{CW}} = +3$ 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 $\chi / B$ follows a Curie-Weiss law. The effective paramagnetic moment $\mu_{\text{eff}} = 7.1 \mu_\text{B}/\text{Eu}$ and antiferromagnetic order with $T_N = 16.5$ K. As the ESR date the inverse susceptibility shows a positive paramagnetic Curie-Weiss temperature $\theta_{\text{CW}} = 21.2$ K. The saturation moment of the magnetization is $5.7 \mu_\text{B}/\text{Eu}$. The reduced values point out the presence of some Eu$^{3+}$ ions in EuZn$_2$As$_2$. The magnetic properties of EuCd$_2$Sb$_2$ were studied on single-crystalline samples. In the temperature range 2 - 300 K the susceptibility $\chi / B$ follows a Curie-Weiss law with a Neel temperature $T_N = 7.4$ K (see Fig.3). The effective paramagnetic moment $\mu_{\text{eff}} = 7.83 \mu_\text{B}/\text{Eu}$ is very close to the $S = 7/2$ value $\mu_{\text{eff}} = 7.94\mu_\text{B}$. This indicates that all Eu ions are in the divalent state, as expected.
from the electron count, when describing this compound within the Zintl concept. With application of an external magnetic field \( T_N \) is shifted downwards and finally suppressed (see Fig. 4). Saturation magnetization at \( \sim 3 \) T and 2.5 K gives an absolute magnetic moments \( \mu_S = 6.6 \mu_B/\text{Eu} \). For divalent europium \( \mu_S = 7 \mu_B/\text{Eu} \) is expected. We found no evidence for ferromagnetic order [5], however the positive Weiss temperature \( \theta_{CW} = +3 \) K points to the existence of FM correlations in this material or quantum phase transition in magnetic field induced by Jan-Teller effect in anionic complex.

2.4. Electrical resistance
The electrical resistivity \( \rho \) of \( \text{EuCd}_2\text{Sb}_2 \) is typical for a metal or semimetal with \( \rho = 0.25 \Omega \text{cm} \) at room temperature (see Fig. 5). This suggests scattering of charge carriers by magnetic fluctuations near \( T_N \) and predominant electron-magnon scattering at lower temperatures. This behavior of resistivity is typically for the 4f compounds with well-localized magnetic moments. The electrical resistivity \( \rho(T) \) from 10 to 300 K for \( \text{EuZn}_2\text{As}_2 \) (Fig. 5) suggests a narrow gap semiconductor. The activation energy is estimated to be \( E_g \approx 0.1 \) eV. The carrier concentrations at room temperature are \( 7.2 \times 10^{18} \) cm\(^{-3} \) for \( \text{EuCd}_2\text{Sb}_2 \) and \( 5.6 \times 10^{18} \) cm\(^{-3} \) for \( \text{EuZn}_2\text{As}_2 \).

![Figure 5. Temperature dependence of the electrical resistance of the polycrystalline \( \text{EuZn}_2\text{As}_2 \) and \( \text{EuCd}_2\text{Sb}_2 \).](image)

3. Conclusion.
The ternary Eu based compounds \( \text{EuCd}_2\text{Sb}_2 \) and \( \text{EuZn}_2\text{As}_2 \) with CaA\(_2\)S\(_2\)-type crystal structures have been synthesized and their magnetic and electric properties were studied. We can conclude on the base of our data that these compounds are antiferromagnets, in which there are strong ferromagnetic correlations in the fields above 1000 Oe. Taking into account that the density of electrons in the conduction band is very low, we believe that g-actor shift is due to hybridization and the formation of bound states of 4f-electrons \( \text{Eu}^{2+} \) 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 [6, 7], is responsibly for anti-ferromagnetism of these compounds. Fluctuations in the density of valence band electrons may well cause fluctuations in the valence state of europium between the magnetic state of \( \text{Eu}^{2+} \) and nonmagnetic \( \text{Eu}^{3+} \). This leads to AFM fluctuation above \( T_N \) and reduce the saturation magnetization.

4. Acknowledgments
This work was supported in part by grants of DFG, ASM, RFBR and Presidium of the RAS.

References
[1] Yu C, Zhu T J, Zhang S N, Zhao X B, He J, Su Z, Tritt T M, 2008 J. Appl. Phys. 104 013705
[2] Zheng C and Hoffmann R 1988 Journal of Solid State Chemistry 72 58
[3] Altshuler S A, Kozhev B M, EPR of the intermediate group compounds.1972 (M.Science), 478
[4] Weber F, Cosee C, Drobnik S, Faiss A, et al., 2006 Phys. Rev. B 73 014427
[5] Artmann A, Mewis A, Roepke M and Michels G 1996 Z. anorg. allg. Chem. 622 679
[6] Ruderman M A, Kittel C, 1954 Phys. Rev. 96 99
[7] Bloembergen N, Rowland T J, 1955 Phys. Rev. 97 1679