Spin and Valence Fluctuation in Eu Compounds with CaAl$_2$Si$_2$-Structure

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We measured the X-band electron spin resonance (ESR) in the family of ternary Eu pnictides with structure CaAl$_2$Si$_2$ – type (sp.gr. P3̅m1). Temperature dependences of position and width of resonance line well described by the contribution of the form \((T-\theta)\frac{1}{\sqrt{2}}\) \((\theta > 0)\) and \(\theta = T_N\) or \(\theta = \theta_{c-w} \); \(T_N\), \(\theta_{c-w}\) - Neel and the Curie-Weiss temperatures). In the case \(\theta_{c-w} > T_N\), experiment obviously indicates the existence of a magnetic phase between the AFM and PM states and relevant quantum critical point. Exchange interaction between localized magnetic moments and the current carriers causes the broadening of the ESR line \(\Delta \delta H\) and the g-factor shift \(\Delta g\) (electronic Knight shift) of Eu$^{2+}$ ions relatively free electron. It is known that linewidth of the ESR due the Dzyaloshinsky-Moriya interaction depends on the correlation length \(\xi\) as \((\xi/a_0)^3\) (\(a_0\) - lattice constant), while the symmetric anisotropic interaction as \((\xi/a_0)\). This allows to conclude that experimental results are explained by the dominant contribution of valence and spin fluctuations caused by mentioned symmetrical anisotropic interaction.

KEYWORDS: spin and valence fluctuation, magnetic resonance, phase transitions, anti-ferromagnetism

1. Introduction

The pnictides intermetallic compounds RMe$_2$Pn$_2$ (R = rare earth; Me = transition metal; Pn = pnictides P, As, Sb, Bi) crystallize in the trigonal CaAl$_2$Si$_2$-type structure (space group P3̅m1: Int. Tab. No. 164) or the tetragonal ThCr$_2$Si$_2$-type structure (space group I4/mmm: No. 139) and exhibit a rich variety of magnetic and transport phenomena. Following the initial characterization of these materials over twenty years ago, interest in the members of this huge 1-2-2 pnictides compound family has been revived by the recent discovery of a large group of superconductors on the basis of iron pnictides. 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 RMe$_2$Pn$_2$ family, where, similar as in the better known tetragonal ThCr$_2$Si$_2$ structure the cations on the R-site form layers interspersed with Me$_2$Pn$_2$-layers, where the Me-ions sit in the center of a Pn$_4$ tetrahedron. The way of packing these layers distinguishes between the ThCr$_2$Si$_2$- and CaAl$_2$Si$_2$-type structures [2]. This indicates a possible structural instability of Me$_2$Pn$_2$-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 latter is yet one reason for local structure instability. The representatives of RM$_2$Pn$_2$ family are EuCd$_2$Pn$_2$ and EuZn$_2$Pn$_2$ whose magnetic properties and the type of magnetic ordering in are still unclear. We report here the results of ESR study of EuZn$_2$Pn$_2$ compounds family.

2. Experiment and discussion

2.1 Experiment details

EuZn$_2$(P,As,Sb)$_2$ were prepared by direct reaction of the stoichiometric amounts of Zn, Sb, As, P (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 P3$\bar{m}$1) was confirmed by X-ray powder diffraction. Unit cell dimensions: EuZn$_2$P$_2$ - $a = b = 4.08710(10)$ Å, $c = 7.0105(4)$ Å; EuZn$_2$As$_2$ - $a = b = 4.2136$ Å, $c = 7.1871$ Å; EuZn$_2$Sb$_2$ - $a = b = 4.4890$ Å, $c = 7.6090$ Å.

The ESR (electron spin resonance) was measured on the powders (size ~ 4 μm) in X-band (9.3 GHz) in TE$_{102}$ rectangular cavity of spectrometer “Bruker” at 4.2 - 300 K. EuZn$_2$Sb$_2$ is semimetal, EuZn$_2$As$_2$ is a semiconductor with gap $E_g$ ~ 0.1Ev by measuring the resistivity and Hall effect [3,4]. There are no data EuZn$_2$P$_2$ yet, but given the strengthening of ionic bonding, the gap should be wider than in EuZn$_2$As$_2$.

2.2 Electron spin resonance

2.2.1 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 [5]. 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 the deviation occurs 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. For instance, for EuZn$_2$As$_2$ this is seen most dramatically in the temperature range 10 – 23 K (see Fig.1), where it was required of additions of the 40% of the admixture of Gaussian shape line for an acceptable description of the shape. 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.

![Fig. 1.](image-url) (Color online) The ESR spectrum of EuZn$_2$As$_2$ powder at low temperatures. The initial part of the spectrum at temperatures near to $T_N$ is interpreted as due to the spin-flop transition.
2.2.2 Resonance fields, linewidth, g-factor

At room temperature the observed single resonance lines of the Eu\(^{2+}\) ions were symmetric and they are described very good by a Lorentzian lineshape with linewidths 450 Oe (EuZn\(_2\)P\(_2\)), 530 Oe (EuZn\(_2\)As\(_2\)) and 730 Oe (EuZn\(_2\)Sb\(_2\)) at temperatures above 120 K. Position and width of the resonance lines were not changed and the g-factors were 2.004 (EuZn\(_2\)P\(_2\)), 2.003 (EuZn\(_2\)As\(_2\)) and 2.011 (EuZn\(_2\)Sb\(_2\)), respectively, in this temperature range. Bivalent europium has the electron spin \(7/2\) and two stable isotopes with a nuclear spin of \(5/2\). 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 was observed an increasing of linewidth (see Fig. 2) and a decreasing of the resonance field (see Fig. 3), indicating the magnification of antiferromagnetic (AFM) fluctuations and the effective molecular Weiss field. The change of shape from Lorentzian to Gaussian indicates also on the magnification of antiferromagnetic fluctuations.

Deviations of the g-factor from 2.0 (g-factor of free electron, see also [6]) points on the magnification of hybridization of the europium f-electron states with the p- s- states of the band electrons. Since ground state of Eu\(^{2+}\) ion is pure spin state \(S = 7/2\), the resultant orbital angular momentum equal to zero. The crystal field may split its main levels. 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 in a crystalline field of cubic symmetry and the ground state ion is completely degenerated in spin. The ion electronic cloud deforms slightly under the influence of crystal field of tetragonal or trigonal symmetry. As a result, the electron cloud energy of the spin-spin interaction depends on the relative orientation of electron spins of magnetic ions, and 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.

Temperature behavior of the line width has fluctuating nature - due to fluctuations of the magnetization, while the exchange field (molecular Weiss field) is equal to half the width of the line. Contribution of Korringa relaxation is almost invisible due to the low carrier concentration. The critical index \(\gamma\) for the mean quadratic fluctuations of the magnetization \(<\delta M^2> \sim |T - \theta_{cw}|^{\gamma}\) in the Landau theory is -1. Hence, at a temperature \(T = \theta_{cw}\) must be a singularity of type \(|T - \theta_{cw}|^{-1/2}\) in the temperature dependence of the linewidth and resonance field. Comparing the temperature dependences of linewidth and
the resonance field (see Fig. 2, 3), we see that the molecular field, resulting from a shift of the resonance line is completely determined by the average quadratic fluctuation of the magnetization in the case of EuZn$_2$As$_2$. In other cases, the shift of the resonance line with decreasing temperature is smaller. Also the deviation from the Lorentzian line shape becomes noticeable with the increase of the fluctuations - the shape of the resonance line becomes closer to Gaussian. The latter is also evidence about the enhancement of stochastic broadening mechanisms of the resonance line.

2.2.3 Intensity of the ESR line

Intensity of the ESR spectrum is proportional to magnetic susceptibility of a spin system. 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. Such causes are absent in our case (the skin layer is much larger than the size of the powder particles in the sample). 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 ferromagnetic order induced by external magnetic field on the background of strong AFM fluctuations. As the Fig.4 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 of paramagnetic Curie-Weiss temperature for the antiferromagnet is confirmed by direct measurements of the dc susceptibility. The obtained values of paramagnetic temperatures $\theta_{\text{ESR}}$ and $\theta_{\text{cw}}$ are quite close. The Neel temperatures $T_N$ and paramagnetic Curie-Weiss temperatures from the ESR data $\theta_{\text{ESR}}$ for the studied compounds were: EuZn$_2$P$_2$: $T_N = 26.3$ K, $\theta_{\text{ESR}} = 29.5$ K [3]. EuZn$_2$As$_2$: $T_N = 12.7$ K, $\theta_{\text{ESR}} = 20.4$ K (DC measurement: $T_N = 16.5$ K, $\theta_{\text{cw}} = 21.2$ K) [3]. EuZn$_2$Sb$_2$: $T_N = 12.0$ K, $\theta_{\text{ESR}} = 1.9$ K, (DC measurement: $T_N = 13.3$ K, $\theta_{\text{cw}} = 6.65 - 8.8$ K weakly anisotropic antiferromagnetic state [4]). Similarly, the positive Curie-Weiss temperatures for antiferromagnets have been observed for other compounds of europium with the same structure [7, 8]. But in work [9] in EuRh$_2$P$_2$ with $T_N = 50$ K it was observed $\theta_{\text{cw}} = -45$ K. In contrast to other case, in EuRh$_2$P$_2$ the ESR signal above 50 K is not practically observed. From a comparison with isostructural EuRh$_2$As$_2$ (the ThCr$_2$Si$_2$ – type structure) authors of work [9] conclude that the absence of the bulk ESR signal is caused by the non-integral valence of Eu: even a small broadening of the 4f -level due to charge fluctuations leads to disappearance of the ESR signal, if the width of the 4f state exceeds the characteristic energy scale of the measurement (0.04 meV at 10 GHz) [8]. From all of these measurements we can conclude unambiguously that the occupancy of the Eu 4f-level in EuRh$_2$P$_2$ is non-integral, i.e. it is not a pure 4f$^7$ state. However, for EuRh$_2$As$_2$ $T_N = 47$ K and $\theta_{\text{cw}} = +12$ K also positive!
According to [10] the magnetic ordering alone does not exclude valence fluctuations. A coexistence of magnetic order and valence fluctuation may be possible, if the fluctuation energy at low temperatures becomes smaller than the magnetic ordering temperature [11]. Nevertheless, the paramagnetic susceptibility data in connection with the magnetic ordering give an argument for the integral valence. The deviations of the susceptibility from an ideal Curie law \( \chi = C/T \) are described by the Curie-Weiss law

\[
\chi = C [T - \theta_{cw}]^{-1} = C [T - (\theta_{mag} - T_{fluct})]^{-1}
\]

Here, the Curie-Weiss temperature \( \theta_{cw} \) is the difference between the valence fluctuation temperature \( T_{fluct} > 0 \) [11], and \( \theta_{mag} \), presenting magnetic correlations; \( \theta_{mag} \), is usually negative for antiferromagnetic and positive for ferromagnetic order. Therefore, without valence fluctuation \( (T_{fluct} = \hbar \nu = 0, \nu - frequency \ of \ fluctuations) \) the susceptibility is enhanced for ferromagnetism and reduced for anti-ferromagnetism. The valence fluctuation results in a reduction of the susceptibility. However, the measurements on all our systems show an enhanced susceptibility compared to the Curie susceptibility of the free Eu\(^{2+} \) ion at low temperatures. This clearly excludes any valence fluctuations in the antiferromagnetic (or meta-magnetic) compounds. For an ideal ferromagnetic system, \( \theta_{mag} \), is expected to be equal to the Curie (Neel) temperature \( T_c \) \((-T_N)\), i.e. \( \theta_{cw} = T_c = -T_N \). In ferromagnetic systems \( \theta_{cw} \) is even larger than \( T_c \), resulting in a further enhancement of the susceptibility and again excluding valence fluctuations. In fact, this observed enhancement of the susceptibility is a strong argument against valence fluctuation in all Eu compounds discussed here.

If we suppose that the difference between \( T_N \) and \( \theta_{cw} \) is due to valence fluctuations, \( T_{fluct} \) is obtained in all cases negative. In the sense of \( T_{fluct} \), it is a positive quantity. That is, version of the valence fluctuations in this way does not work. If we talk about the valence fluctuations in one of the sublattices of the antiferromagnet, these fluctuations as well as in the case of a ferromagnet will lead to increased susceptibility and to increasing molecular field in the antiferromagnet. Given that in these compounds the indirect exchange interaction between magnetic ions occurs through the electrons of both bands (the conduction band and the valence band, for example, the Kimball-Falicov model [12,13], and the modified-RKKY Bloembergen-Rowland model [14,15]) the role of the valence instability in these interactions increases. Thus, the above indicates that there is a special class of compounds of europium, in which the valence instability leads to a new type of magnetic behavior and, consequently, to the possible existence of new magnetic phases and quantum phase transitions. Near the quantum critical point, depending on the parameter tuning can change the correlation length and the magnitude of the order parameter fluctuations. Depending on the type of exchange interaction will lead to different types of connections between corresponding contributions in g-factor \( \Delta g \) and
linewidth $\Delta(\delta H)$ of the ESR.

In [16, 17] is made a comparative calculation of the linewidth of the ESR in the two-dimensional Heisenberg antiferromagnet $S = 1/2$ for the cases with skyrmions antisymmetric anisotropic exchange interaction (Dzyaloshinsky-Moriya) and symmetric anisotropic exchange interaction. In the first case, the dependence on the correlation length has the form $\Delta(\delta H) \sim (\xi/a)$; in the second - $\Delta(\delta H) \sim (\xi/a)^3$ (where $\xi$ - the correlation length, $a$ – the lattice constant). Mean square deviation the g-factor induced by spin fluctuations $\Delta g_{f}^2 \sim (\xi/a)^3$. Excluding the correlation length in dependence of $\Delta(\delta H)$ for the Dzyaloshinsky-Moriya case we get $\Delta g_{f} \sim \Delta(\delta H)^{3/2}$. This corresponds to our experiment.

3. Conclusion

We have studied the magnetic properties of the Zintl compounds EuZn$_2$(P, As, Sb)$_2$ by ESR. At the temperature decreasing well before the antiferromagnetic ordering temperature we have observed an increasing of linewidth and a decreasing of the resonance fields, which in our case is very good described by the Landau theory of magnetic fluctuations. The paramagnetic temperature $\theta_p$, obtained from the temperature dependence of the ESR signal intensity, has the positive sign. We believe that such behaviour of $\theta_p$ is connected with the proximity to quantum critical point and with the relevant instability of magnetic and crystal structures (instability Me$_2$Pn$_2$-layers, competition between nonmagnetic 4f$^6$ and magnetic 4f$^7$ states of Eu). We consider that the magnetic properties of studied compounds are due to the instability of the CaAl$_2$Si$_2$-type structures (similar compounds with bismuth and nitrogen are unknown), the interplay of spin and valence fluctuations (nonmagnetic 4f$^6$ and magnetic 4f$^7$ states of Eu), and the differences of interactions in comparison with Rh-Eu pnictides with the ThCr$_2$Si$_2$ - type structure. Europium has nonintegral valence in Rh-Eu pnictides and g-factor substantially smaller than 2.0 [9]. We conclude that the valence instability can lead to a new type of magnetic behavior and, consequently, to the possible existence of new magnetic phases and quantum phase transitions in a specific class of compounds.

References