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# Resonant Indirect Exchange Interaction between Localized Spin States in 3D Dirac semimetal

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The paper considers the question of the exchange interaction of localized spin states of Eu impurities in the Dirac semimetal  $\alpha$ -Cd<sub>3</sub>As<sub>2</sub> by means donor electrons originating from these impurities. Being in a state of chemical compression, the divalent europium ion is inclined, by donating an electron to the conduction band, to pass into a trivalent state with a smaller ionic radius. The existence of europium in the non-magnetic trivalent state occurs only a small part of the time. However, it leads to a slight decrease in its effective local magnetic moment and an increase in the  $g$ -factor due to interaction with Dirac electrons. The change in the degree of chemical compression with temperature explains the previously observed temperature dependences of the  $g$ -factor and EPR linewidth for impurity Eu<sup>2+</sup> ions ( $g \sim 2.2$  and  $g \sim 4.4$ ). Taken together, this indicates the presence of a crystallographically selective indirect exchange interaction between localized spins of Eu<sup>2+</sup> ions mediated by the donor conduction electrons

**Keywords:** magnetic resonance, Dirac semimetals, magnetic impurities, exchange interaction.

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## 1. Introduction

Ever since the understanding of the mechanisms [1] of formation of atomic localized magnetic moments in solids has come up, the problem of the mechanisms of indirect exchange interactions between these magnetic moments has also arisen [2–6]. The most commonly known of these interactions is the Ruderman–Kittel–Kasuya–Yosida (RKKY) interaction. The nature and long-range action of this interaction is mainly affected by the spectrum of excitations in the electronic system of current carriers. For example, the effects caused by these features in superconductors and highly paramagnetic metals are well known. From this point of view, the behavior of magnetic impurities in Dirac topological materials is of great interest. The topological protection of band states that have a linear spectrum of electronic excitations results in such a feature of the scattering of band electrons by impurities as suppression of backscattering. This can introduce certain changes into the nature of the indirect exchange interaction of impurity localized spin states through band electrons. For example, in [7] it is shown that in the RKKY interaction in a Dirac semimetal there appears not an oscillating part, similar to that in superconductors, but of a part with ferromagnetic sign. EPR studies [8] of the behavior of europium impurities in the  $\alpha$ -Cd<sub>3</sub>As<sub>2</sub> Dirac topological semimetal have shown that most likely the ferromagnetic type of coupling is prevailing between magnetic impurities. However, at the same time, this study has pointed to some problems. Facts indicating the existence of a mechanism associated with the emission and absorption of donor electrons by Eu<sup>2+</sup>

impurities are considered. Doping with Eu<sup>2+</sup> changes the sign of the Cd<sub>3</sub>As<sub>2</sub> magnetoresistance [8]. This may be indicative of the presence of a small-scale phase separation. Indeed, two lines with significantly different  $g$ -factors and absolutely identical behavior of the width and position of these resonance lines are observed in EPR. It has been established that these lines relate to the magnetic moments of europium, located, respectively, in the substitution positions of cadmium ions and interstitial positions in the antiferrotype lattice [9]. Thus, it turns out that europium ions, on the one hand, are randomly located in the above-mentioned crystallographic positions, and on the other hand, form magnetic phases identified in the magnetic susceptibility and EPR lines with significantly different and anomalously large  $g$ -factors. We need to resolve the issues that arise in this context: If the normal value of the  $g$ -factor of the pure spin state Eu<sup>2+</sup> is 2.0, then what is the nature of the EPR lines observed in [8] with  $g$ -factors near 2.2 and 4.4 and what is the explanation of their strong temperature dependences?

## 2. Discussion

### 2.1. Deficiency of donor electrons upon $\alpha$ -Cd<sub>3</sub>As<sub>2</sub> doping with europium

$\alpha$ -Cd<sub>3</sub>As<sub>2</sub> is a low-temperature tetragonal modification of Cd<sub>3</sub>As<sub>2</sub> [9,10] with space symmetry group I4<sub>1</sub>cd and lattice parameters  $a = 12.654(5)$  Å,  $c = 25.465(3)$  Å (when doped with Eu [8]). The crystal cell consists of 16 distorted crystalline subcells of the antiferrotype type, about 6.33 Å in size, with Cd in tetrahedral coordination and ordered

Cd vacancies. Each  $\text{cm}^3$   $\alpha\text{-Cd}_3\text{As}_2$  contains  $2.564 \cdot 10^{20}$  crystal cells. Each cell contains 160 atoms, including 96 ions of  $\text{Cd}^{2+}$  and 64 ions of  $\text{As}^{3-}$  in stoichiometric positions. In addition, tetrahedral vacancies of a crystal cell can formally contain up to 0.16 ions of  $\text{Cd}^{2+}$  or impurity ions of  $\text{Eu}^{2+}$ . I.e. about 6 „extra“ cadmium atoms per cell. However, the electrons from these cadmium ions do not enter the conduction band, because their concentration is 2 orders of magnitude higher than the concentration of conduction electrons measured in the pure sample [8]. For the doping level of 0.1–0.2 at.% Eu

$$\begin{aligned} n &= 160 \cdot (0.001 \dots 0.002) \cdot 2.564 \cdot 10^{20} \\ &= (4.1 \dots 8.2) \cdot 10^{19} \text{ cm}^{-3}, \end{aligned}$$

which is close to the concentration measured in [8], i.e.  $n_e = 2.2 \cdot 10^{19} \text{ cm}^{-3}$ , but indicates a significant deficiency of donor electrons. From this a conclusion can be made that the valence electrons of the  $\text{Eu}^{2+}$  ion, like  $\text{Cd}^{2+}$ , are included in the valence band, and the electrons associated with the partial transition of the  $\text{Eu}^{2+}$  ion into  $\text{Eu}^{3+}$  are a source of electrons in the conduction band. However, the energies of removal of the second and the third Eu electrons from the crystal are 11.25 eV and 24.7 eV, respectively. The same values for Cd are 16.908 eV and 36.48 eV. This energy can be compensated by the energy of lattice stresses during the transition of  $\text{Eu}^{2+}$  to  $\text{Eu}^{3+}$ , which are different for the substitution and interstitial positions.

## 2.2. Comparative assessment of stress energies in the crystal lattice caused by $\text{Eu}^{2+}$ and $\text{Eu}^{3+}$ ions

The elastic energy arising when the  $\text{Eu}^{2+}$  ion is placed in the tetrahedral coordination position of the  $\text{Cd}^{2+}$  ion or in the tetrahedral vacancy can be estimated from the following formal considerations using the data from [11] according to the parameters of the Lennard–Jones potential:

$$U(r) = U_0 [(\sigma/r)^{12} - (\sigma/r)^6] \quad (1)$$

taking into account the difference in melting temperature and ionic radii of  $\text{Cd}_3\text{As}_2$ . Equilibrium states in the corresponding positions are determined by the energy parameter  $U_0 \sim 4\epsilon \sim 0.416 \text{ eV}$  (in the notation of [11]) and the formal interionic distance (geometric parameter  $\sigma$ , determined as a minimum of  $U_0$  in the formula for the Lennard–Jones potential), equal to the sum of the ionic radii of the  $\text{Cd}^{2+}$  and  $\text{As}^{3-}$  ions ( $\sigma = 0.99 + 1.91 = 2.9 \text{ \AA}$ ) in the case of substitution of a cadmium ion inside the tetrahedron of  $\text{As}^{3-}$  ions. Thus, the initial equilibrium molecular structures are: 1) a tetrahedron of  $\text{As}^{3-}$  ions with an internal  $\text{Cd}^{2+}$  ion and 2) the same tetrahedron of the same  $\text{As}^{3-}$  ions without the internal  $\text{Cd}^{2+}$  ion. When the  $\text{Eu}^{2+}$  ion is implanted, it will be assumed that the distances between the surrounding ions remain nearly unchanged and the geometric parameter that determines the position of the

potential minimum becomes equal to the sum of radii of  $\text{Eu}^{2+}$  and  $\text{As}^{3-}$  ions ( $\sigma = 1.47 + 1.91 = 3.38 \text{ \AA}$ ) or  $\text{Eu}^{3+}$  and  $\text{As}^{3-}$  ions ( $\sigma = 0.97 + 1.91 = 2.88 \text{ \AA}$ ). That is, the replacing  $\text{Cd}^{2+}$  with  $\text{Eu}^{3+}$  is almost equivalent, and the replacing  $\text{Cd}^{2+}$  with  $\text{Eu}^{2+}$  transfers the ionic system to a position corresponding to strong repulsion. For the substitution position, the excess repulsion energy of four  $\text{As}^{3-}$  ions will be 6.285 eV. A similar calculation is performed for the interstitial position. Assuming that the energy parameter  $\epsilon$  is the same for all bonds in the described molecular structure, we find that a decrease in the geometric parameter of the bonds of the internal ion leads to unloading of the bonds of this ion with  $\text{As}^{3-}$  ions and the same load to compress the bonds between  $\text{As}^{3-}$  ions. The length  $\tilde{a}$  of the tetrahedron edges and the length  $R$  of internal bonds of  $\text{As}^{3-}$  ions with this ion can be estimated based on the size of the  $\text{As}^{3-}$  ion,  $\tilde{a} = 1.91 + 1.91 = 3.82 \text{ \AA}$  and the edge size of the antifluorite subcell of the crystal lattice  $a = 6.33 \text{ \AA}$ . In the latter case (estimated from the lattice constant), the distance from the Cd vacancy to the As ion is found to be  $R'' = 2.74 \text{ \AA}$ . From this value and the geometric parameter  $\sigma$  in (1), equal to the sum of radii of  $\text{Eu}^{2+}$  and  $\text{As}^{3-}$  ions of  $3.38 \text{ \AA}$ , the excess repulsion energy in the interstice is found to be  $U(r) = 14.8 \text{ eV}$ . The real pattern, of course, is somewhat more complicated and features, for example, such details as the non-central location of the metal ion in the tetrahedron of  $\text{As}^{3-}$  ions and the distortion of the tetrahedron itself, leading to different values of the lengths of internal bonds with the  $\text{As}^{3-}$  ions. However, these values presented in [10] are close to the value mentioned above.

It is absolutely clear that a displacement of the atoms surrounding the tetrahedron occurs and the excess energy is localized in a very small area. If the calculation is carried out taking into account the displacements of atoms located at long distances, then it is obvious that the displacement of atoms (ions) in the first coordination sphere will lead to the unloading of the tension of these bonds, to the transfer of stresses, both positive and negative, to the next coordination spheres. Both types of stress, however, contain positive excess energy. So, the assuming immobile the ions in the first coordination sphere, does not take into account this excess energy but by increasing the tension in the nearest bonds the excess energy contained in them is increased. That is, this approach for estimating the excess energy when implanting the  $\text{Eu}^{2+}$  ion cannot greatly distort the value of the calculated excess energy. This also supports another approach to such estimates. Namely: the replacement of a cadmium ion with a divalent or a trivalent europium ion comes down to the addition of a spherical layer of electron density. Naturally, this layer displaces outside the electron density previously located in this place. And this displaced electron density cannot have a volume noticeably different from the added density. So, already in the next coordination sphere the thickness of the layer of excess electron density will be an order of magnitude smaller than the original one. Also, the displacements of atoms caused by this displaced electron density will be

an order of magnitude smaller. The compressive stresses described by the first term of the Lennard–Jones potential will decrease by 12 orders of magnitude. Thus, the fears that taking into account the stresses only in the direct bonds of the implanted ion with the position of the ions in the environment remaining unchanged will underestimate the excess energy, are groundless. Similar values of  $U(r)$  for the  $\text{Eu}^{3+}$  ion are:  $-0.065$  eV (instead of  $6.285$  eV for  $\text{Eu}^{2+}$ ),  $0.78$  eV ( $14.8$  eV for  $\text{Eu}^{2+}$ ). In the latter case, this value for the  $\text{Cd}^{2+}$  ion radii used turns out to be equal to  $0.95$  eV. This means that the  $\text{Eu}^{3+}$  ion makes the crystal lattice „subsided“ in both positions and, in any case, it is energetically unfavorable for the europium ion to be in the trivalent state.

Assuming that the valence electrons of Cd determine the bottom of the conduction band, we find that the transfer of the third europium electron to this level requires an energy of about  $24.7 - 16.908 \approx 7.792$  eV. This energy is slightly higher than the lattice energy released when the valence state of the europium ion changes in the substitution position, and is significantly less than in the interstitial position. Due to these circumstances, the lifetimes of Eu ions in the magnetic divalent state and their effective magnetizations in these positions differ significantly. An electron emitted by the  $\text{Eu}^{2+}$  magnetic ion in the corresponding position, due to conservation laws, transfers energy and angular momentum to the  $\text{Eu}^{3+}$  ion located in the same crystallographic position, and, being accepted by it, restores the magnetic state the resulting  $\text{Eu}^{2+}$  ion. Thus, a resonant exchange interaction occurs between  $\text{Eu}^{2+}$  ions located in the same crystallographic positions, under conditions of suppression of the backscattering of emitted electrons and more effective preservation of their spin states obtained during emission. The resonance conditions are determined by the energy and mode of crystal lattice vibrations accompanying the changes in the valence state of the europium ion in the corresponding crystallographic position.

### 2.3. The effect of Dirac electrons on $g$ -factor of $\text{Eu}^{2+}$ ions

Assuming that the value of the  $g$ -factor of the  $\text{Eu}^{2+}$  ion is the result of interaction with the magnetic momenta of current carriers, and using the results of [12] for the effective  $g$ -factor in the case of two interacting electronic systems, we obtain the following:

$$g_{\text{eff}} = (g_1 S_1 + g_2 S_2) / (S_1 + S_2), \quad (2)$$

$$g_{\text{eff}} = g_{\text{Eu}} \cdot [1 - \mu^* (g_e / g_{\text{Eu}})] / (1 - \mu^*),$$

where  $\mu^* = [\mu_{\text{Eu}} - \mu_0] / \mu_{\text{Eu}}$ .

For  $g_e = 16$ ,  $g_{\text{Eu}} = 2$ ,  $0$  depending on the degree of decrease in  $\mu_{\text{Eu}} / \mu_0$  of the magnetic momentum of the  $\text{Eu}^{2+}$  ion due to the episodic transition of  $\text{Eu}^{3+}$  to a non-

magnetic state we obtain the following effective  $g$ -factors

$$\text{for } \mu_{\text{Eu}} / \mu_0 = 0.99 \quad g_{\text{eff}} = 2.154;$$

$$\text{for } \mu_{\text{Eu}} / \mu_0 = 0.98 \quad g_{\text{eff}} = 2.28;$$

$$\text{for } \mu_{\text{Eu}} / \mu_0 = 0.85 \quad g_{\text{eff}} = 4.2.$$

The degree of decrease in  $\mu_{\text{Eu}} / \mu_0$  of the magnetic momentum of the  $\text{Eu}^{2+}$  ion is different for different positions in the crystal lattice and determines the resonant conditions for electron emission at one site during the transition of  $\text{Eu}^{2+}$  to  $\text{Eu}^{3+}$  and its absorption at another site during the transition from  $\text{Eu}^{3+}$  to  $\text{Eu}^{2+}$ . As follows from the above, if the Eu ion is in the  $\text{Eu}^{3+}$  state for 15% of time at the interstitial position and 2% of time at the substitution position, then this explains the observed values of the  $g$ -factors. The change in the degree of chemical compression with a change in temperature explains the temperature dependences of the  $g$ -factor and EPR linewidth observed in [8], i.e. values of  $g$ -factors ( $g \sim 2.2$  and  $g \sim 4.4$ ) of  $\text{Eu}^{2+}$  impurity ions, and, thus, the value of  $g$ -factor of conduction electrons can be determined from these values as  $g_e \sim 16$ , which turns out to be close to that obtained in other experiments [13]. It can be seen from the temperature behavior of the EPR lines that the two spin ensembles corresponding to them are ordered at different temperatures. This is indicative of the existence of an indirect exchange interaction of  $\text{Eu}^{2+}$  spins [14,15] through donor conduction electrons that is selective for the crystallographic position. In this case, the parent electrons of the matrix constitute an insignificant fraction of the donor electrons, and the donor electrons originating from interstitial positions have a greater effect, because in these positions, the europium ion spends more time in the  $\text{Eu}^{3+}$  state. Accordingly, this resonant channel of the exchange interaction has a high exchange energy [15] and, as a consequence, a high Curie-Weiss temperature:  $\sim 130$  K versus  $\sim 6$  K for ions at the substitution position [8].

The latter fact excludes a possible explanation of the values of  $g$ -factors due to the formation of exchange-coupled pairs or clusters of europium ions, because in this case, due to the low average concentration of impurity europium ions and conduction electrons, the classical RKKY interaction of clusters would have to occur at even greater distances, excluding a simple explanation for the narrowing of resonance lines with increasing temperature and the linear temperature dependences of the EPR parameters for each ensemble of spins.

### 3. Conclusion

The above description reveals the mechanism of selective indirect exchange interaction of magnetic impurities and spin diffusion in subsystems with identical spin states. The selectivity of interaction consists in the fact that impurities located in crystal lattice sites with the same local symmetry and the degree of chemical compression of the magnetic impurity ion determined by it selectively interact with each

other. This may mean that we are dealing with a new type of long-range indirect exchange interactions of magnetic ions in topological semimetals. The RKKY interaction of magnetic impurities (localized spins) is possible only in the presence of „freely“ moving spins of current carriers (electrons, holes). No carriers — no RKKY. There are very few such carriers in a pure semimetal. When doped, such carriers appear. However, the valence  $s$ -electrons of impurities also go to the valence band and almost do not enter the conduction band. In order for a free electron to appear in the conduction band, which would revive the RKKY interaction, this electron must be raised from deep levels to the conduction band. This requires energy. And this energy is in no way connected with the RKKY interaction, it is significantly greater than anything that the RKKY can provide. Where does such energy come from? The assumption that this may be an excess energy of the crystal lattice is confirmed by the simplest estimates made.

It is natural to ask about the implementation of the described scenario for other magnetic impurities. The closest analogue could be the  $Mn^{2+}$  ion, which, like  $Eu^{2+}$ , is in a purely spin state and has no magnetic momentum in the trivalent state. However, the manganese ion has a size smaller than the cadmium ion, and therefore the scenario associated with strong chemical compression of the ion is not realized. Moreover, the value of its  $g$ -factor is exactly equal to the  $g$ -factor of free electron, indicating the absence of an electron Knight shift and, accordingly, a zero density of  $s$ -electrons in substitution positions. Considering that a small electron Knight shift of the signal from  $Mn^{2+}$  is observed for interstitial positions, it can be said that there is a nonuniform distribution of the conduction electron density and the possibility of small-scale phase separation, considered in [16].

The lack of chemical compression also occurs for other iron group ions. For the main  $Fe^{2+}$  and  $Cr^{2+}$  impurity ions, no EPR is observed at a frequency of 9 GHz. However, weak EPR signals from the  $Fe^{3+}$  and  $Cr^{3+}$  ions are observed, and this indicates that the sample contains a certain amount of donor electrons resulting from the transition of the main divalent ion to the trivalent state. In the case of doping with iron, as in the case of doping with manganese, a  $g$ -factor is observed that is almost equal to the  $g$ -factor of a free electron, and the implementation of a scenario with resonant indirect exchange interaction can not be expected. In the case of doping with chromium, a more complex and diverse nature of interactions between impurity ions can be expected. The chromium ion has a non-zero orbital momentum and is a Jahn-Teller ion, i. e. an ion capable of changing the symmetry and nature of bonds in the immediate environment and, accordingly, participating in the exchange interactions where the impurity ion has a direct effect on the configuration of the immediate environment [17].

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## Conflict of interest

The authors declare that they have no conflict of interest.

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