

Ferromagnetic superexchange in Cr-based diluted magnetic semiconductors

J. Blinowski

Institute of Theoretical Physics, Warsaw University, ul. Hoża 69, 00-681 Warszawa, Poland

P. Kacman

Institute of Physics, Polish Academy of Sciences, al. Lotników 32/46, 02-668 Warszawa, Poland

J. A. Majewski

Walter Schottky Institut, Technische Universität München, Am Coulombwall, D-85748 Garching, Germany

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A theory of superexchange in Cr-based $A_{II}B_{VI}$ diluted magnetic semiconductors (DMS's) is presented. The spin interaction between Cr^{2+} ions, calculated numerically for zinc chalcogenides, exhibits properties unique in DMS's, it is ferromagnetic, and depends on the relative orientations of the ionic Jahn-Teller distortions. We explain the origin of this unusual behavior and predict a ferromagnetic character of the superexchange in other Cr-based $A_{II}B_{VI}$ DMS's.

The discovery of diluted magnetic semiconductors (DMS's) has created the possibility to study the magnetic phenomena in crystals with a simple band structure and excellent magneto-optical and transport properties. The well-developed technology of these semiconductors allows also for tuning of their magnetic properties not only by an external magnetic field but by varying the band structure and/or carrier, impurity, and magnetic ion concentrations. This makes DMS's a valuable test ground for various theoretical ideas and opens doors for numerous device applications. The most spectacular feature of DMS's, i.e., the giant spin splitting of the free-carrier spectrum in a magnetic field, results from the strong spin-dependent interaction of the band carriers with the localized spins of the magnetic ions ($sp-d$ exchange interactions). The pursuit after maximum spin splittings in DMS's runs in two directions: either to increase the concentration of magnetic ions or to look for new materials with larger exchange constants. Still, several years of considerable effort did not bring satisfactory progress. Despite the larger exchange constants found in DMS's with Fe and Co ions (see Refs. 1–3, and the references therein) the spin splittings remain in these materials similar to those in Mn-based DMS's, since the spin of the Mn^{2+} ion is larger. On the other hand, the increase of the magnetic-ion content enhances the role of the ion-ion ($d-d$) interactions. The latter, being antiferromagnetic in all known $A_{II}B_{VI}$ DMS's, reduces the average ionic magnetic moment. They impose, therefore, an upper limit to the increase of the free-carrier spin splitting with the growing number of magnetic ions. There are materials with ferromagnetic ion-ion interactions and very large spin splittings (magnetic semiconductors like, e.g., Eu-chalcogenides or $ZnCr_2Se_4$ spinels), which were known well before the DMS's systems have come into play (see, e.g., Ref. 4 and the references therein). However, in contrast to DMS, these materials exhibit rather complex crystallographic and band structures together with poor optical and

transport properties. Obviously, a material combining the known³ virtues of the DMS family with ferromagnetic $d-d$ interactions would be very interesting from both fundamental and applicational points of view.

In Mn-based DMS's the ion-ion spin interactions have been both theoretically and experimentally investigated by many authors (for a review see Ref. 5). The indirect exchange^{6–8} as well as the superexchange^{9,10} were invoked to account for the observed isotropic (Heisenberg) and anisotropic (Dzyaloshinsky-Moriya) exchange constants. Larson *et al.*⁹ have shown, using a perturbative k -space approach, that the superexchange, resulting from the $sp-d$ hybridization, is by far the dominant spin-spin interaction in $A_{II}B_{VI}$ DMS's. In Refs. 9,10 they calculated the isotropic and the anisotropic spin-spin interaction constants and obtained a good agreement with experimental data for a selected set of model parameters.

Within the k -space perturbational approach the $sp-d$ hybridization can be thought about in terms of virtual transitions of an electron between sp bands and the ionic d shell. With this respect, the 6S ion with the half-filled d shell, Mn^{2+} , is quite an exception. Each of its five d orbitals is occupied by one electron. Thus, every orbital can participate in the hybridization-induced virtual transitions of both types: involving the creation and the annihilation of a band electron. Moreover, all these virtual transitions decrease the total spin of the Mn^{2+} ion. The unique properties of Mn^{2+} lead to considerable simplifications in the theoretical description of the hybridization-induced spin interactions, making the results inapplicable to other transition-metal ions. This fact, clearly demonstrated^{11–14} for the kinetic exchange (i.e., hybridization mediated spin-dependent $p-d$ interaction), has to be taken into account in the theory of $d-d$ interactions.

For ions with some hybridizing orbitals empty (doubly occupied), the virtual transitions involving creation (annihilation) of a d electron cannot only decrease but also increase

the total spin of the ion. In such cases the theory has to account properly for the many-electron intrashell correlations responsible for the Hund's rule. Using the rotationally invariant many-electron Parmenter Hamiltonian¹⁵ for the description of the unperturbed magnetic ions, we have shown in Ref. 14 that, depending on the filling of ionic d shell, the kinetic exchange Hamiltonian evolves from the antiferromagnetic (for Mn^{2+} , Fe^{2+} , and Co^{2+} ions) to the ferromagnetic Kondo-like (for Sc^{2+} and Ti^{2+}) via more complicated forms (Cr^{2+} , V^{2+} , Ni^{2+} , and Cu^{2+} ions). The results for Cr^{2+} ions, for which the kinetic exchange interaction was shown to depend strongly on the relative number of ions with the Jahn-Teller distortions along different, equivalent crystallographic directions,¹² stimulated technological efforts in obtaining Cr-based DMS's. Up to now the materials obtained by equilibrium methods have rather low Cr ion content, too low to study experimentally the d - d interactions. In zinc chalcogenides, however, the concentration of Cr^{2+} ions was high enough for the discovery of the unusual ferromagnetic type of the p - d spin interactions.¹⁶ The theoretical analysis of the superexchange in Cr-based $A_{\text{II}}B_{\text{VI}}$ DMS's, presented below, shows that in these materials one should expect the ion-ion interactions to be also ferromagnetic.

The most general effective spin-spin interaction between two Cr^{2+} impurity ions occupying two crystal sites separated by the vector \mathbf{R}_{12} is described by the operator

$$\hat{H}_S = -2 \sum_{\alpha, \beta} J_{\alpha\beta}^{\gamma\delta}(\mathbf{R}_{12}) \hat{S}_{1\alpha} \hat{S}_{2\beta}, \quad (1)$$

where $\hat{S}_{i\alpha}$ is the α th component ($\alpha = x, y, z$) of the spin operator of the ion i .¹⁷ The ground state of the Cr^{2+} ion in zinc-blende type DMS's can be one of the three possible orbital singlets corresponding to different directions (x , y , or z) of the tetragonal Jahn-Teller distortions. In each of these orbital singlets, four out of five ionic d orbitals are singly occupied (the two e_g and two t_{2g} orbitals). The indices γ and δ specify which of the t_{2g} orbitals (yz , xz , or xy) remain empty in the 1 and 2 ion, respectively.

To calculate the superexchange, one has to determine the fourth-order perturbation matrix for the hybridization Hamiltonian applied to the system of two ions in a crystal with completely filled valence bands. This hybridization results primarily from the mixing of the d orbitals of the paramagnetic ion occupying a cation site in the lattice with the sp orbitals of the nearest-neighbor anions.¹⁸ For the description of the unperturbed magnetic ions we use the rotationally invariant Parmenter Hamiltonian,¹⁵ which attributes different energies E_N^S to the states with different total spin values S of the N d electrons. The unperturbed band states are described in the frame of the empirical tight-binding method. Applying this approach to the $A_{\text{II}}B_{\text{VI}}$ crystal with Cr^{2+} ions we obtain the superexchange tensor J consisting of three terms F , H , and G ,

$$J_{\alpha\beta}^{\gamma\delta}(\mathbf{R}_{12}) = F_{\alpha\beta}^{\gamma\delta}(\mathbf{R}_{12}) + H_{\alpha\beta}^{\gamma\delta}(\mathbf{R}_{12}) + G_{\alpha\beta}^{\gamma\delta}(\mathbf{R}_{12}). \quad (2)$$

These terms describe the contributions to the superexchange tensor coming from occupied orbitals of the two interacting

ions (F), occupied orbitals of one ion and the empty orbital of the second ion (H), and empty orbitals of both ions (G), and they read

$$F_{\alpha\beta}^{\gamma\delta}(\mathbf{R}_{12}) = \sum_{\nu, \nu'}^{\text{occ}} \exp(i\mathbf{k}_{\nu\nu'} \cdot \mathbf{R}_{12}) \mathcal{F}_{\nu\nu'}^{\alpha\gamma} (\mathcal{F}_{\nu\nu'}^{\beta\delta})^* \mathcal{F}_{\nu\nu'}, \quad (3)$$

$$H_{\alpha\beta}^{\gamma\delta}(\mathbf{R}_{12}) = - \sum_{\nu, \nu'}^{\text{occ}} \exp(i\mathbf{k}_{\nu\nu'} \cdot \mathbf{R}_{12}) [I_{\nu\nu'}^{\alpha\gamma} (\mathcal{F}_{\nu\nu'}^{\beta\delta})^* \mathcal{H}_{\nu\nu'} + \mathcal{F}_{\nu\nu'}^{\alpha\gamma} (I_{\nu\nu'}^{\beta\delta})^* \mathcal{H}_{\nu\nu'}], \quad (4)$$

$$G_{\alpha\beta}^{\gamma\delta}(\mathbf{R}_{12}) = - \sum_{\nu, \nu'}^{\text{occ}} \exp(i\mathbf{k}_{\nu\nu'} \cdot \mathbf{R}_{12}) I_{\nu\nu'}^{\alpha\gamma} (I_{\nu\nu'}^{\beta\delta})^* \mathcal{G}_{\nu\nu'}, \quad (5)$$

where ν indicates the valence-band state with the energy ε_ν [we lumped the band index n and the wave vector \mathbf{k} together, $\nu \equiv (n, \mathbf{k})$], $\mathbf{k}_{\nu\nu'} = \mathbf{k} - \mathbf{k}'$, and the matrices \mathcal{F} , \mathcal{H} , \mathcal{G} , I , and \mathcal{S} are

$$\mathcal{F}_{\nu\nu'} = \frac{1}{16} w_\nu^0 w_{\nu'}^0 \left(w_\nu^0 + w_{\nu'}^0 + \frac{1}{e_2 + e_1} \right), \quad (6)$$

$$\mathcal{H}_{\nu\nu'} = \frac{1}{20} \left[w_\nu^0 w_{\nu'}^0 \left(w_{\nu'}^1 - w_{\nu'}^0 - w_\nu^0 - \frac{1}{e_2 + e_1} \right) + w_\nu^1 w_{\nu'}^1 \left(w_\nu^0 + \frac{1}{e_2 - \Delta + e_1} \right) \right], \quad (7)$$

$$\mathcal{G}_{\nu\nu'} = \frac{1}{25} (w_\nu^1 + w_{\nu'}^1 - w_\nu^0 - w_{\nu'}^0) (w_\nu^1 w_{\nu'}^1 - w_\nu^0 w_{\nu'}^0), \quad (8)$$

$$I_{\nu\nu'}^{\alpha\gamma} = \sum_{\sigma\sigma'} V_\nu^{\gamma\sigma} \hat{\sigma}_{\sigma\sigma'}^\alpha (V_{\nu'}^{\sigma'\gamma})^*, \quad \mathcal{F}_{\nu\nu'}^{\alpha\gamma} = \sum_{\gamma' \neq \gamma} I_{\nu\nu'}^{\alpha\gamma'}. \quad (9)$$

Here, $\hat{\sigma}^\alpha$ are the Pauli matrices, $\sigma\sigma'$ the spin indices, and $V_\nu^{\gamma\sigma}$ the hybridization matrix elements between the valence-band state $|\nu\rangle$ and the d orbital $|\gamma\sigma\rangle$.⁹

The elements $\mathcal{F}_{\nu\nu'}$, $\mathcal{H}_{\nu\nu'}$, and $\mathcal{G}_{\nu\nu'}$ depend strongly on the excitation energies of the system. The energy denominators in w_ν^1 and w_ν^0 differ by the ionic spin-excitation energy $\Delta = E_5^{3/2} - E_5^{5/2}$:

$$w_\nu^i = (e_2 - \varepsilon_\nu - i\Delta + \varepsilon_0)^{-1}, \quad (10)$$

i.e., they represent the energy required to transfer a band electron with the energy ε_ν to the d shell of the Cr^{2+} ion decreasing ($i=0$) or increasing ($i=1$) the total spin of the ion, respectively. The symbols e_1 and $e_2 - \Delta$ have been assigned to the unperturbed energies of the charge transfers between the valence-band top (with energy ε_0) and the $3d$ shell of the ion ($e_1 = E_3^{3/2} - E_4^2 + \varepsilon_0$, $e_2 - \Delta = E_5^{5/2} - E_4^2 - \varepsilon_0$). These energies differ from the experimentally observed positions of the ionic $3+/2+$ and $2+/1+$ charge states since in the latter the second- and higher-order hybridization-induced crystal-field corrections are already embodied.¹⁹ The stability of the ground-state configuration (two Cr^{2+} ions and completely filled valence bands) imposes the condition that all energy denominators in Eqs. (6)–(8) have to be positive.

TABLE I. The dominant superexchange tensor components in zinc chalcogenides (in K).

	$V_{pd\sigma}$ (eV)	e_1 (eV)	e_2 (eV)	$J_{xx}^{xy,xy}$	$J_{xx}^{yz,yz}$	$J_{xx}^{xy,yz}$	$J_{xx}^{xz,yz}$
ZnS	-0.98	-1.7	6.2	0.55	0.06	1.06	0.37
ZnSe	-0.85	-0.75	5.25	0.62	0.40	1.20	0.71
ZnTe	-0.64	0.0	4.5	0.33	0.42	0.80	0.67

We have performed numerical calculations of the superexchange tensor for the Cr^{2+} ions in ZnS, ZnSe, and ZnTe crystals. The bands were described in the framework of Vogl's sp^3s^* tight-binding model²⁰ with the spin-orbit interaction,²¹ and the model's parameters taken from Ref. 22. We used the universal Harrison's parameters $V_{pd\sigma}$ (Ref. 18) to describe the $sp-d$ hybridization (the universal relations $V_{pd\pi} = -0.45V_{pd\sigma}$ and $V_{sd\sigma} = 1.08V_{pd\sigma}$ were imposed). For the charge transfer energies e_1 and $e_2 - \Delta$, we took the values deduced from experimental data on the position of donor and acceptor Cr^{2+} levels relative to the bands of the host material.²³ For the spin-excitation energy Δ , we used the average free-ion value of 3 eV.²⁴ The values of the diagonal tensor component $J_{xx}^{\gamma\delta}$ [with $(\gamma, \delta) = (xy, xy)$, (xy, yz) , (yz, yz) , and (yz, xz)] for the two nearest-neighbor Cr^{2+} ions lying in the $z=0$ plane are presented in Table I. When the spin-orbit splitting of the valence band is neglected the superexchange tensors acquire the scalar form, and these four components determine by symmetry the superexchange tensors for arbitrary nearest neighbors, γ and δ . The off-diagonal tensor components and the differences in the diagonal matrix elements, proportional to the spin-orbit splitting of the valence band even in ZnTe, are smaller than the diagonal components by 1 and 2 orders of magnitude, respectively. All diagonal components in all zinc chalcogenides turned out to be positive. According to the definition (1), positive exchange constants correspond to the ferromagnetic interactions. The calculated ferromagnetic superexchange for Cr ions seems to be much weaker than the observed antiferromagnetic interaction between Mn ions. We note, however, that Harrison's universal parameters $V_{pd\sigma}$ give also too small values to account for the observed exchange constants in Mn-based DMS's.^{9,10}

Of course, as in any model, there is some degree of uncertainty and arbitrariness in the choice of the model param-

eters. We verified, however, that the main features of the results are parameter independent. $V_{pd\sigma}$, entering in fourth power via a multiplicative factor, has no effect on the sign of the interaction, but it essentially influences the magnitude of the superexchange tensor. Therefore, for comparisons between various compounds, it is advantageous to eliminate this factor and to consider $J_{xx}^{\gamma\delta}/V_{pd\sigma}^4$. The dependence of the $J_{xx}^{xy,xy}/V_{pd\sigma}^4$ on the energy parameters e_1 and e_2 for the three zinc chalcogenides is presented in Fig. 1. (For other tensor components and configurations the plots are qualitatively similar.) One can see that the interactions remain ferromagnetic in an extensive range of parameters, the sign changes only for unrealistically large values of the charge-transfer energies.

The origins of the ferromagnetic character of the obtained ion-ion interactions can be traced by a careful analysis of Eqs. (3)–(8) and (10). Despite the fact that e_1 is negative in Cr-based DMS's (as confirmed by the observed ferromagnetic character of the $p-d$ exchange) all energy denominators in Eqs. (6)–(8) are positive by the aforementioned stability of the ground-state configuration. Consequently, for any ν and ν' the contributions to the superexchange tensor coming from the occupied orbitals only [Eq. (3)] and those involving the empty orbitals [Eqs. (4) and (5)] differ in sign, in agreement with the semiempirical Anderson-Goodenough-Kanamori rules for the sign of the superexchange in magnetic insulators.²⁵ Note that the ferromagnetic contributions $H_{\alpha\beta}^{\gamma\delta}$ and $G_{\alpha\beta}^{\gamma\delta}$ would vanish if the energy splittings between the ionic states of different total spin were neglected. Then, the superexchange tensor would be equal to the $F_{\alpha\beta}^{\gamma\delta}$, and it would acquire the antiferromagnetic form, very much similar to that obtained for Mn-based⁹ and for Fe- and Co-based²⁶ DMS's. Actually, for Cr^{2+} ions in $A_{II}B_{VI}$ DMS the contributions from empty orbitals ($H_{\alpha\beta}^{\gamma\delta}$ and $G_{\alpha\beta}^{\gamma\delta}$) prevail over the Mn-like contribution from the occupied orbitals ($F_{\alpha\beta}^{\gamma\delta}$) for a wide range of the charge transfer energies e_1 and e_2 , as depicted in Fig. 2.

The essential results of the present paper are as follows: (1) the superexchange between two nearest-neighbor Cr^{2+} ions is dominated by the isotropic Heisenberg-type interaction; (2) these Heisenberg-type interactions turn out to be ferromagnetic in all materials considered, in contrast to the

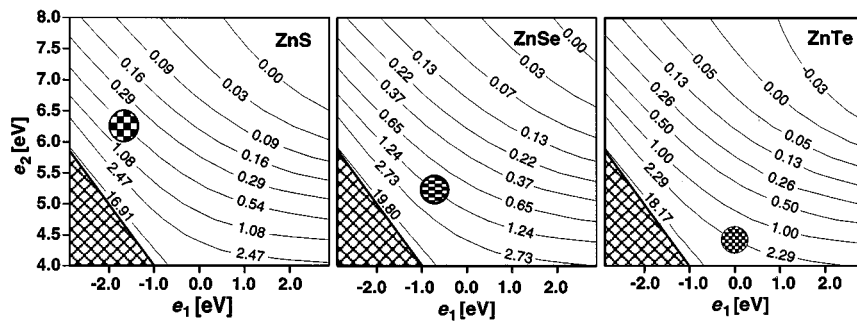


FIG. 1. Contour graphs showing the dependence of the J_{xx} superexchange tensor component on the model energies e_1 and e_2 for two nearest-neighbor Cr^{2+} ions in $z=0$ plane (in ZnSe, ZnS, and ZnTe) with Jahn-Teller distortions mutually parallel and perpendicular to the plane ($\gamma=xy$, $\delta=xy$). The shaded circles define approximately the areas of the e_1 and e_2 values compatible with the positions of Cr $3+/2+$ and $2+/1+$ levels given in Ref. 23. The cross-hatched triangles indicate the unphysical region of e_1 and e_2 , where $e_2 - \Delta + e_1 \leq 0$.

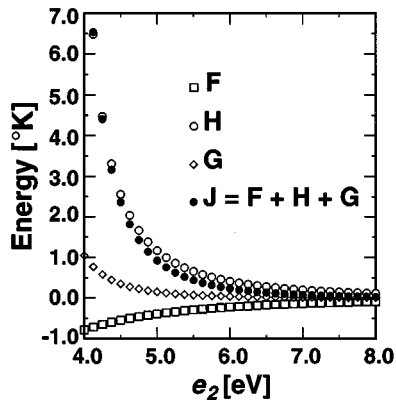


FIG. 2. Typical dependence of the ferromagnetic (H and G) and antiferromagnetic (F) contributions to a superexchange tensor component (J) on the charge transfer energy e_2 for Cr^{2+} ions in zinc chalcogenides exemplified for $J_{xx}^{xy,xy}$, ZnSe, and for $e_1 = -0.75$ eV.

case of Mn^{2+} , Fe^{2+} , and Co^{2+} studied so far; (3) the strength of the interaction depends on the relative orientations of the Jahn-Teller distortions of the interacting chromium ions, so that the $d-d$ interactions in Cr-based DMS may not be characterized by a single nearest-neighbor exchange constant J_1 .

We expect the above results for Cr^{2+} ions to be valid in other $A_{\text{II}}B_{\text{VI}}$ compounds, since the charge-transfer energies in zinc and cadmium chalcogenides are nearly the same, and $J_{\alpha\beta}^{\gamma\delta}/V_{pd\sigma}^4$ shows relatively weak dependence on the band-structure details. Finally, it has to be emphasized that, whatever the strength of the $d-d$ interactions in Cr-based DMS's, the very fact that they are not antiferromagnetic should motivate technological efforts directed towards obtaining the $A_{\text{II}}B_{\text{VI}}$ alloys with a high Cr content.

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