



Ferromagnetism in Cr-based diluted magnetic semiconductors

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Abstract

The antiferromagnetic ion–ion interactions observed in $A_{II}B_{VI}$ diluted magnetic semiconductors (DMS) impose an upper limit to the increase of the giant free carrier spin-splitting with the growing content of the magnetic ions. In this paper we report the first calculations of the superexchange in Cr-based DMS and we predict the ion–ion interactions to be ferromagnetic in these materials. Within the same model we clarify the origins of the recently discovered ferromagnetic p–d interactions in zinc chalcogenides with Cr^{2+} paramagnetic ions.

The most spectacular feature of diluted magnetic semiconductors (DMS), i.e., the giant spin splitting of the free-carriers 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). In the diluted limit this splitting is proportional to the concentration of the magnetic ions. The increase of the magnetic-ions content enhances however the role of the ion–ion (d–d) interactions. These interactions, being antiferromagnetic in all known DMS, reduce the average ionic magnetic moment and impose, therefore, an upper limit to the increase of the free-carrier spin-splitting with the growing number of magnetic ions. It is evident that a material with ferromagnetic d–d interactions would open really new perspectives and allows one to profit fully from the excellent magneto-optical properties of $A_{II}B_{VI}$ DMS.

Unusual ferromagnetic p–d interactions have recently been discovered in zinc chalcogenides with Cr^{2+} paramagnetic ions [1,2]. A theoretical analysis of the kinetic exchange in Cr-based $A_{II}B_{VI}$ DMS [3,4] indicated that these interactions should be strongly affected by the static Jahn–Teller effect observed in these materials, i.e., the interaction should depend on the relative population of Cr^{2+} ions with different orientations of the tetragonal Jahn–Teller distortions. The experiment reported in Ref. [1] seems to correspond to the situation when none of the possible equivalent directions of these distortions is significantly privileged. According to Eq. (30) in Ref. [3] the mean field p–d exchange constant for Γ_8 bands ($N_0\beta$) should thus be proportional to $(2B - C)$.

The exchange constant B (given by Eq. (19) in Ref. [3]), collects the contributions from virtual transitions involving singly occupied ionic orbitals, i.e., the charge transfers from the ion into the valence band and from the valence band onto the ionic d-shell, in both cases reducing the total spin of the chromium ion to $S = 3/2$. In the following, we

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denote the corresponding transfer energies by e_1 and e_2 , respectively.

The constant C , Eq. (21) in Ref. [3], describes the contribution from virtual transitions involving the empty t_{2g} orbital only, i.e., the charge transfers from the valence band to the ground ($S = 5/2$) and excited ($S = 3/2$) states of the Cr^{1+} ion, with the corresponding transfer energies $e_2 - \Delta$ and e_2 , respectively.

In Fig. 1 we present the contour plots of the calculated p–d exchange constants $N_0\beta$ versus e_1 and e_2 for zinc and cadmium chalcogenides with Cr^{2+} paramagnetic ions. Please note that e_1 and e_2 are the charge transfer energies of the unperturbed system and their exact values are rather difficult to establish, since the experimentally observed energies already incorporate the second and higher order corrections. In Fig. 1 the centers of the shaded circles correspond to the values experimentally deduced in Ref. [5] for the given compound, whereas the parameter uncertainty radius was chosen rather arbitrarily. One can see from Fig. 1 that the theory correctly accounts for the observed ferromagnetic character of

the p–d exchange in ZnSe and ZnS. Surprisingly enough, when the universal Harrison's values of hybridization matrix elements and the free ion value $\Delta = 3$ eV [6] are used, the resulting $N_0\beta$ values for these compounds are in excellent agreement with the existing experimental results (0.57 ± 0.1 for ZnS and 0.83 ± 0.1 for ZnSe) [2]. ZnTe and CdTe are situated at the borderline $e_1 = 0$ between very large ferromagnetic and very large antiferromagnetic exchange constants. Our result indicates that one can expect large values and unusual concentration and pressure dependencies of the p–d exchange constants in these materials. It has to be mentioned, however, that the conclusions concerning ZnTe and CdTe are purely qualitative, since in Ref. [3] the p–d interaction was derived within the perturbational approach, hardly applicable to the case $e_1 = 0$.

The essential purpose of the above comparison between the theoretical and experimental results on $N_0\beta$ was to test the model parameters. The main objective of the present study is the theoretical, qualitative and quantitative, analysis of the superexchange interactions between Cr^{2+} ions in $A_{II}B_{VI}$

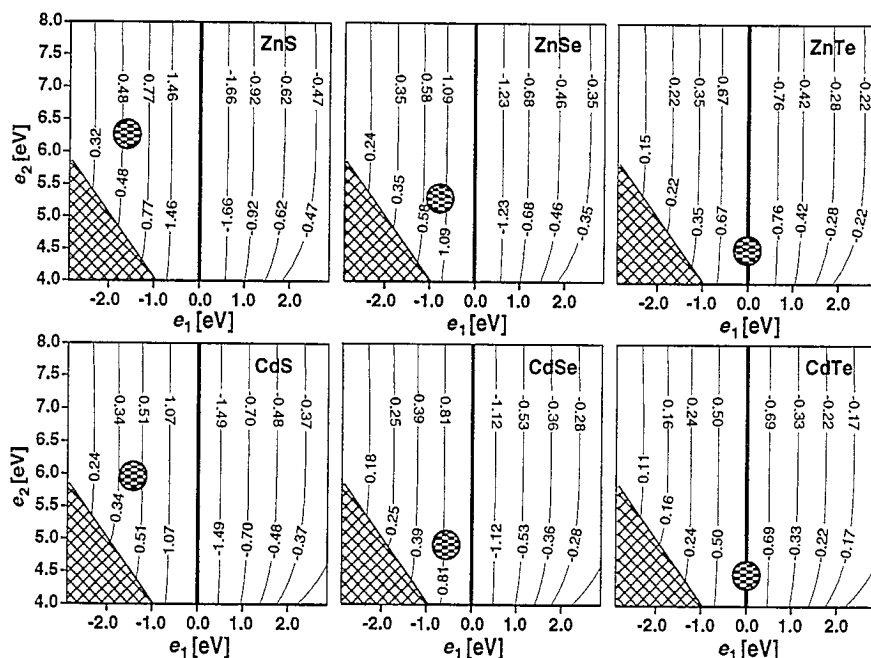


Fig. 1. Contour graph presenting ($N_0\beta$) (in eV) as a function of transfer energies e_1 and e_2 for zinc and cadmium chalcogenides. The shaded circles define approximately the areas of the e_1 and e_2 values compatible with the positions of the Cr $3+/2+$ and $2+/1+$ levels given in Ref. [5]. The cross-hatched triangles indicate the unphysical region of e_1 and e_2 , where $e_2 - \Delta + e_1 \leq 0$, i.e., the region for which the situation with 5 electrons in the d-shell of one chromium ion and 3 in the d-shell of the other would be energetically favored.

compounds within the same model as used previously [3] for the calculation of the kinetic (p - d) exchange in these materials. To calculate the superexchange using the perturbative k -space approach of Larson and Ehrenreich [7], 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. The unperturbed ions are described, as in Ref. [3], by the rotationally invariant Parmenter Hamiltonian. For the itinerant electrons, in contrast to what was needed for the calculations of kinetic exchange, one has to describe the band structure in the entire Brillouin zone. We describe the bands within Vogl's sp^3s^* empirical tight-binding model [8] taking into account the spin-orbit interaction [9].

The 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 . The indices γ and δ define the Jahn-Teller singlet states of the interacting ions. The numerical 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 neighbour Cr^{2+} ions lying in the $z = 0$ plane in various zinc and cadmium chalcogenides [10] are presented in Table 1. The off-diagonal tensor components and the differences in the diagonal matrix elements, proportional to the spin-orbit splitting of the valence band, are smaller than the diagonal components by one and two orders of magnitude, respectively. All diagonal components in all chalcogenides studied turned out

to be positive, what, according to the definition (1), corresponds to the ferromagnetic interactions.

The superexchange tensor J consists of three terms 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), all with appropriate charge transfer energies in the denominators. The sign of the two latter terms (H and G) is opposite to the sign of the term F . The term F collects the contributions involving virtual transitions only to the excited spin states ($S = 3/2$) of the Cr^{1+} ion with the charge transfer energies exceeding e_2 . The terms G and H collect as well the contributions from virtual transitions to the ground spin state ($S = 5/2$) of Cr^{1+} ion with the charge transfer energies down to $(e_2 - \Delta)$. This is why, for Cr^{2+} ions in $A_{II}B_{VI}$ crystals for a wide range of the charge transfer energies, the ferromagnetic contributions from empty orbitals (H and G) prevail over the antiferromagnetic Mn-like contri-

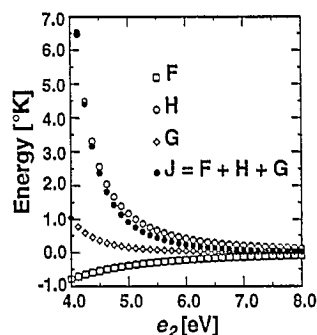


Fig. 2. Typical dependence of the ferromagnetic (H and G) and antiferromagnetic (F) contributions to a superexchange tensor component (J) on the charge transfer energy e_2 for Cr^{2+} ions in zinc and cadmium chalcogenides exemplified for $J_{xx}^{xy,xy}$, ZnSe, and for $e_1 = -0.75$ eV.

Table 1
The dominant superexchange tensor components in various Cr-based DMS (in K)

	e_1 (eV)	e_2 (eV)	$J_{xx}^{xy,xy}$	$J_{xx}^{yz,yz}$	$J_{xx}^{xy,yz}$	$J_{xx}^{xz,yz}$
ZnS	-1.7	6.2	0.55	0.06	1.06	0.37
ZnSe	-0.75	5.25	0.62	0.40	1.20	0.71
ZnTe	0.0	4.5	0.33	0.42	0.80	0.67
CdS	-1.5	6.0	0.17	0.76	0.61	0.33
CdSe	-0.55	5.05	0.20	0.20	0.66	0.47
CdTe	0.0	4.5	0.15	0.15	0.38	0.28

bution from the occupied orbitals F , as depicted in Fig. 2. Finally, we note also that the origin of the ferromagnetic character of the superexchange in Cr-based $A_{II}B_{VI}$ DMS is different from that of the ferromagnetic kinetic exchange observed in these compounds. The latter, as shown in Fig. 1 is essentially due to the fact that the charge transfer energy e_1 is negative.

In summary, we have presented a model that explains the observed ferromagnetic p–d exchange constants in Cr-based zinc chalcogenides. In cadmium chalcogenides, for which the transfer energies are almost identical as in the corresponding zinc compounds, we predict the p–d exchange to have the same ferromagnetic character as in zinc chalcogenides. The superexchange between two nearest neighbour Cr^{2+} ions obtained within the same model is dominated by the isotropic Heisenberg-type interaction, ferromagnetic in all materials studied. 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 may not be characterized by a single nearest neighbor exchange constant J_1 . Although the ferromagnetic d–d interactions in Cr-based DMS seem to be much weaker than those in Mn-, Fe- or Co-based materials, the very fact that they are not antiferromagnetic should motivate technological efforts directed towards obtaining the $A_{II}B_{VI}$ alloys with a high Cr content.

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