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SUPEREXCHANGE IN $\mathrm{A^{II}B^{VI}}$ DILUTED MAGNETIC SEMICONDUCTORS WITH Mn, Fe AND Co IONS

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A theory of superexchange, the dominant ion–ion spin interaction, for Mn-, Fe- and Co-based DMS is presented. The theory takes into account the band structure of $\mathrm{A^{II}B^{VI}}$ compounds, the orbital dependence of the hybridization and the intra shell correlations of the d-electrons, which are essential in the case of the non-S-state ions. The general formulae relating the superexchange to the band structure and the ionic energy spectrum were obtained — the dominant part of the superexchange turns out to be inversely proportional to the square of the ionic spin. This explains the observed increase in the average values of d–d exchange constants, when passing from Mn via Fe to Co ions in DMS.

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The ion–ion (d–d) spin interactions in diluted magnetic semiconductors (DMS) have been theoretically investigated by many authors (for a review on this subject and a list of references see K.C. Hass in Ref. [1]). The indirect exchange [2–4], as well as the superexchange [5, 6] were invoked to account for the observed isotropic (Heisenberg) and anisotropic (Dzyaloshinski–Moriya) exchange constants. Using a perturbative k-space approach Larson et al. [5] have shown that the superexchange, resulting from sp–d hybridization, is by far the dominant spin–spin interaction mechanism in $\mathrm{A^{II}B^{VI}}$ DMS. In papers [5] and [6] the authors, considering the case of the S-like $\mathrm{Mn^{2+}}$ magnetic ion, have used the simplest Anderson model to approximate the ionic energy spectrum. Furthermore, in the calculations of isotropic exchange [5] the ionic orbital dependence of the hybridization Hamiltonian was neglected. In the case of Mn-based DMS the above approximations are justified and the results obtained account well for both the isotropic and anisotropic spin–spin interactions experimentally observed in these materials.

One of the trends in the current DMS research is to study systems containing magnetic ions other than Mn^{2+}. A considerable number of experimental data is already accumulated for DMS with Fe^{2+} and Co^{2+} ions [7–10]. The experimentally determined *d–d* exchange constants in Fe-based DMS turned out to be significantly larger than in the corresponding Mn-based DMS and a still further increase has been observed in DMS with Co ions. In the absence of the theoretical model of *d–d* spin interactions for non-*S*-state ions, the observed results are tentatively interpreted by modifying the energy denominators [1] and/or hybridization matrix elements [11] in the existing theory for Mn-DMS.

The purpose of the present paper is to derive general formulae describing the superexchange interactions, both isotropic and anisotropic, for Fe and Co based $A^{II}B^{VI}$ DMS. For comparison, in the same framework we derive the formulae for Mn based DMS. Following Larson et al. [5], we employ the perturbative *k*-space approach. We observe, however, that the two aforementioned approximations used in Ref. [5] may lead to erroneous results in the case of non-*S*-state ions. Thus, for DMS with such ions we use a model similar to that in Ref. [12]. The ionic energy spectrum E_N^S is described by the rotationally invariant Parmenter Hamiltonian whereas the one-electron *d*-orbitals are chosen in the form of e_g-doublet and t_{2g}-triplet. On the other hand, the band states are constructed in the spirit of empirical tight-binding method from *s* and *p* orbitals of anions and cations. The hybridization of ionic and band states results primarily from the mixing of *d*-orbitals with *p*-orbitals of nearest-neighbour anions, depending on the two Harrison integrals $V_{pd\rho}$ and $V_{pd\pi}$ [13]. Even though all *d*-orbitals do hybridize with all *p*-orbitals of a given neighbour, in the vicinity of the centre of the Brillouin zone the contributions from e_g orbitals of all neighbours mutually cancel whereas each t_{2g} orbital does hybridize with a single tight-binding *p*-like basis function.

To calculate the superexchange one has to go to the fourth-order perturbation theory with respect to the hybridization Hamiltonian H_h applied to the system of two ions and the crystal with the completely filled valence bands. In the subspace of degenerate states $|m\rangle$ with the energy E_0 a general fourth-order Hamiltonian matrix reads

$$-\sum_{n,n',l}\frac{\langle m'|H_\mathrm{h}|n'\rangle\langle n'|H_\mathrm{h}|l\rangle\langle l|H_\mathrm{h}|n\rangle\langle n|H_\mathrm{h}|m\rangle}{(E_n-E_0)(E_{n'}-E_0)(E_l-E_0)}. \tag{1}$$

The derivation of the spin-spin superexchange Hamiltonian starts with the proper selection of the intermediate states in (1). In states $|n\rangle$ and $|n'\rangle$ one of the valence band electrons was transferred into a *d*-orbital of one of the magnetic ions. In the next step, to reach the intermediate state $|l\rangle$, either another band electron is transferred into the other ion (the state $|l\rangle$ is then a state of two holes in the valence band and an extra electron on each of the two magnetic ions) or an electron from the *d*-orbital of the second ion is transferred into the band (no holes in the valence band, $N+1$ and $N-1$ electrons on the ions in the state $|l\rangle$). The resulting matrix can be expressed in an operator form

$$H_s=\sum_{i,j=x,y,z}J_{ij}(\boldsymbol{R}_2-\boldsymbol{R}_1)\hat{S}_{1i}\hat{S}_{2j}, \tag{2}$$

where $\boldsymbol{S}_1$ and $\boldsymbol{S}_2$ are the spin operators of the ion 1 and 2, respectively. For the components of the tensor we obtain

$$
\begin{aligned}
J_{ij}(\boldsymbol{R}_2-\boldsymbol{R}_1) &= \sum_{n,n'}\int_{\mathrm{BZ}}\frac{\mathrm{d}^3\boldsymbol{k}}{(2\pi)^3}\int_{\mathrm{BZ}}\frac{\mathrm{d}^3\boldsymbol{k}'}{(2\pi)^3} \\
&\times\left\{(2S)^{-2}W_{nn'}I^{i}_{nn'}I^{j^*}_{nn'}+(2S)^{-1}(2S+1)^{-1}U_{nn'}\left[K^{i}_{nn'}I^{j^*}_{nn'}+K^{j^*}_{nn'}I^{i}_{nn'}\right]\right\} \\
&\times\frac{\exp[\mathrm{i}(\boldsymbol{k}'-\boldsymbol{k})(\boldsymbol{R}_2-\boldsymbol{R}_1)]}{\left[E^{S}_{N}+\varepsilon_n(\boldsymbol{k})-E^{S-1/2}_{N+1}\right]\left[E^{S}_{N}+\varepsilon_{n'}(\boldsymbol{k}')-E^{S-1/2}_{N+1}\right]},
\end{aligned}
\tag{3}
$$

where

$$
\begin{aligned}
W_{nn'} &= \left[E^{S-1/2}_{N+1}-E^{S}_{N}-\varepsilon_n(\boldsymbol{k})\right]^{-1}+\left[E^{S-1/2}_{N+1}-E^{S}_{N}-\varepsilon_{n'}(\boldsymbol{k}')\right]^{-1} \\
&\quad +2\left[E^{S-1/2}_{N+1}-E^{S-1/2}_{N-1}-2E^{S}_{N}\right]^{-1}
\end{aligned}
$$

and

$$
U_{nn'}=\left[E^{S-1/2}_{N+1}-E^{S+1/2}_{N-1}-2E^{S}_{N}\right]^{-1}-\left[E^{S-1/2}_{N+1}-E^{S-1/2}_{N-1}-2E^{S}_{N}\right]^{-1}.
$$

From the components of the tensor the isotropic (Heisenberg), the pseudo-dipolar and the anisotropic (Dzyaloshinski–Moriya) exchange constants can be directly determined. The $\boldsymbol{k},\boldsymbol{k}'$-dependent functions $I^{i}_{nn'}$ and $K^{i}_{nn'}$ describe the hybridization of the many-electron ionic states with the Bloch functions of the bands n and n'. The former represent the contribution from all singly occupied ionic orbitals, whereas the latter the contribution from the doubly occupied e_{g} orbitals. After putting $S=5/2$ and noting that in Mn^{2+} ions all $5d$-orbitals are singly occupied, one gets from (3) the results compatible with those of Larson and Ehrenreich [6].

For Fe^{2+} and Co^{2+} ions all terms in Eq. (3) should be taken into account. The detailed, numerical calculations of $J_{ij}(\boldsymbol{R}_2-\boldsymbol{R}_1)$ are in progress. Here we note that even when weaker hybridization of ionic e_{g} orbitals with the p-like valence bands is completely disregarded (and the expressions for the tensor $J_{ij}(\boldsymbol{R}_2-\boldsymbol{R}_1)$ become the same for Mn^{2+}, Fe^{2+} and Co^{2+} ions) one should still expect the exchange integrals to vary from ion to ion and from compound to compound, owing to differences in Harrison's hybridization matrix elements, ionic and crystal energy spectra and the ionic spin S. Surprisingly enough, it is the factor $(2S)^{-2}$ alone which seems to be decisive for the explanation of the observed increase in the average isotropic exchange constants, when passing from Mn^{2+} ($S=5/2$) ions via Fe^{2+} ($S=2$) to Co^{2+} ($S=3/2$) ions.

References

[1] *Semimagnetic Semiconductors and Diluted Magnetic Semiconductors*, Eds. M. Averous, M. Balkanski, World Scientific, Singapore 1991.

[2] G. Bastard, C. Lewiner, *Phys. Rev. B* **20**, 4256 (1979).

[3] J. Ginter, J. Kossut, L. Swierkowski, *Phys. Status Solidi B* **96**, 735 (1979).

[4] V.-C. Lee, L. Liu, *Phys. Rev. B* **29**, 2125 (1984).

[5] B.E. Larson, K.C. Hass, H. Ehrenreich, A.E. Carlsson, *Solid State Commun.* **56**, 347 (1985); *Phys. Rev. B* **37**, 4137 (1988).

[6] B.E. Larson, H. Ehrenreich, *Phys. Rev. B* **39**, 1747 (1989).

[7] Y. Shapira, in Ref. [1], p. 121.

[8] A. Twardowski, in: *Diluted Magnetic Semiconductors*, Ed. M. Jain, World Scientific, Singapore 1991, p. 275.

[9] A. Lewicki, A.I. Schindler, J.K. Furdyna, T. Giebultowicz, in: *Diluted Magnetic Semiconductors*, Ed. M. Jain, World Scientific, Singapore 1991, p. 409.

[10] A. Twardowski, H.J.M. Swagten, W.J.M. de Jonge, in: *II–VI Semiconductor Compounds*, Ed. M. Jain, World Scientific, Singapore 1993, p. 227.

[11] K.C. Hass, in Ref. [1], p. 59.

[12] J. Blinowski, P. Kacman, *Phys. Rev. B* **46**, 12298 (1992).

[13] W.A. Harrison, *Electronic Structure and the Properties of Solids*, H. Freeman and Co., San Francisco 1980.