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# *s-p-d-f* EXCHANGE INTERACTIONS IN Mn AND Eu BASED IV–VI SEMIMAGNETIC SEMICONDUCTORS*

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We evaluated exchange integrals which describe the spin dependent coupling between effective mass electrons and localized spins in the IV–VI semimagnetic semiconductors taking into account contributions from the direct Coulomb exchange as well as from the hybridization between band states and magnetic shells. The obtained constants compare favorably with the experimental values for both the Mn- and the Eu-based compounds. We also discuss some peculiarities of IV–VI semimagnetic semiconductors, which may render the virtual-crystal approximation invalid.

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Since the pioneering work of Niewodniczańska-Zawadzka et al. [1] on magnetotransport properties of $Pb_{1-x}Mn_xTe$, several studies of IV–VI semimagnetic semiconductors have been carried out [2]. These studies, particularly interband magnetotransmission [3, 4], coherent anti-Stokes Raman scattering [3, 5] as well as laser emission [6] have unambiguously demonstrated the existence of an appreciable spin-dependent coupling between effective mass electrons and open magnetic shells in IV–VI compounds containing either Mn [3, 4, 6] or Eu [5]. A similar conclusion emerges from the free-carrier-induced ferromagnetic phase transition in $Pb_{1-x-y}Sn_yMn_xTe$ [7].

The magnetooptical experiments referred to above [3–5] were interpreted quantitatively in terms of an elaborated six-band $\boldsymbol{k}\cdot\boldsymbol{p}$ model [2], which took the presence of magnetic ions into account in the framework of the mean-field and virtual-crystal approximations. According to that model the exchange interaction $-J\boldsymbol{s}\cdot\boldsymbol{S}$ introduces four additional $\boldsymbol{k}\cdot\boldsymbol{p}$ parameters, two for holes ($L^{6+}$ double-group representation):

$$a_1 = \cos^2\Theta^+\langle R|J|R\rangle \quad \text{and} \quad A = a_1 - \sin^2\Theta^+\langle S_\pm|J|S_\pm\rangle,$$

and two for electrons ($L^{6-}$):

$$b_1 = \cos^2\Theta^-\langle Z|J|Z\rangle \quad \text{and} \quad B = b_1 - \sin^2\Theta^-\langle X_\pm|J|X_\pm\rangle,$$

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where in tellurium compounds $\cos\Theta^-$ should be replaced by $\sin\Theta^-$ and vice versa.

In the above equations $\Theta^{\pm}$ are the spin-orbit mixing parameters computed in Ref. [8], while $|R\rangle$, $|S_{\pm}\rangle$, $|Z\rangle$ and $|X_{\pm}\rangle$ denote the Luttinger amplitudes, which transform according to $L_{1+}$, $L_{3+}$, $L_{2-}$, and $L_{3-}$, single-group representations, respectively.

The experimental values of the exchange parameters, summarized in Table, lead to an interesting conclusion that the exchange integrals are of opposite signs in the case of Mn and Eu compounds [4, 5] but in the both groups of materials the exchange coupling is much stronger for holes than for electrons [3–6]. Furthermore, the exchange parameters of holes were found to exhibit an unexpected dependence on the magnetic ion concentration [3, 5] and temperature [3], a behavior taken as indicative for the breakdown of the mean-field approximation [3].

TABLE

Experimental and calculated values of the exchange energies (in meV) for IV–VI semimagnetic semiconductors.

| | | $Pb_{1-x}Mn_xTe$ | $Pb_{1-x}Mn_xSe$ | $Pb_{1-x}Eu_xSe$ |
|---|---|---|---|---|
| $a_1$ | expl. | $-330 \div -265$ [3] | $-270 \div -180$ [4] | $+24 \div +106$ [4, 5] |
| | calc. | $-245$ | $-470$ | $+65$ |
| $A$ | expl. | $-210 \div -35$ [3] | $-200 \div -140$ [4] | $+26 \div +112$ [4, 5] |
| | calc. | $-240$ | $-450$ | $+60$ |
| $b_1$ | expl. | $+22 \div +64$ [3] | $+60 \div +90$ [4] | $+4 \div +29$ [4, 5] |
| | calc. | $+40$ | $+100$ | $+15$ |
| $B$ | expl. | $-23 \div -61$ [3] | $+7 \div +14$ [4] | $+3 \div +36$ [4, 5] |
| | calc. | $-65$ | $+55$ | $+10$ |

In order to establish the dominant mechanisms of the spin dependent interaction we have extended for IV–VI compounds a tight-binding model (see for instance [9]) of the exchange coupling in covalent solids. Within this model the coupling between carriers and localized spins depends on the type of magnetic-ion orbitals which hybridized with the band state. If symmetry allows the *non*-magnetic orbitals of the magnetic ion to contribute to the carrier wave function, the direct Coulomb ferromagnetic exchange interaction operates. If, on the other hand, the magnetic orbitals are involved, the spin dependent coupling proceeds via a second-order hybridization process, i.e., via the so-called kinetic exchange mechanism. Taking both contributions into account the exchange integral for compounds containing ions with half filled magnetic shells can be written in the form

$$\langle u_{\boldsymbol{k}}|J|u_{\boldsymbol{k}}\rangle = \sum_{l} |a_{\boldsymbol{k}}(l)|^2 J_{l-d(f)} - \sum_{j} \left| \sum_{l,i} a_{\boldsymbol{k}}(l) \langle l_{\boldsymbol{R}_i} \mathrm{e}^{\mathrm{i}\boldsymbol{k}\boldsymbol{R}_i} |H| d^{(j)}(f^{(j)})\rangle \right|^2 S^{-1}$$
$$\times [(E_{\boldsymbol{k}} - E_{d(f)})^{-1} + (U_{\mathrm{eff}} - E_{\boldsymbol{k}} + E_{d(f)})^{-1}],$$

where $J_{l-d(f)}$ are the intra-atomic exchange energies, for which we take values resulting from the known spectra (see for instance [10]) of the free $\mathrm{Mn}^{1+}$ and $\mathrm{Eu}^{1+}$ ions: $J_{4s-3d} = 392$ meV, $J_{4p-3d} = 196$ meV, $J_{4d-3d} = 107$ meV, $J_{6s-4f} = 52$ meV, $J_{6p-4f} = 33$ meV, $J_{5d-4f} = 215$ meV. The coefficients $|a_{\boldsymbol{k}}(l)|^2$ denote fractional contributions of cation or anion atomic wave functions $|l_{\boldsymbol{R}_i}\rangle$ in the Bloch wave function $|u_{\boldsymbol{k}}\rangle$. In order to estimate their magnitude we carried out a tight binding model calculation of the lead-chalcogenides band-structure at the $L$ point of the Brillouin zone (see for instance [11]). We find out that the hole amplitude $|R\rangle$ contains approximately equal contributions from the anion $p$ and cations $s$ wave functions, while $|S_{\pm}\rangle$ is built mostly from the anion $p$ wave function. However, both $|R\rangle$ and $|S_{\pm}\rangle$ can contain an admixture of the cation $d$ wave functions. The latter has two important consequences in the case of the semimagnetic alloys. First, the low lying Eu $5d$ level participates in bonding and gives a significant contribution to the hole wave function (about 25% to $|R\rangle$ and 50% to $|S_{\pm}\rangle$). Secondly, in the Mn compounds the kinetic exchange takes place due to the nearest neighbor anion–cation $p$–$d$ hybridization and, in the case of $L_{1+}$ state, due to the next nearest neighbor cation–cation $s$–$d$ hybridization. The magnitude of this exchange depends on the Slater–Koster interatomic matrix elements $\langle l_{\boldsymbol{R}_i} \mathrm{e}^{\mathrm{i}\boldsymbol{k}\boldsymbol{R}_i}|H|d\rangle$, which we evaluate following Harrison and Straub [12]. Furthermore, in the absence of experimental information, we take for the energy denominators the values determined for II–VI semiconductors, i.e., $E_{\boldsymbol{k}} - E_d \approx 0.5U_{\mathrm{eff}} \approx 3.5$ eV. Turning to the electrons we remark that the odd parity $|Z\rangle$ and $|X_{\pm}\rangle$ consist of the cation $p$ ($\approx$ 75%), and also anion $d$ wave functions. Those wave functions do not hybridize with the cation $d$ orbitals but, in principle, may hybridize with the $f$ ones. This hybridization appears, however, to be small enough to be neglected.

Results of numerical calculations performed according to the above procedure are compared to the experimental findings in Table. Inspection of the data indicates that our model embodies the essential features of the exchange interactions in IV–VI semimagnetic semiconductors. Within its framework the effect of the Mn spins upon the holes comes from the kinetic exchange, mediated by the anion–cation $p$–$d$ and cation–cation $s$–$d$ hybridization, somewhat reduced by the ferromagnetic $s$–$d$ intra-atomic exchange. In the case of electrons the relatively weak intra-atomic $p$–$d$ exchange is involved. In the Eu compounds, in turn, the holes experience the strong $d$–$f$, while the electrons the weak $p$–$d$ intra-atomic exchange interaction.

We also analyzed possible origins of the unusual dependence of the hole exchange integrals on the magnetic ion concentration and temperature. We note that the existence of the semimagnetic IV–VI alloys, i.e., the possibility of substitution of the group-IV element by the group-II element without creating acceptor states can hardly be reconciled with the virtual-crystal approximation [13] and, therefore, calls into question its straightforward applicability for a description of electronic states in the alloys under consideration. This concerns, first of all, cation $s$ states and, in particular, causes that the sign and magnitude of the coefficient $a_{\mathbf{k}}(s)$ may depend on the local cation configuration. For clusters rich in PbTe $a_{\mathbf{k}}(s)/a_{\mathbf{k}}(p) \approx +1$, as the Pb $s$ states reside below the anion $p$ states. In MnTe and EuTe, however, the ordering of these states is reverse and, therefore, $a_{\mathbf{k}}(s)/a_{\mathbf{k}}(p) \approx -1$. This may have a rather dramatic effect on the exchange integrals: the magnitude of $A$ calculated for the above two values of $a_{\mathbf{k}}(s)/a_{\mathbf{k}}(p)$ is $-236$ and $+126$ meV, respectively, a trend consistent with the experimental findings [3]. The same effect may account for the temperature dependence of the exchange integrals as, because of antiferromagnetic interactions among magnetic ions, their effective concentration increases with the temperature.

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