Ferromagnetic *p-d* Exchange in $Zn_{1-x}Cr_xSe$ Diluted Magnetic Semiconductor

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We measured free exciton splitting and Faraday rotation of the diluted magnetic semiconductor $Zn_{1-x}Cr_xSe$ ($x < 0.005$) and found valence band splitting which is reversed relative to the materials with Mn, Co, or Fe. This fact indicates a ferromagnetic *p-d* exchange, observed for the first time in II-VI diluted magnetic semiconductors.

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Diluted magnetic semiconductors (DMS) constitute a broad class of materials based on typical semiconductors (e.g., II-VI compounds) where a fraction of nonmagnetic cations is randomly substituted by magnetic ions (typically Mn, Co, or Fe) [1]. One of the most important features of these materials is a strong *s,p-d* exchange interaction between delocalized band electrons and localized electrons of magnetic ions. This interaction results in large splittings of conduction and valence bands in a magnetic field, which leads to spectacular effects (such as giant Faraday rotation or giant exciton splitting) [1]. As the key physical mechanism of the phenomena distinguishing DMS, *s,p-d* exchange interaction has been attracting the attention of many theoreticians. Although the efforts aimed at understanding the mechanism of that interaction resulted in tens of publications, the problem is still alive and substantial disagreement remains [2–7]. The available experimental data cannot further advance our understanding of the exchange mechanism since the electronic structure of the magnetic ions incorporated so far in DMS is rather similar. Therefore new materials containing ions of significantly different electronic structure should constitute a precious source of new information.

Let us recall that the exchange interaction between conduction band *s*-type electrons and *d* electrons represents the so-called direct exchange case and favors ferromagnetic *s-d* coupling. On the other hand interaction between valence band *p*-type electrons and *d* electrons is dominated by *p-d* hybridization [2–7]. At the center of the Brillouin zone (BZ) only *d* electrons of *t*-type symmetry can hybridize with *p* electrons (*e*-type orbitals hybridize only away from the BZ center). This makes the occupancy of *t*-type orbitals of the magnetic ion *d*-level crucial for the *p-d* exchange [2]. It turns out that for Mn (d^5 electronic configuration), Co (d^7), and Fe (d^6) ions, the occupancy of *t*-type orbitals is the same: all spin-up *t*-type orbitals (t_+) are occupied and all spin-down *t*-type orbitals (t_-) are empty (Mn: $d^5 = e_+^2 t_+^3 e_-^0 t_-^0$, Fe: $d^6 = e_+^2 t_+^3 e_-^1 t_-^0$, Co: $d^7 = e_+^2 t_+^3 e_-^2 t_-^0$). This means that only spin-down electrons from the valence band can jump onto the *d* level, which finally leads to the antiferromagnetic *p-d* coupling observed for all the Mn-, Co-, and Fe-based DMS studied so far. Moreover single occupancy of *t*-type orbitals in the case of Mn, Fe, and Co ions implies a simple isotropic Heisenberg-type Hamiltonian describing the *s,p-d* exchange [2, 6],

$$H \sim \mathbf{S}\sigma \, , \tag{1}$$

where $\mathbf{S} = (S_x, S_y, S_z)$ is the spin of the magnetic ion and $\sigma = (\sigma_x, \sigma_y, \sigma_z)$ is the spin operator of the band electron. Summing the interactions over randomly distributed magnetic ions one finds that the total conduction-valence band splitting reads [1]

$$\Delta E = (N_0\alpha - N_0\beta)x\langle S\rangle \, , \tag{2}$$

where x is the ion concentration, $\langle S\rangle$ is the thermodynamic average of the ion spin component along the applied magnetic field, and $N_0\alpha, N_0\beta$ are exchange parameters for the conduction and valence bands, respectively. As noted above for Mn, Co, and Fe DMS $N_0\alpha > 0$ [ferromagnetic (F) coupling] and $N_0\beta < 0$ [antiferromagnetic (AF) coupling]. Additionally it was shown that $\langle S\rangle$ is in fact measured by macroscopic magnetization [8]. The proportionality between band splittings and magnetization of the crystal was considered to be a proof of the simple form (1) of exchange interaction [8–11].

In contrast to the magnetic ions introduced so far in DMS, the Cr^{++} ion with its d^4 configuration ($d^4 = e_+^2 t_+^2 e_-^0 t_-^0$) offers a new possibility: hopping of both spin-down and spin-up valence band electrons is possible in this case. The new exchange channel can yield ferromagnetic *p-d* coupling [6], and consequently, band splittings different from those observed for Mn-, Co-, and Fe-based DMS. Moreover, the exchange Hamiltonian is predicted in a more complicated form than given by Eq. (1) [3, 7].

In view of the perspectives outlined above we studied the band splittings of newly grown $Zn_{1-x}Cr_xSe$. The crystals were grown by a modified Bridgman technique. Single phase crystals were obtained only for $x < 0.005$. We studied the crystals with $x = 0.0011$, 0.0025, 0.0035, and 0.0045 (as detected by atomic absorption and chemical analysis). X-ray experiments performed on the samples showed a cubic structure with some stacking faults,

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resulting in a certain axial anisotropy along one of the (111) axes. To estimate the crystal quality we measured transmission of samples placed between crossed polarizers, resulting from depolarization and birefringence. For the magneto-optical experiments we chose samples whose transmission did not exceed 0.02, corresponding to long wave birefringence below 10^{-4}, 2 orders of magnitude less than typical values in hexagonal II-VI compounds.

A straightforward way of studying band splittings is free exciton spectroscopy. We recall that the exciton line typically splits in a magnetic field (Faraday configuration, circularly polarized light) into four components [1, 11]: two in σ^+ (lines A and B) and two in σ^- polarizations (lines C and D) [see Fig. 1(b), $Zn_{0.95}Mn_{0.05}Se$]. Lines A and D are stronger than B and C (approximately 3 times) and in the compounds studied so far are much more sensitive to the magnetic field. The total line splitting ($\Delta E = E_D - E_A$) is given by Eq. (2) [12].

Another way of getting information about band splitting is to measure the Faraday rotation of linearly polarized light. It was shown that in the case where the rotation is driven by exciton splitting resulting from s,p-d exchange, the rotation angle Θ is proportional to $(3N_0\alpha - 5N_0\beta)x\langle S\rangle$ [12]. We applied both these methods to our crystals. The magnetic field was along the (110) crystallographic direction.

Examples of $Zn_{1-x}Cr_xSe$ excitonic magnetoreflectance spectra are shown in Fig. 1(a). We observe splitting into two components: one in σ^+ and one in σ^- (where the σ^- component has a lower energy than the σ^+ component), instead of the typical four-line structure. The pronounced four-line structure is, however, only observed if the splitting is significantly larger than the exciton linewidth, which is usually the case for $x > 0.01$ [see Fig. 1(b)]. In our case the Cr concentration is low, and consequently the exciton splitting is so small that the lines in the same polarization are not resolved and we observe only one line, being a sum of A and B (or C and D). Such a situation is also encountered for crystals with higher magnetic ion content at low fields or high temperature, as demonstrated in Fig. 1(c) for $Zn_{0.95}Mn_{0.05}Se$. We believe that in such a case the observed structures should be rather associated with lines A and D, having in mind the relative strength of the A,D and B,C lines. A possible correction for this effect is given below.

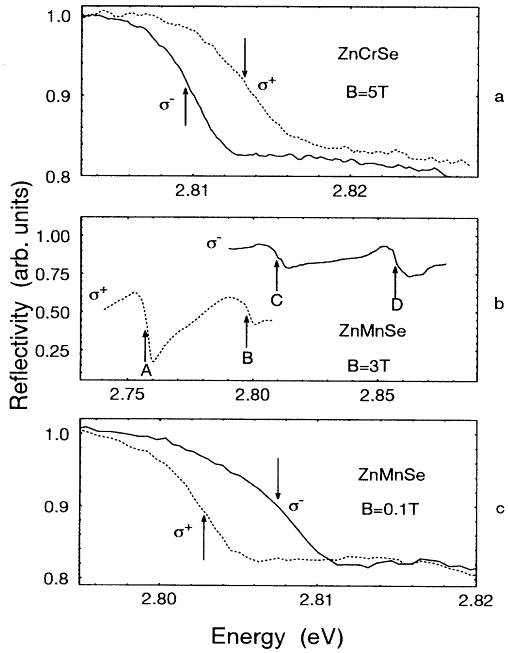

FIG. 1. Reflectance spectra of ZnCrSe and ZnMnSe at $T = 1.9$ K. (a) $Zn_{0.996}Cr_{0.004}Se$ at $B = 5$ T, (b) $Zn_{0.95}Mn_{0.05}Se$ at $B = 3$ T, and (c) $Zn_{0.95}Mn_{0.05}Se$ at $B = 0.1$ T. The arrows indicate exciton energies and σ^+, σ^- denote circular right and left polarizations of light.

Exciton splitting versus magnetic field is displayed in Fig. 2. The curves represent Eq. (2), with the spin average value $\langle S\rangle$ calculated for an isolated Cr^{++} ion [13]. The value of the coefficient $N_0\alpha - N_0\beta$ was the only adjustable parameter and will be discussed below.

We notice that Zeeman exciton splitting of pure ZnSe is negligible. We performed a checking experiment on pure ZnSe and observed no exciton splitting larger than 0.1 meV up to 5 T. This is in agreement with the reported g factor for ZnSe [14, 15].

The essential difference between ZnCrSe and the other DMS is the sense of the exciton splitting. For all Mn, Co, and Fe DMS studied so far [1], σ^+ exciton components have lower energies than the σ^- ones ($E_A < E_D$). In our case this sequence is reversed: $E_A > E_D$. This unusual behavior is corroborated by Faraday rotation results. In Fig. 3 we show the rotation angle as a function of magnetic field for ZnCrSe and ZnMnSe, for reference. The

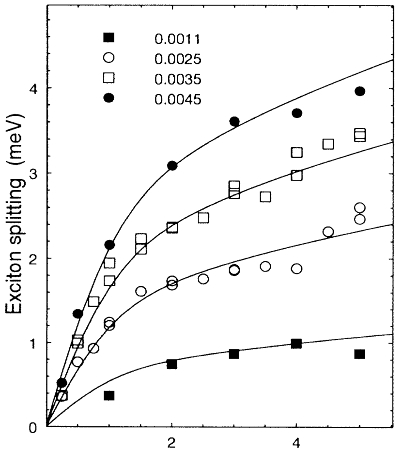

FIG. 2. Exciton splitting $E(\sigma^+) - E(\sigma^-)$ of $Zn_{1-x}Cr_xSe$ versus magnetic field at $T = 1.9$ K. The lines are calculated using Eq. (2) with $N_0\alpha - N_0\beta = -0.64$ eV and calculated spin $\langle S\rangle$ value [13].

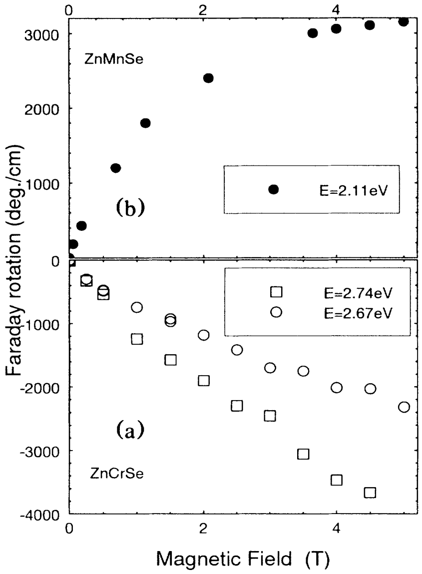

FIG. 3. Faraday rotation as a function of magnetic field at $T = 1.9$ K for (a) $\mathrm{Zn}_{0.997}\mathrm{Cr}_{0.003}\mathrm{Se}$ at photon energies 2.67 eV and 2.74 eV and (b) $\mathrm{Zn}_{0.95}\mathrm{Mn}_{0.05}\mathrm{Se}$ at 2.11 eV.

rotation in ZnCrSe has a negative sign with respect to ZnMnSe. We notice that the rotation was measured for the light energy as close to the exciton energy as possible, to provide as large an exciton contribution as possible, so that rotation is dominated by exciton splitting [16]. It was done for photon energies of 2.67 eV and 2.74 eV, which are above the maximum of the Cr^{++} photoionization band, occurring around 2.48 eV [17]. The increase of the Faraday rotation while approaching the free exciton transition proves that the excitonic dichroism dominates the measured Faraday effect [13]. We should note, however, that photoionization contributes to Faraday rotation sizably, which results in rotation field dependence different than expected for a pure excitonic contribution [cf. Figs. 2 and 3(a)].

Completing the optical data with magnetization results measured on the same samples we found that the total band splitting is proportional to the macroscopic magnetization (Fig. 4), with a proportionality coefficient of 8.7 ± 0.9 meV g/emu. This result suggests a simple form of the exchange interaction [Eq. (1)], the same as for all the other DMS known so far.

Associating our exciton splitting with lines A and D and assuming that this splitting is expressed by Eq. (2) one can evaluate $N_0\alpha - N_0\beta$. Detailed calculations of Cr^{++} spin [18] show that in our field range the Cr ion spin is proportional to the magnetic moment $\langle M\rangle = \langle L+2S\rangle$: $\langle S\rangle = k\langle M\rangle$ with $k = 0.535$ (we recall that $k = 1/2$ for spin-only case, i.e., $\langle L\rangle = 0$). Therefore, the spin $\langle S\rangle$ can be expressed by macroscopic magnetization M_m,

$$M_m = \langle M\rangle(\mu_B x/m) = (\langle S\rangle/k)(\mu_B x/m) \ , \qquad (3)$$

where $m = (1-x)m_{\mathrm{Zn}} + x m_{\mathrm{Cr}} + m_{\mathrm{Se}} = m_{\mathrm{mole}}/N_{\mathrm{Av}}$ is the mass of a DMS molecule and μ_B is the Bohr magneton.

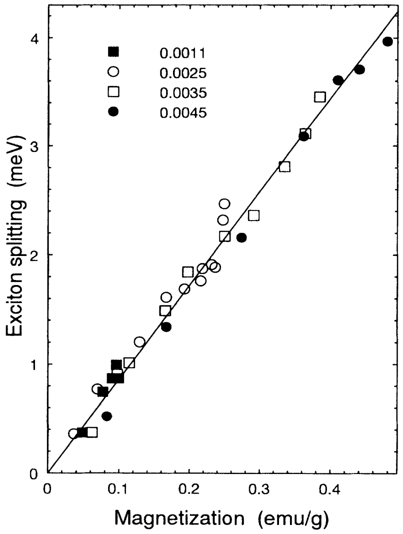

FIG. 4. Exciton splitting versus magnetization of $\mathrm{Zn}_{1-x}\mathrm{Cr}_x\mathrm{Se}$ for x =0.0011, 0.0025, 0.0035, and 0.0045. The straight line represents $N_0\alpha - N_0\beta = -0.64$ eV.

Finally, from Eqs. (2) and (3) we get

$$N_0\alpha - N_0\beta = (E_{\mathrm{D}} - E_{\mathrm{A}})/M_m(\mu_B/mk) \ , \qquad (4)$$

which results in $N_0\alpha - N_0\beta = -0.65 \pm 0.1$ eV. Since we observe only two exciton lines we cannot give separate values of $N_0\alpha$ and $N_0\beta$. However, $N_0\alpha$ is expected to be positive (as resulting from a direct, ferromagnetic exchange [1–7]), which means that $N_0\beta$ must be positive, indicating ferromagnetic *p-d* coupling in ZnCrSe. This is the first observation of F *p-d* exchange in II-VI DMS [19, 20].

Since $N_0\alpha \approx 0.2$ eV for all the DMS studied so far [1], it is reasonable to adopt this value for ZnCrSe and obtain an estimate for $N_0\beta \approx +0.85$ eV. To take into account the fact that the σ^+ (σ^-) line corresponds to unresolved A and B (C and D) lines, one can assume that the energy of the σ^+ (σ^-) line is given as an average $3/4E_{\mathrm{A}} + 1/4E_{\mathrm{B}}$ ($1/4E_{\mathrm{C}} + 3/4E_{\mathrm{D}}$), where weighting factors 3/4 and 1/4 reflect the intensity ratio for A and B lines. Under this assumption the $\sigma^+ - \sigma^-$ exciton splitting reads [12] $3/4(N_0\alpha - N_0\beta) + 1/4(-N_0\alpha - N_0\beta/3)$. With $N_0\alpha = +0.2$ eV one gets $N_0\beta = +0.9$ eV. The difference between an uncorrected and a corrected $N_0\beta$ value is less than experimental accuracy. These estimates for $N_0\alpha$ and $N_0\beta$ produce the same sign of exchange factors in both exciton splittings ($N_0\alpha - N_0\beta$) and Faraday rotation ($3N_0\alpha - 5N_0\beta$). This means that reversed exciton splitting should result in reversed rotation, which is in fact encountered in experiment, as presented above.

As mentioned above, the problem of interaction of a Cr^{++} ion with band electrons has been treated theoretically by Blinowski and Kacman [7] and Bhattacharjee [4]. Blinowski and Kacman have found an additional contribution to the indirect *p-d* exchange, predicted to be of ferromagnetic sign. One of the possible explanations of our result ($N_0\beta > 0$) is the domination of that contribution over the usual (antiferromagnetic) exchange term. The authors of Ref. [7] do not state which of the terms (AF or F) is greater. A second possibility is a change of the sign of the $N_0\beta$ due to location of the d^4/d^5 level above the top of the valence band (contrary to the situation encountered in Mn-, Co-, and Fe-based DMS) resulting in the change of sign of the energy denominator in the expression for the exchange constant [Eqs. (19) and (21) in Ref. [7]]. Available information on the positions of d levels of transition ions in semiconductors [21] supports this possibility. Within the model of Bhattacharjee [4] the second of the two explanations discussed above is also valid, whereas the first one is not applicable. A non-Heisenberg term found for Cr^{++} ions in Ref. [4] leads to a magnetization induced heavy-hole–light-hole splitting, not confirmed by our experiments. However, the Jahn-Teller effect (known to be important for Cr in ZnSe [18, 22]) is not taken into account in [4]. Therefore the model in its actual form cannot be precisely verified experimentally. Although our results do not indicate any non-Heisenberg terms in the *p-d* Hamiltonian, more precise experimental tests of this problem are possible, in particular using magneto-optical measurements under uniaxial stress. On the other hand, more detailed theoretical calculations are desirable.

Finally we comment on the perspectives for ferromagnetic *d-d* exchange in Cr DMS. In view of a new *p-d* exchange mechanism we cannot exclude F *d-d* coupling, which would be extremely important for possible applications. One should, however, remember that the final character of the *d-d* interaction will result from F and AF contributions, since the latter one is still effective in our case. We cannot make a statement about *d-d* exchange based solely on the present data, since no theoretical model was developed for d^4-d^4 exchange. Anyway it is beyond question that the situation for Cr DMS is very promising and hopefully will stimulate development of both *p-d* and *d-d* exchange theory, as well as experimental investigations, which should establish the character of *d-d* exchange.

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