

# Anomalously large $p$ - $d$ exchange interaction in magnetically mixed $\text{Cd}_{1-x}\text{Mn}_x\text{S}$ crystals

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Experiments reveal that  $\text{Cd}_{1-x}\text{Mn}_x\text{S}$  crystals have a  $p$ - $d$  exchange interaction constant anomalously large in comparison with those of other semimagnetic semiconductors. The value of the exchange integrals for crystals with a manganese mole fraction  $x = 0.001$  is  $N_0 J_h = 3.3$  eV or more than three times known values for magnetically mixed semiconductors based on II–VI compounds.

The exchange interaction with localized spin moments of magnetic impurities gives rise to a huge spin splitting of electronic states in the valence and conduction bands of magnetically mixed semiconductors.<sup>1–3</sup> The basic parameters characterizing the exchange interaction in magnetically mixed semiconductors are the values of the  $s$ - $d$  and  $p$ - $d$  exchange integrals, which describe the exchange interaction of the localized spin moments of the manganese with the electron and hole states. So far, the exchange interaction has been studied thoroughly in Cd and Zn tellurides and selenides.<sup>4–8</sup> For sulfides, we have no reliable information on the  $p$ - $d$  exchange interaction. A huge spin splitting of exciton states in  $\text{CdMnS}$  crystals was studied in Ref. 9. Although it was not possible in that study to distinguish between the contributions of hole and electron states on the sole basis of experimental data on the exciton magnetoreflexion, it was established that the splitting of the valence band is substantially greater than the splitting of the conduction band. In the present study we have obtained information on the spin splitting in the valence and conduction bands by comparing data on exciton magnetoreflexion and spin-flip Raman scattering of light by shallow donor centers. It has thus become possible to independently determine the magnitude of the spin splitting of the conduction band and the ratio of the  $p$ - $d$  and  $s$ - $d$  exchange integrals.

In the experiments we used  $\text{Cd}_{1-x}\text{Mn}_x\text{S}$  crystals with manganese mole fractions  $x = 0.001$ , 0.005, and 0.014. The exciton reflection spectra and the spin-flip Raman spectra are measured in the Faraday configuration, along the direction of the magnetic field, normal to the surface of the sample. The direction of the magnetic field is the direction of the  $C_6$  hexagonal axis of the crystal. Experiments are carried out at  $T = 1.7$  K in magnetic fields up to 50 kOe. The photoelectric measurements are taken in a photon-counting mode with multichannel storage, with subsequent numerical processing.

As was shown in Refs. 9–11, the magnitude of the spin splitting of the exciton term in crystals with the wurtzite structure in the geometry  $\mathbf{H} \parallel C_6$  is equal to the sum of the spin splittings of the valence and conduction bands:

$$\Delta E_{\text{exc}}^A = \Delta E_e + \Delta E_h, \quad (1)$$

$$\Delta E_e = N_0 x^* J_e \langle S_M^z \rangle_{H, T} + \mu_B g_e H, \quad (2)$$

$$\Delta E_h = N_0 x^* J_h \langle S_M^z \rangle_{H, T} + \mu_B g_h H, \quad (3)$$

where  $J_{e, h}$  is the exchange integral,  $x^*$  is the effective concentration of the magnetic impurity,  $N_0$  is the number of cation states per cubic centimeter,  $\langle S_M^z \rangle_{H, T}$  is the average magnetization of the magnetic-impurity subsystem, and  $g_{e, h}$  is the effective  $g$ -factor of the carrier (electron or hole). It can be seen from (2) and (3) that the spin splitting of the electron state results from two factors: first, the exchange interaction with the magnetic-impurity subsystem, which is determined by the exchange integral, the effective concentration of the magnetic impurity, and the average magnetization of the magnetic-impurity subsystem; second, the direct effect of the magnetic field on the spin of the carrier. The latter depends on only the strength of the external magnetic field and the effective  $g$ -factor of the carrier. For the case of valence-band electrons, the exchange interaction is usually significantly greater than the direct effect of the magnetic field. This direct effect can quite accurately be ignored. For states in the conduction band, in contrast, the exchange contribution at magnetic-impurity concentrations  $x \sim 0.001$  may be comparable to the Zeeman term, and it must be taken into account.

Figure 1 shows spin-flip Raman spectra for  $\text{Cd}_{1-x}\text{Mn}_x\text{S}$  crystals with a manganese mole fraction  $x = 0.001$ . We clearly see two lines,  $L_1$  and  $L_2$ . The line  $L_1$ , which is further removed from the laser line, constitutes spin-flip Raman scattering of light by a shallow neutral donor. This line is considerably broader than the laser line, because of fluctuations in the local Mn concentration and in the local magnetization within the range of the donor wave function. The line  $L_2$  is Raman scattering of light with a flipping of the Mn spin. The magnitude of the spectral shift of  $L_2$  is proportional to the magnetic field and is the same as the Zeeman splitting of the localized spin moment of

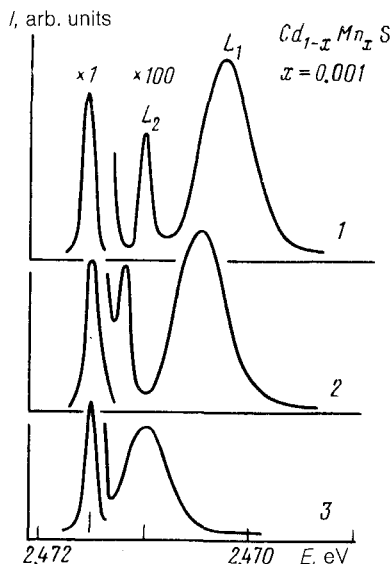


FIG. 1. Spin-flip Raman-scattering spectra in  $\text{Cd}_{1-x}\text{Mn}_x\text{S}$  ( $x = 0.001$ ) crystals in magnetic fields of several strengths: 1— $H = 45$  kOe; 2— $H = 30$  kOe; 3— $H = 6$  kOe.  $T = 1.7$  K. The arrow shows the position of the exciting laser.

Mn. The spectral width of this line, which is the same as the width of the Rayleigh line of the laser, reflects the instrumental width of the spectral instrument. By measuring the spectral shift of  $L_1$ , and subtracting the magnitude of the Zeeman term,  $\Delta_z = \mu_B g_D H$ , from it, we can determine the magnitude of the exchange contribution to the spin splitting of the donor state. Since the wave function of a shallow donor center is constructed from conduction-band wave functions, the magnitude of the exchange splitting of a donor state is quite accurately the same as the magnitude of the exchange splitting of the conduction band.

Figure 2 shows the spin splitting of the  $A$ -exciton term, determined from the reflection spectra of the crystal, along with the spin splitting of the donor center, determined from the spin-flip Raman spectra, as functions of the magnetic field. Subtracting the Zeeman terms from these curves, we find the exchange contributions to the spin splitting in both the valence and conduction bands. For the CdMnS crystals with a magnetic-impurity mole fraction  $x = 0.001$ , these values are  $\Delta E_{s-d}^{ex} = 0.82$  meV and  $\Delta E_{p-d}^{ex} = 12.4$  meV in the region of saturating magnetic fields. Correspondingly, the ratio of the absolute values of the exchange integrals is  $J_h/J_e \approx 15$ —well above the values observed in other II-IV semiconductors, where  $J_h/J_e$  varies from 4.0 for CdMnTe (Ref. 4) to 5.7 for ZnMnTe (Ref. 7). Using the value of the exchange integral ( $N_\sigma J_j = 0.22$  eV) found in Ref. 12 for CdMnS crystals, we can now find the value of the  $p$ - $d$  exchange integral:  $N_\sigma J_h = 3.3$  eV. This value agrees with an estimate based on (3) and the assumption that all the magnetic impurities are effective, i.e., under the assumption  $x^* \approx x$ . Consequently, the anomalously large ratio of exchange integrals in CdMnS,  $J_h/J_e = 15$ , is due primarily to the anomalously large  $p$ - $d$  exchange interaction.

The ratio of exchange integrals  $J_h/J_e$  determined for crystals with a higher Mn concentration is  $\approx 13$  at  $x = 0.005$  and  $\approx 9.5$  at  $x = 0.014$ , decreasing slightly with

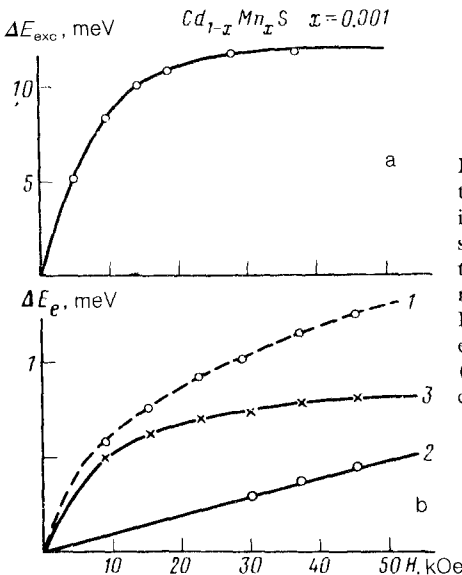


FIG. 2. (a)  $H$  dependence of the magnitude of the splitting of the  $\sigma^+$  and  $\sigma^-$  components of the  $A$ -exciton term in the exciton reflection spectra. (b)  $H$  dependence of the spin splitting. 1—For a shallow donor center (line  $L_1$  in the spin-flip Raman spectra); 2—for a localized spin moment of the magnetic impurity (line  $L_2$  in the spin-flip Raman spectra). Curve 3 shows the contribution of the exchange interaction to the splitting of the donor center (found by subtracting the Zeeman terms  $\mu_B g_D H$  from curve 1, where  $g_D$  is taken to be 1.76).<sup>13</sup>

increasing concentration of the magnetic impurity, but apparently remaining substantially larger than in the tellurides and selenides.

The magnitude of the  $p$ - $d$  exchange integral in CdMnS crystals,  $N_0/J_h = 3.3$  eV, is comparable to the width of the valence band of the semiconductor. Under these conditions we would expect the electron density of valence electrons in a unit cell of the crystal to depend on the spin state of the magnetic impurity, with the possible formation of spin-polaron bands. The dependence of the ratio of exchange integrals  $J_h/J_e$  on the magnetic-impurity concentration which has been found indicates correlations of this sort in these crystals. However, a definite conclusion regarding the mechanism for the intensification of the  $p$ - $d$  exchange interaction in  $\text{Cd}_{1-x}\text{Mn}_x\text{S}$  crystals will require further experiments.

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