Asymmetry of *p-d* exchange interaction in magnetically mixed $Cd_{1-x}Mn_xS$ crystals

S. I. Gubarev and M. G. Tyazhlov
Institute of Solid State Physics, Academy of Sciences of the USSR

(Submitted 5 September 1988)
Pis'ma Zh. Eksp. Teor. Fiz. **48**, No. 8, 437–440 (25 October 1988)

An anomalous behavior of the widths of exciton resonances has been observed in magnetically mixed $Cd_{1-x}Mn_xS$ crystals ($x = 0.001$). Under conditions corresponding to a giant spin splitting of exciton states, the width of the Γ_5^+ and Γ_5^- exciton resonances changes by nearly an order of magnitude, from 1.2 meV to 8 meV. The observed behavior indicates an asymmetry of the exchange interaction for the states of carriers with different spin directions.

The exchange interaction with the magnetic-impurity subsystem leads to a giant spin splitting of exciton states in magnetically mixed semiconductors based on II-VI semiconducting compounds.[1,3] Among the semiconductors of this class which have been studied, $Cd_{1-x}Mn_xS$ crystals occupy a special position, since the constant of their *p-d* exchange interaction is anomalously large.[4–7] The presence of randomly positioned magnetic moments in the matrix of the semiconductor leads to not only a giant spin splitting but also fluctuations in the exchange interaction in the exciton-(magnetic impurity) system and to an additional broadening of exciton resonances. In this letter we are reporting a study of the effect of fluctuations in the *p-d* exchange interaction on the width of exciton terms as a function of the magnetization of the magnetic subsystem.

For the experiments we used $Cd_{1-x}Mn_xS$ crystals with $x = 0.001$ grown from the melt by the Bridgman method. We studied the reflection spectra of the crystal with normally incident light. Measurements were taken in the σ^+ and σ^- polarizations in the direction of the magnetic field, along the C_6 hexagonal axis of the crystal. The measurements were taken at liquid-helium temperature in magnetic fields up to 5 T.

In the absence of a magnetic field, the reflection spectra clearly exhibit features associated with *A*-, *B*-, and *C*-exciton states. The structural feature associated with an *A*-exciton term is seen most prominently in the reflection spectra. This term corresponds to optical transitions from the upper valence band and determines the optical properties of the crystals near the fundamental absorption edge. In a magnetic field, the *A*-exciton line splits into two lines, Γ_5^+ and Γ_5^-, which are active in the σ^+ and σ^- polarizations (Fig. 1a). One of the components of exciton term Γ_5^+ shifts down the energy scale and broadens, while the Γ_5^--exciton term shifts up the energy scale and becomes substantially sharper. The changes in the widths of the σ^+- and σ^--polarized exciton resonances can be seen most vividly in the differential reflection spectra $dR/d\lambda$, shown in Fig. 1b. We should emphasize that our experiments differ from the experiments carried out on other magnetically fixed semiconductors, such as

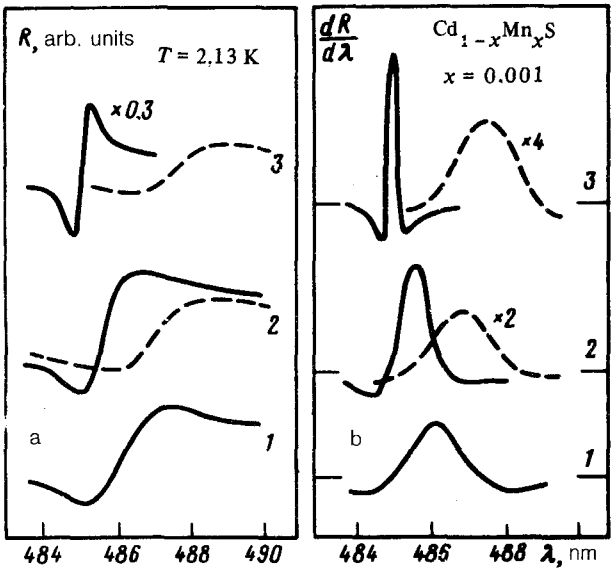

FIG. 1. a—Reflection spectra R; b—differential-reflection spectra $dR/d\lambda$ of the A-exciton term in (solid lines) the σ^+ polarization and (dashed lines) the σ^- polarization in several magnetic fields: 1) $H = 0$ T; 2) $H = 1$ T; 3) $H = 5$ T.

$Cd_{1-x}Mn_xTe$ (Ref. 8) and $Cd_{1-x}Mn_xSe$ (Ref. 9), in that there is a substantial sharpening of the exciton term which shifts up the energy scale, i.e., in the direction of energies corresponding to dissociated states of the Γ_5^+ exciton. Figure 2 shows the width (Γ) of the exciton resonance found from the differential reflection spectra $dR/d\lambda$ as a function of the energy shift of the exciton term with respect to the position in a zero magnetic field. It can be seen from this figure that the dependence is monotonic, and the widths of the exciton resonances in saturating magnetic fields differ by a factor of more than seven, having the values 1.2 meV for the σ^- component and 8 meV for the σ^+-polarized component of the A-exciton. We should also point out that

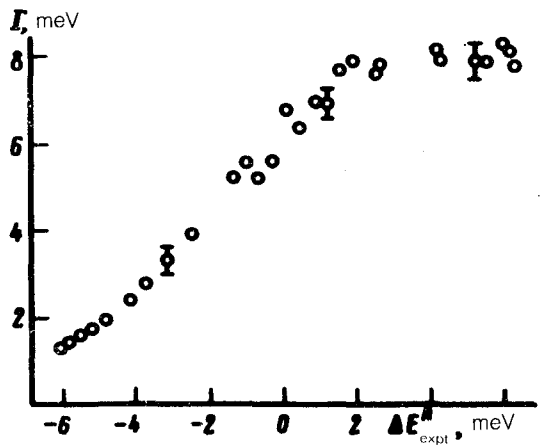

FIG. 2. Half-width of the A-exciton resonance, Γ, as a function of the shift of the exciton term from its position in a zero magnetic field.

the sharpness and the range of the dispersion of the Γ_5^--exciton term in saturating magnetic fields are comparable to the corresponding quality characteristics of the exciton-reflection spectra which are observed in high-quality CdS crystals. On the one hand, this result is evidence of a high structural quality of the crystals of these experiments; on the other hand, it indicates that the anomalous changes which we have observed in the widths of the exciton resonances stem exclusively from an exchange interaction with the magnetic-impurity subsystem.

It was shown in Ref. 7 that the *p-d* exchange interaction in $Cd_{1-x}Mn_xS$ crystals with $x = 0.001$ is stronger than the *s-d* exchange interaction by a factor of nearly 15. It is thus reasonable to link the changes in the widths of the exciton resonances observed here with fluctuations in the energy position of specifically the valence band of the crystal.

According to Refs. 10 and 11, the nature of the strong *p-d* exchange interaction in magnetically mixed semiconductors is caused by a hybridization of $3d$ states of Mn with states of the valence band of the crystal. The $Cd_{1-x}Mn_xS$ valence band is formed from the orbitals of sulfur. With regard to the $3d$ states of Mn, we note that intraatomic correlations split these states by an amount $U \sim 5$–7 eV (Ref. 11). The energy position of the filled $3d_+$ states of Mn coincides with the position of the valence band of the crystal, while the unfilled $3d_-$ orbitals lie well above the edge of the valence band, falling in the band gap or the conduction band of the semiconductor.

A spin splitting of the valence band results from a hybridization of p states of sulfur and d_+ and d_- terms of Mn. The constant of the *p-d* exchange interaction is written in the form[10]

$$J_{pd} = -2|V_{pd}|^2\left[\frac{1}{\epsilon_p - \epsilon_d} + \frac{1}{\epsilon_d + U - \epsilon_p}\right], \qquad (1)$$

where V_{pd} is the matrix element of the *p-d* hybridization, ϵ_p is the energy of the edge of the valence band, and ϵ_d and $\epsilon_d + U$ are the energies of the d_+ and d_- terms of Mn in the crystal. The first term in expression (1) describes the hybridization of p states of the valence band with a filled shell of Mn ($3d_+$), and the second term describes the hybridization with unfilled $3d_-$ states of Mn.

According to estimates in Ref. 11, the value of $\epsilon_p - \epsilon_d$ in $Cd_{1-x}Mn_xS$ is ~ 1.5 eV. In this case we have $\epsilon_p - \epsilon_d \ll \epsilon_d + U - \epsilon_p$; the hybridization with d_+ states is of a resonant nature; and the exchange interaction is caused primarily by the hybridization of p states with $3d_+$ states of Mn. In strong magnetic fields, all the spins of the magnetic impurity are polarized, and the $p\uparrow$ states of the valence band are highly perturbed by fluctuations of the exchange interaction, since they hybridize in a resonant fashion with $d_+\uparrow$ states of Mn. The broadening of the $p\downarrow$ states of the valence band due to fluctuations of the exchange interaction turns out to be far weaker, since the $d\downarrow$ states correspond to unfilled orbitals of Mn, with which the exchange interaction is weakened because of the large value of the denominator $\epsilon_d + U - \epsilon_p$ in expression (1). The resonant nature of the *p-d* exchange interaction is thus the primary cause of both the anomalously strong *p-d* exchange interaction in $Cd_{1-x}Mn_xS$ crystals and the asymmetry of this interaction with respect to the spin states of the valence band.

[1]A. V. Komarov, S. I. Ryabchenko, O. V. Terletskiĭ *et al.*, Zh. Eksp. Teor. Fiz. **73**, 608 (1977) [Sov. Phys. JETP **46**, 318 (1977)].
[2]R. R. Galazka, in Proceedings of the Fourteenth International Conference on the Physics of Semiconductors, Edinburgh, 1978, p. 133.
[3]N. V. Brand and V. V. Moshchalkov, Adv. Phys. **33**, 139 (1984).
[4]S. I. Gubarev, Zh. Eksp. Teor. Fiz. **80**, 1174 (1981) [Sov. Phys. JETP **53**, 601 (1981)].
[5]V. G. Abramishvili, S. I. Gubarev, A. V. Komarov, and S. M. Ryabchenko, Fiz. Tverd. Tela (Leningrad) **26**, 1095 (1984) [Sov. Phys. Solid State **26**, 666 (1984)].
[6]M. Nawrocki, J. P. Lascaray, D. Coquillat, and M. Demianiuk, Proc. Mat. Res. Soc. **89**, 65 (1986).
[7]S. I. Gubarev and M. G. Tyazhlov, Pis'ma Zh. Eksp. Teor. Fiz. **44**, 385 (1986) [JETP Lett. **44**, 494 (1986)].
[8]J. A. Gaj, J. Ginter, and R. R. Galazka, Phys. Status Solidi **b89**, 655 (1978).
[9]A. V. Komarov, S. M. Ryabchenko, Yu. S. Semenov *et al.*, Zh. Eksp. Teor. Fiz. **79**, 1554 (1980) [Sov. Phys. JETP **52**, 783 (1980)].
[10]A. K. Bhattacherjee, G. Fisherman, and B. Coglin, Physica **B117**, **118**, 449 (1983).
[11]Su-Huai Wei and A. Zunger, Phys. Rev. **B35**, 2340 (1987).

Translated by Dave Parsons