Magneto-optical investigation of CdS crystals doped with Mn

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The effect of magnetic-impurity atoms on the magneto-optical properites of CdS:Mn crystals is investigated. It is shown that the anomalously large circular dichroism of the absorption and the giant Faraday rotation near the edge of the fundamental absorption edge, which are observed in these crystals, are due to splitting of the lowest exciton state (*A*-exciton). This splitting is due to the strong exchange interaction of the band electrons with electrons localized on the atoms of the magnetic impurity. The value of the exchange integral for the valence electrons, obtained from a comparison of the splittings of the *A* and *B* exciton states, is more than five times larger than the exchange integral for the conduction-band electrons and amounts to 5.6 ± 0.8 eV. The experimental results are readily explained within the framework of the quasicubic approximation with allowance for Heisenberg-Dirac exchange Hamiltonian that describes the interaction of the band-electron magnetic moments with the magnetic moments localized on the impurities.

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§1. INTRODUCTION

Doping with magnetic impurities influences strongly the magnetooptical properties of semiconductors.[1,2] The exchange interaction of the band electrons with the *d* electrons localized on the magnetic-impurity atoms modifies strongly the energy spectrum of the carriers, which turn out to be very sensitive to the spin state of the magnetic impurities. When a magnetic field is applied, the magnetic moments localized on the impurity become oriented, and this alters substantially the electron and hole states in the crystal. Thus, the presence of Mn atoms in the mixed narrow-band semiconductors $Hg_{1-x}Mn_xTe$ and $Hg_{1-x}Mn_xSe$ (Refs. 3 and 4) leads to giant carrier effective *g* factors that depend on the temperature and on the magnetic field. In the wide-band cubic crystals GdTe : Mn and ZnTe : Mn (Refs. 2, 5–7) the interaction of the band electrons with the manganese *d* electrons leads even in weak magnetic fields to a considerable splitting of the exciton state, as manifest in their anomalous magneto-optical properties.

Up to now, the investigations of the interaction of band carriers with magnetic impurities were made on II–VI semiconductors with sphalerite structure. In these crystals the lowest valence band is quadruply degenerate in spin ($j = \frac{3}{2}$), therefore the picture obtained for the splitting of the hole band upon interaction of the valence electrons with the Mn atoms is relatively complicated. The aim of this paper is to study the interaction of a magnetic impurity with carriers in crystals with wurtzite structure. In these crystals the noncubic crystal field lifts the degeneracy of the valence band. Both bands, valence and conduction, are simple, so that the obtained splitting picture is simple and the interpretation of the experimental results is easier.

We show in this paper, with CdS doped with Mn as the example, that the exchange interaction of the band electrons with the localized Mn electrons does indeed alter greatly the carrier energy spectrum in hexagonal crystals and produce anomalies in their magneto-optical properties.

CdS crystals were chosen for a number of reasons, First, it is one of the most thoroughly investigated II–VI compounds with well known band parameters. Second, as shown by a number of workers,[8,9] the band structure of CdS can be described with good accuracy in the quasicubic approximation, so that the theoretical calculations are much simpler. At helium temperatures, the optical properties of the semiconductors near the fundamental absorption edge are determined by the exciton transitions. Therefore the strong interaction of the carriers with the localized electrons of the magnetic impurity manifests itself as an anomalously large splitting of the exciton terms; this splitting depends on the concentration of the atomic-impurity atoms and on the average magnetic moment localized on them. The splitting of the exciton states is particularly well observed in experiments on the Faraday rotation of the polarization vector, on circular dichroism of the absorption and reflection spectra near the fundamental absorption edge, and in the region of the exciton resonance. These are precisely the experimental procedures used in the present study.

§2 is devoted to the experimental procedure and to the crystals. The principal experimental results are reported in § 3. In § 4 are considered theoretically the changes of the band spectrum of a wurtzite-structure crystal under the influence of exchange interaction with a magnetic impurity. The values splittings of the exciton states and the selection rules for *A*, *B*, and *C* exciton transitions are discussed in § 5.

§2. EXPERIMENTAL PROCEDURE

CdS crystals doped with Mn in the density range 10^{17}–10^{19} cm^{-3} were grown by the Bridgman-Stockbarger method from the melt in argon at a pressure ~100 bar. The dopant was introduced in the form of previously synthesized MnS powder mixed with the initial charge. The content of all the remaining impurities in the

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initial material did not exceed 10–3 wt.%. The Mn density in the samples for which the principal experimental results were obtained was 4.7×10^{-2} wt.% in the batch. Atomic-absorption analysis yields 4.3×10^{-2} wt.%, corresponding to an Mn fraction $x\approx0.001$ and a density $N_{Mn}\approx(2.2\pm0.3)\times10^{19}\,\text{cm}^{-3}$.

Samples measuring 5 × 5 × 1 mm were cut from the ingot in such a way that the hexagonal sixfold axis was normal to the surface of the large face. The crystal surfaces were mechanically polished and then treated with a concentrated solution of CrO_3 in hydrochloric acid. The crystals were placed inside a superconducting solenoid in liquid helium. The work was performed in magnetic fields up to 50 kOe. The direction of the magnetic field coincided with the observation direction (Faraday configuration). The experiments were made in paraxial beams normal to the crystal surface and directed along the hexagonal axis C_6 ($H\|C_6$).

The spectral instrument was a high-aperture MDR-2 monochromator with linear dispersion 20 Å/mm, the resolution being not worse than 0.4 meV when 50-μm spectral slits were used. The light source was a DATs-50 zirconium lamp. In addition, we used an argon laser, one emission line of which, $\lambda_2=496.5$ nm, was located on the fundamental absorption edge of the sample. The circularly polarized light was separated with an analyzer consisting of a quarter-wave plate and a polaroid. For better separation of the polarizations, the light from the source was made circularly polarized of the same sign as used for the registration.

The measurements performed on CdS samples with Mn density in the range from 4×10^{17} to $2\times10^{19}\,\text{cm}^{-3}$ revealed no qualitative differences in the magneto-optical phenomena. It was established that the splitting of the exciton states, the shift of the fundamental absorption edge, and the angle of rotation of the polarization vector in the magnetic field are approximately linear functions of the Mn density. All the experimental results that follow pertain therefore to crystals with Mn density $2.2\times10^{19}\,\text{cm}^{-3}$, for which all the magneto-optical anomalies connected with the presence of the Mn manifested themselves most clearly.

§3. RESULTS

The dependence of the angle of rotation of the transmitted-light polarization angle on the wavelength and on the magnetic field was investigated for crystals 1 mm thick along the C_6 axis at a temperature $T=1.75$ K (Figs. 1a, 1b). The Faraday rotation (FR) in crystals doped with Mn is many times larger than in the pure crystals, and unlike in the latter it is essentially nonlinear in the magnetic field.

Starting with fields $H=15$ kOe, the FR saturates, and when the magnetic field is increased from 20 to 40 kOe the polarization-vector rotation angle remains practically unchanged. In weak fields the dependence is close enough to linear. At the wavelength $\lambda=496.5$ nm the Verdet constant, i.e., the coefficient of proportionality of the field to the polarization-vector rotation angle, is $320\ \text{deg}\cdot\text{mm}^{-1}\cdot\text{kOe}^{-1}$, which is approximately 45 times the value observed in pure crystals (Fig. 1a, b). The field dependence of the Faraday rotation is well approximated by the Brillouin function $B_{5/2}(\mu_B gH/kT)$ [see (6)], which describes a Boltzman distribution of the state with spin $\frac{5}{2}$ over the Zeeman components. Since the Faraday rotation near the fundamental absorption edge is determined mainly by the splitting of the lowest of the exciton resonances (A exciton), this behavior indicates that the magnitude of this splitting depends both on the density of the Mn atoms in the crystal and on the average value of the magnetic moment localized on them.

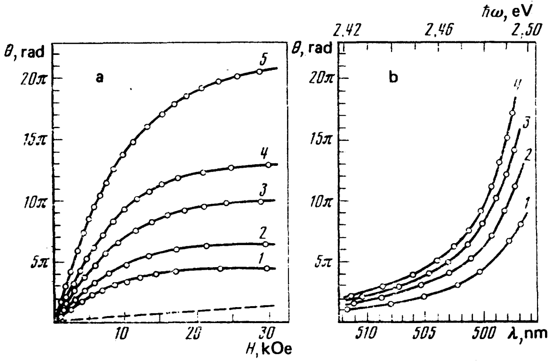

FIG. 1. Rotation angle θ of polarization vector vs.: a) the magnetic field H for wavelengths λ equal to; 1) 505.0 nm, 2) 502.5, 3) 500.0, 4) 489.5, 5) 496.5; b) the wavelength λ in fields: 1) 5.2 kOe, 2) 8.6, 3) 14.7, 4) 47.5. Temperature $T=1.75$ K, sample thickness 1 mm, ($N_{Mn}=2.2\times10^{19}\,\text{cm}^{-3}$) The dashed curve shows the FR in a pure CdS crystal at $\lambda=496.5$ nm.

The appreciable splitting of the A-exciton state should lead to a strong circular dichroism of the magnetoabsorption. Indeed, when a magnetic field is applied the sample transmission increases strongly for the σ^+ polarization, and decreases strongly for the σ^- polarization. The light passing through the sample is then up to 80% circularly polarized. This behavior can be attributed to the fact that in the external magnetic field the edge of the fundamental absorption in CdS : Mn for the components σ^+ and σ^- of circularly polarized light is shifted in opposite directions relative to the position at $H=0$ (Fig. 2). The splitting has a nonlinear dependence on H, reaching a value ~8 meV in saturating fields.

The appreciable splitting of the A-exciton term is confirmed by experiments on circular dichroism of the

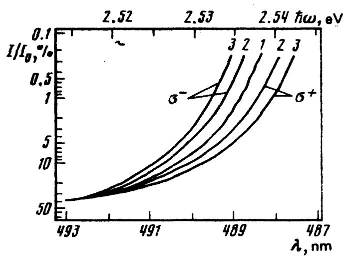

FIG. 2. Spectral dependence of the transmission I/I_0 of samples 0.1 mm thick at $T=1.75$ K in polarizations σ^+ and σ^-: 1) $H=0$, 2) $H=9$ kOe, 3) $H=45$ kOe, $N_{Mn}=1.5\times10^{19}\,\text{cm}^{-3}$.

spectra of exciton reflection in a magnetic field. In the investigated samples, the experimental reflection spectra reveal exciton resonance connected only with the A and B valence subbands. Without a magnetic fields, singularities connected with either the A or the B exciton resonance are strongly smeared out. In a magnetic field, the exciton resonance corresponding to the A exciton becomes sharper and shifts towards higher energies in the σ^+ polarization, and conversely becomes smoother and shifts towards lower energies in the σ^- polarization. As for the B exciton, in the σ^+ polarization the singularity in the reflection spectrum becomes smoothed out and in the σ^- polarization, on the contrary it becomes sharper, the spectral positon remaining practically unchanged.

Special notice should be taken of the strong sharpening of the A-exciton term, which shifts towards higher energies in magnetic fields. The sharpness and the extent of the dispersion of this resonance are comparable with the reflection spectra observed in the purest and most perfect CdS crystals. This circumstance is evidence of the structural perfection of the CdS : Mn samples used in the present study, and indicates that the anomalous behavior of the width of the exciton-reflection spectrum and the large change of the dispersion of the exciton resonance are due to the orientation of the magnetic moments of the Mn in the magnetic field.

If the spectral position of the exciton resonance, determined from the reflection spectra in different circular polarizations, is plotted as a function of the magnetic field (Fig. 4), then it can be seen that the shift of the A-exciton resonance in the different polarizations is practically symmetrical relative to the position in a zero field. This shift is well described by the Brillouin function $B_{5/2}(\mu_B gH/kT)$ [see (6)]. The spacing between the σ^+ and σ^- exciton terms in a saturating field is 12 ±0.5 meV.

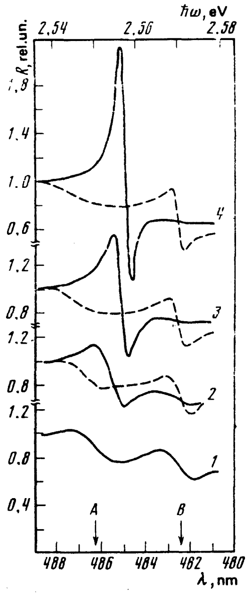

FIG. 3. Reflection spectrum of CdS:Mn ($N_{\mathrm{Mn}}=2.2\times10^{19}$ cm^{-3}) in polarizations σ^+ (solid curve) and σ^- (dashed) at temperature $T=1.75$ K. 1) $H=0$, 2) $H=5.2$ kOe, 3) 14 kOe, 4) 43 kOe. The arrows show the spectral positions of the A and B excitons in a zero magnetic field.

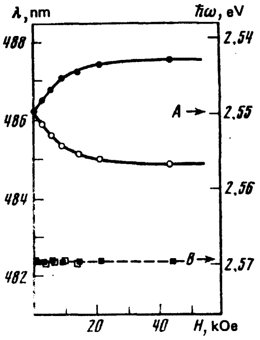

FIG. 4. Spectral position of A and B excitonic resonances in polarizations σ^+ (○,□) and σ^- (●, ■) as functions of the magnetic field.

§4. CHANGE OF BAND SPECTRUM OF WURTZITE STRUCTURE CRYSTALS UNDER THE INFLUENCE OF EXCHANGE INTERACTION WITH A MAGNETIC IMPURITY

In cadmium sulfide, the Mn^{++} ion replaces a Cd^{++} ion in the lattice and is thus an isoelectronic impurity; the d shell of the Mn^{++} ion is half-filled and consists of five electrons. Because of the quenching of the orbital angular momentum by the crystal lattice field, these electrons form an ^6S configuration with total spin $S_{\mathrm{Mn}}=\frac{5}{2}$. The g factor of the d electrons for Mn^{++} in CdS, according to the ESR data,[10] differs little from the g factor of the free electron, and is equal to $g_{\mathrm{Mn}}=2.020$.

According to the $s-d$ interaction theory,[11] the Hamiltonian of the system of localized and free electrons can be broken up into three parts corresponding to different interactions: H_{ll}-between localized states, H_{cc}-between free carriers, and H_{cl}-between band and localized electrons,

$$H=H_{ll}+H_{cc}+H_{cl}. \tag{1}$$

As for localized magnetic moments, since the Mn concentration is small in the investigated crystals ($x \leq 0.001$) and the average distance between the magnetic-impurity atoms amounts to many (~10) lattice constants, and the spin states of these atoms can be regarded as independent. Then H_{ll} reduces to a direct action of the external magnetic field on the magnetic moments localized on the Mn atoms (in $\mathrm{Hg}_{1-x}\mathrm{Mn}_x\mathrm{Te}$ the interaction between the Mn atoms comes into play only at $x \geq 0.02$, Ref. 3).

At low excitation levels, the collective effects in a system of photoexcited carriers can be neglected. Then H_{cc} is simply the Hamiltonian of an exciton in a magnetic field

$$H_{\mathrm{ex}}=p^2/2\mu-e^2/\varepsilon r+H_{\mathrm{exch}}+H_1, \tag{2}$$

where H_1 includes terms that take into account the direct influence of the magnetic field on the magnetic moments that make up the exciton, as well as on their orbital motion, while H_{exch} is responsible for the electron-hole interaction in the exciton; in fields up to 50 kOe the two contributions do not exceed 0.5 meV,[12] and we shall hereafter take into account in (2) only the first two terms, which represent the pure Coulomb interaction of the carriers in the exciton.

Following Ref. 3, the interaction between the spin $\boldsymbol{\sigma}$ of the band electron and the magnetic moment $\mathbf{S}_i$, localized on an Mn atom in the site $\mathbf{R}_i$, will be described within the framework of the Heisenberg-Dirac vector model:

$$H_{cl}=\sum_{\mathbf{R}_i} J(\mathbf{r}-\mathbf{R}_i)\mathbf{S}_i\boldsymbol{\sigma}, \tag{3}$$

where $J(\mathbf{r})$ is the exchange integral with center at $\mathbf{R}_i$.

Since $J(\mathbf{r})$ drops to zero within the limits of the cell, we can approximate (3) by the expression[3]

$$A_{uu}=[H_{cl}]_{uu}=\sum_{\mathbf{R}_i} f_N^*(\mathbf{R}_i)f_N(\mathbf{R}_i)\mathbf{S}_i\int_{\Omega_0} d\Omega\langle u|J(\mathbf{r})\sigma|u\rangle, \tag{4}$$

where $f_N(\mathbf{R}_i)$ is a function that describes the distribution of the impurity over the lattice site, and u is the periodic part of the Bloch function of the band electrons.

The expression must be averaged over all the random positions of the impurity and over the magnitude of the spin moment localized on Mn. In an external magnetic field, the energy level of the magnetic impurity splits into a Zeeman multiplet with $j=\frac{5}{2}$. In this case

$$\langle S_i^+\rangle=\langle S_i^-\rangle=0, \quad \langle S_i^z\rangle=B_{5/2}(\mu_B gH/kT), \tag{5}$$

where $B_j(t)$ is the Brillouin function corresponding to the spin j

$$B_j(t)=\frac{2j+1}{2}\coth\left(\frac{2j+1}{2}t\right)-\frac{1}{2}\coth\frac{t}{2}. \tag{6}$$

After averaging we obtain[3]

$$A_{uu}=N_0x\langle S_i^z\rangle J_{uu}, \tag{7}$$

$$J_{uu}=\frac{1}{\Omega}\int_{\Omega_0} d\Omega\langle u|J(\mathbf{r})\sigma_z|u\rangle, \tag{8}$$

where N_0 is the number of cells per unit volume and x is the molar fraction of the Mn in the CdS.

The conduction band of CdS is a simple one of the S type. The interaction (3) lifts the spin degeneracy and splits the conduction band, according to (7), into two with energies

$$E_e=E_g+\frac{k^2}{2m_e}\pm A, \quad A=\frac{1}{2}\frac{N_{\text{Mn}}}{\Omega_0}\langle S_i^z\rangle\langle S|J|S\rangle, \tag{9}$$

N_{Mn} is the Mn concentration in the sample, Ω_0 the volume of the unit cell, and $\alpha=\langle S|J|S\rangle$ is the value of the exchange integral (8) on the S-wave functions of the conduction band.

We consider now the valence band. The wave functions in the valence band transform like atomic wave functions of p-type. If initially the wave functions transforms at the extremum point in accord with the representation Γ_{15} (antisymmetrical state of p-type), then inclusion of the spin-orbit interaction lifts the degeneracy in the total angular momentum j and splits $\Gamma_{15}(x,y,z)$ into the quadruply degenerate Γ_8 $(j=\frac{3}{2})$ and doubly degenerate Γ_7 $(j=\frac{1}{2})$ with a splitting Δ_{so}. On the other hand, in crystals with wurtzite structure the states are split even if $\Delta_{\text{so}}=0$, inasmuch as there are initially two energy states, $\Gamma_5(x,y)$ and $\Gamma_1(z)$. It can be assumed that both stem from $\Gamma_{15}(x,y,z)$ following the action of the noncubic crystal field Δ_{cr}.

In the quasicubic approximation it is assumed that the real structure of the valence band in hexagonal crystals, which consists of three doubly degenerate bands, is the result of the combined influence of both perturbations of the "crystal field" and the "spin-orbit interaction," with the wave functions for each of the bands expressible in the form of a linear combination of p_x, p_y, and p_z and of the spin functions (or of the functions $p_{3/2}$ and $p_{1/2}$), if the interaction of the levels with the conduction band is disregarded (i.e., $\Delta_{\text{cr}}, \Delta_{\text{so}}\ll E_g$).

At the point $\mathbf{k}=0$ the band Hamiltonian of the valence band with wurtzite structure can then be written in the form[13]

$$\begin{bmatrix} \Delta_1+\Delta_2 & 0 & 0 \\ 0 & \Delta_1-\Delta_2 & \sqrt{2}\Delta_3 \\ 0 & \sqrt{2}\Delta_3 & 0 \end{bmatrix}, \tag{10}$$

where Δ_1 is the crystal splitting constant, and Δ_2 and Δ_3 are the constants of the spin-orbit interaction (in the quasicubic approximation, $\Delta_2=\Delta_3=(\frac{1}{3})\Delta_{\text{so}}$). The corresponding values for CdS are $\Delta_1=29.4$ meV, $\Delta_2=20.9$ meV, and $\Delta_3=20.7$ meV. In contrast to tellurides and selenides of cadmium and zinc, the constants of the crystalline and spin-orbit interactions in CdS turn out to be comparable, and this leads to a strong mixing of the wave functions of the Γ_7 states.

The Hamiltonian (10) leads to the secular equation

$$(\Delta_1+\Delta_2-\varepsilon)(\varepsilon^2-(\Delta_1-\Delta_2)\varepsilon-2\Delta_3^2)=0. \tag{11}$$

The eigenvalues of the energies of the valence-band extrema, obtained from this equation, are

$$\begin{gathered} E_A{}^0=\Delta_1+\Delta_2, \\ E_B{}^0={}^1/_2\{(\Delta_1-\Delta_2)+[(\Delta_1-\Delta_2)^2+8\Delta_3^2]^{1/2}\}, \\ E_C{}^0={}^1/_2\{(\Delta_1-\Delta_2)-[(\Delta_1-\Delta_2)^2+8\Delta_3^2]^{1/2}\}. \end{gathered} \tag{12}$$

The wave functions of the electron in these bands at $\mathbf{k}=0$ are the following:

$$\begin{gathered} \psi_{A+3/2}=X_+\uparrow, \ \psi_{A-3/2}=X_-\downarrow, \\ \psi_{B+1/2}=C_1X_+\downarrow+C_2z\uparrow, \ \psi_{B-1/2}=C_1X_-\uparrow+C_2z\downarrow, \\ \psi_{C+1/2}=-C_2X_+\downarrow+C_1z\uparrow, \ \psi_{C-1/2}=-C_2X_-\uparrow+C_1z\downarrow, \end{gathered} \tag{13}$$

where $X_\pm=(x\pm iy)/\sqrt{2}$, and x, y, and z are wave functions that transform like the atomic wave functions p_x, p_y, and p_z. The coefficients C_1 and C_2 depend on the crystal and spin-orbit interactions and are equal to

$$\begin{gathered} C_1=E_B{}^0/((E_B{}^0)^2+2\Delta_3^2)^{1/2}, \\ C_2=\sqrt{2}\Delta_3/((E_B{}^0)^2+2\Delta_3^2)^{1/2}. \end{gathered} \tag{14}$$

Allowance for the influence of the magnetic impurity reduces in first-order perturbation theory to calculation of the diagonal matrix elements of the operator (8) on wave functions of the form (13), and this leads to splitting of the extrema of the valence bands

$$\begin{gathered} E^1_{A\pm 3/2}=E_A{}^0\pm B, \quad E^1_{B\pm 1/2}=E_B{}^0\pm(C_2^2-C_1^2)B, \\ E^1_{C\pm 1/2}=E_C{}^0\pm(C_1^2-C_2^2)B; \quad B={}^1/_2(N_{\text{Mn}}/\Omega_0)\langle S_{\text{Mn}}{}^z\rangle\beta, \end{gathered} \tag{15}$$

where $\beta = \langle p_x | J | p_x \rangle$ is the value of the exchange integral on the p-type valence wave functions. For CdS we have $C_1^2 = 0.56$ and $C_2^2 = 0.44$, and the splittings are equal to $2B$ and $0.24B$ for the bands $\Gamma_9(A)$ and Γ_7 (B and C), respectively.

In crystals with large Mn content, the splitting due to the introduction of the magnetic impurity may turn out to be comparable with or even larger than the initial splitting in the valence band. In this case perturbation theory does not hold, and the terms connected with the exchange interaction should be included in the initial Hamiltonian (10) together with the crystal field and the spin-orbit interaction. This leads to a new secular equation for the energy eigenvalues at $\mathbf{k} = 0$:

$$(\Delta_1+\Delta_2\pm B-\varepsilon)[(\varepsilon\pm B)(\Delta_1-\Delta_2\pm B-\varepsilon)-2\Delta_3^2]=0. \tag{16}$$

The roots of this secular equations are

$$\begin{gathered} E'_{A\pm 1/2}=\Delta_1+\Delta_2\pm B, \\ E'_{B\pm 1/2}={}^1/_2\{(\Delta_1-\Delta_2)+[(\Delta_1-\Delta_2)^2+8\Delta_3^2+4B^2\pm 4B(\Delta_1-\Delta_2)]^{1/2}\}, \\ E'_{C\pm 1/2}={}^1/_2\{(\Delta_1-\Delta_2)-[(\Delta_1-\Delta_2)^2+8\Delta_3^2+4B^2\pm 4B(\Delta_1-\Delta_2)]^{1/2}\}. \end{gathered} \tag{17}$$

For small B, expanding the radicand in a Taylor series and confining ourselves to terms linear in B, we obtain for the B and C valence subbands

$$\begin{gathered} E_{B\pm 1/2}=E_B^0\mp(\Delta_1-\Delta_2)B/[(\Delta_1-\Delta_2)^2+8\Delta_3^2]^{1/2}, \\ E_{C\pm 1/2}=E_C^0\pm\frac{(\Delta_1-\Delta_2)B}{[(\Delta_1-\Delta_2)^2+8\Delta_3^2]^{1/2}}, \end{gathered} \tag{18}$$

which coincides with (15).

Figure 5 shows the energy CdS : Mn energy spectrum calculated from formulas (17) and (15) for the valence band vs the exchange interaction B. Besides the splitting of the valence band, allowance for the interaction with the Mn atoms lead to a shift, quadratic in B, of the B and C valence bands. The size of this shift becomes comparable with the splitting at $B \geq 10$ meV, so that Eqs. (17) must be used at large B.

The splitting of the valence band in crystals with sphalerite structure is obtained as a particular case of relations (9)–(17). If we put in these formulas $\Delta_1 = \Delta_{\rm cr} = 0$ and $\Delta_2 = \Delta_3 = (\frac{1}{3})\Delta_{\rm so} \gg B$, then we obtain $C_1^2 = \frac{1}{3}$, $C_2^2 = \frac{2}{3}$, and for the splitting of the lower valence band

$$E^{3/2}_{\pm 3/2}=E_0^{3/2}\pm B, \qquad E^{1/2}_{\pm 1/2}=E_0^{1/2}\pm B/3 \tag{19}$$

in accord with Refs. 6 and 7.

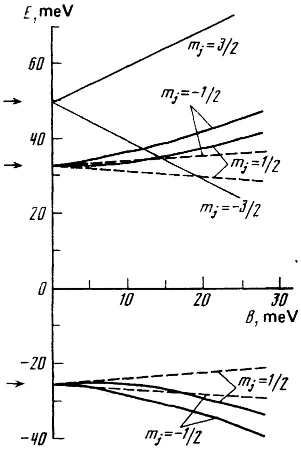

FIG. 5. Energy position of extrema of A, B, and C valence bands vs. the exchange interaction B calculated from formulas (17) (solid line) and (15) (dashed).

§5. SPLITTING OF EXCITON STATES AND SELECTION RULES

It was shown in §4 that exchange interaction of the carriers with a magnetic impurity lifts completely the spin degeneracy both in the conduction band, according to (9), and in the valence band (17). The Coulomb interaction (2) between the electrons and the holes causes them to be bound into an exciton. Out of the twelve exciton-transition energies obtained in this manner, only six are spectroscopically active in the case of a Faraday configuration, and these correspond to transitions with change of the magnetic quantum number $\Delta m = \pm 1$ (Fig. 6).

Kostler's table for the matrix elements of the exciton transitions takes the form

$$\begin{gathered} \langle S|p_+|X_-\rangle=P, \quad \langle S|p_-|X_-\rangle=0, \\ \langle S|p_+|X_+\rangle=0, \quad \langle S|p_-|X_+\rangle=-P, \end{gathered} \tag{20}$$

where $p_\pm$ is the dipole-transition operator for $\sigma^\pm$ polarized light. The initial (ψ_i) and final (ψ_f) states of the electron in the exciton transition, the energy ε, the polarization σ, and the probability W of these transitions are listed for the Faraday configuration in Table I.

The magnitude of the splitting between the σ^+ and σ^- polarized exciton transitions is

$$\Delta_A=2B-2A, \quad \Delta_B=2A-2(C_1^2-C_2^2)B, \quad \Delta_C=2A+2(C_1^2-C_2^2)B. \tag{21}$$

Assuming $|\Delta_B| < 1$ meV (Fig. 4), we obtain from the splitting $\Delta_A = 12 \pm 0.5$ meV of the A-exciton state the values $B = 7 \pm 1$ meV and $A = 0.9 \pm 1$ meV, i.e., we find that the s–d exchange interaction between the manganese d electrons and the valence electrons is several times larger than the exchange interaction between the

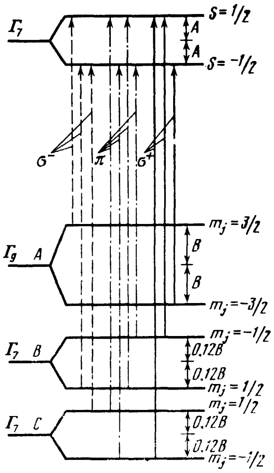

FIG. 6. Level scheme of optically allowed transitions between A, B, and C valence bands and the conduction band with allowance for the exchange interaction of the carriers with the magnetic impurity.

TABLE I. Initial (ψ_i) and final (ψ_f) states of an electron in an exciton transition, and the energy ε, the polarization σ, and the probability W of such a transition for the Faraday configuration.

ψ_i	ψ_f	σ	ε	W
$\psi_A+{}^3/_2$	$S\vert+{}^1/_2\rangle$	σ^-	ε_A-B+A	$\vert P\vert^2$
$\psi_A-{}^3/_2$	$S\vert-{}^1/_2\rangle$	σ^+	ε_A+B-A	$\vert P\vert^2$
$\psi_B+{}^1/_2$	$S\vert-{}^1/_2\rangle$	σ^-	$\varepsilon_B+(C^2{}_1-C^2{}_2)B-A$	$C^2{}_1\vert P\vert^2$
$\psi_B-{}^1/_2$	$S\vert+{}^1/_2\rangle$	σ^+	$\varepsilon_B-(C^2{}_1-C^2{}_2)B+A$	$C^2{}_1\vert P\vert^2$
$\psi_C+{}^1/_2$	$S\vert-{}^1/_2\rangle$	σ^-	$\varepsilon_C-(C^2{}_1-C^2{}_2)B-A$	$C^2{}_2\vert P\vert^2$
$\psi_C-{}^1/_2$	$S\vert+{}^1/_2\rangle$	σ^+	$\varepsilon_C+(C^2{}_1-C^2{}_2)B-A$	$C^2{}_2\vert P\vert^2$

Note. Here $\psi_{A,B,C}$ are the wave functions of the valence electrons (13), and $\varepsilon_{A,B,C}$ are the energies of the exciton transitions for the A, B, and C excitons at $H=0$.

conduction-band electrons. The splitting of the exciton states in CdS : Mn in a magnetic field is therefore due mainly to the splitting of the valence band. The exchange integral for the valence electrons amounts to $N_0=N_0\langle p_x|J|p_x\rangle=5.6\pm0.8$ eV.

Particular notice should be taken of the anomalous behavior of the width and amplitude of the exciton resonances of CdS : Mn as functions of the magnetic field (Fig. 3). In contrast to the $Cd_{1-x}Mn_xTe$ crystals, the exciton term that broadens is the one that shifts towards the lower energies, while the exciton resonances that shifts towards higher energies are sharper and more distinct in the spectra. The reason for this is not quite clear. It may be due to the inhomogeneous distribution of the Mn atoms over the crystal. At a concentration ~2×10^{-19} cm^{-3} the wave function of the exciton spans over a crystal region containing three or four magnetic-impurity atoms. Therefore the fluctuations of the exchange interaction can be appreciable. Another possible mechanism is connected with the inelastic scattering of the carriers by the magnetic impurity, since the scattering probability should depend strongly on the magnitude and sign of the magnetic moment localized on the impurity, and is significantly different for carriers with different spins.

Semiconductors doped with magnetic impurities constitute systems with very unusual properties. In such a system the *s–d* exchange interaction influences only the spin variables, without touching upon the orbital motion of the carriers in the crystal. This interaction is so strong that even in weak magnetic field it leads to a spin-state splitting corresponding to fields of tens and hundreds of kilooersteds. Great interest attaches therefore to the behavior of multiparticle, collective formations in such semiconductors, namely exciton-impurity complexes, biexcitons, and electron-hole drops. The lifting of the spin degeneracy in both the valence and conduction bands should alter radically the binding energies of these formations, and possibly make them energywise unprofitable.

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