Exciton emission and emission by exciton-impurity complexes in $Cd_{1-x}Mn_xSe$ crystals

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The state of an exciton complex on a neutral donor is energetically unstable due to the exchange interaction with a magnetic impurity. As a result, the line corresponding to recombination of exciton-impurity complexes disappears in the emission spectrum of $Cd_{1-x}Mn_xSe$ in a magnetic field and the emission line of free excitons is excited.

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Exchange fields, which arise when carriers interact with magnetic impurity atoms in semimagnetic semiconductors (SMSS) in a magnetic field, remove the spin degeneracy in the valence and conduction bands.[1,2] Giant spin splittings, which occur in SMSS

($\Delta_{e,h} \sim 10^1$–10^2 meV with a molar fraction of magnetic impurity $x \sim 10^{-2}$), can greatly alter the form of the energy spectrum of free and bound excitons in these compounds.[3,4] This work is concerned with the effect of strong spin splittings on the energy spectrum and stability of an exciton-impurity complex (EIC) on a neutral donor in SMSS with the structure of wurtzite $Cd_{1-x}Mn_xSe$.

The experiments were performed on $Cd_{1-x}Mn_xSe$ crystals ($x \sim 10^{-2}$), grown by Bridgman's method from the melt. The reflection spectra and the recombination radiation spectra (RR) were studied both in the Faraday geometry (in σ^+ and σ^- polarizations) and in the Voigt geometry (in σ and π polarizations). In both cases, the orientation of the magnetic field coincided with the hexagonal axis of the crystal $\mathbf{H} \| \mathbf{C}_6$. The experiments were performed at a temperature of 1.5 K in magnetic fields up to 40 kOe. The crystals were excited with the help of a 2-mW He-Ne laser. The spectral resolution was no worse than 0.2 meV.

Introduction of a magnetic impurity into the semiconductor matrix slightly increases the width of the forbidden band.[5] The energy position of the X-exciton line and the RR line of EIC on the neutral donor D_0X is shifted relative to the position in pure CdSe by approximately 18 meV and is $E_x = 1.8435$ eV and $E_{D_0X} = 1.839$ eV. The difference in the energies of A and B excitons in the specimen studied is ~ 25 meV, which agrees well with the known magnitude for pure CdSe.

The change in the energy spectrum of excitons in SMSS with a hexagonal structure under the action of strong carrier-impurity exchange interaction was studied previously in Refs. 6 and 7. In the $\mathbf{H} \| \mathbf{C}_6$ geometry, the spectroscopically active state A of the Γ_5 exciton splits into two Γ_5^+ and Γ_5^- excitons active in σ^+ and σ^- polarizations. In addition, in the reflection spectrum, the exciton line in σ^+ polarization is displaced toward lower energies, while in σ^- polarization, it is displaced toward higher energies (Fig. 1a). The magnitude of the splitting between Γ_5^+ and Γ_5^- due to the exciton is ~ 44 meV in a field 40 kOe. The weak singularity at the low-frequency edge of the reflection spectrum at $H = 0$ is due to resonant excitation of EIC. Donor electrons are rapidly polarized in a magnetic field and in fields > 2 kOe, the EIC line is present only in the σ^- polarized component of the reflection spectrum.

Only the I_2 line, which corresponds to the radiative decay of EIC on the neutral donor D_0X, is observed in the emission spectrum of the crystal at $H = 0$. In a magnetic field, the σ^+ component of RR is shifted toward low energies, increasing slightly in width and decreasing in intensity (Fig. 1b). In σ^- polarization, the RR D_0X line is shifted toward high energies. Its intensity drops rapidly and in fields > 5 kOe, the σ^- component of RR D_0X is not observed. Beginning at fields ~ 8 kOe, a new line with half-width ~ 1 meV, whose spectral position essentially coincides with the position of the lowest exciton term determined from the reflection spectra of the crystal, arises at the high-frequency edge of the D_0X emission line. As the field is increased, the intensity of this line increases, whereas the intensity of the I_2 line drops rapidly, and in the region of saturating magnetic fields, emission lines of free excitons dominate in the RR spectrum (curve 4 in Fig. 1b).

The magnetic-field dependence of the energy position of oppositely polarized components of the A and B exciton lines and the emission lines of the D_0X complex

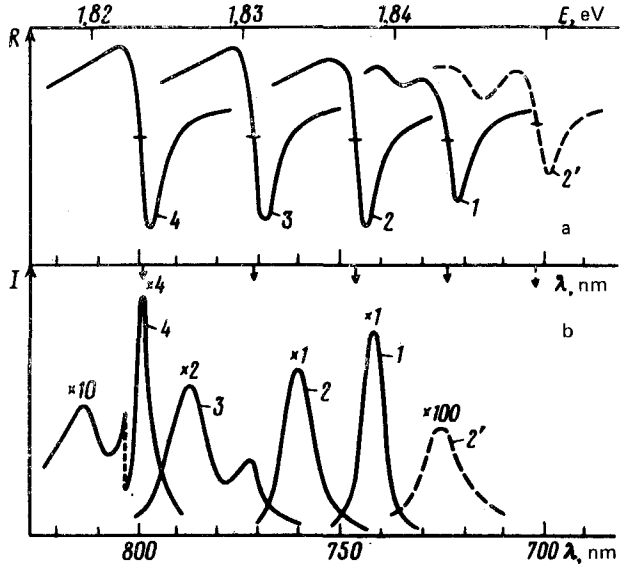

FIG. 1. Reflection spectrum (a) and RR spectrum (b) of $Cd_{1-x}Mn_xSe$ crystals with $x = 0.01$ in σ^+ (solid curve) and σ^- (dashed curve) polarizations in a magnetic field: 1—$H = 0$ kE, 2,2'—$H = 4$ kE, 3—$H = 9$kE, 4—$H = 23$ kE. $T = 1.5$ K. The arrows in Fig. 1b indicate the position of the exciton term, determined from the reflection spectra of the crystal.

exhibits saturation (Fig. 2). This saturation is attributable to the exchange splittings in the valence and conduction bands of SMSS on the magnetization of the magnetic

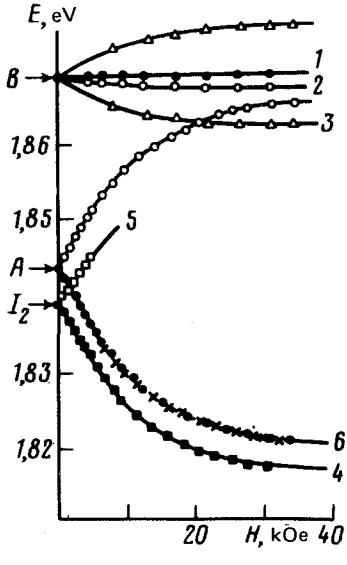

FIG. 2. Energy position of the reflection lines of A and B excitons in the $\sigma^+(1)$, $\sigma^-(2)$, $\pi(3)$ polarizations, as well as of the emission lines of EIC on the neutral donor in the σ^+ and σ^- polarizations (4,5) and emission lines of free excitons (6) as a function of the magnitude of the magnetic field H. The arrows indicate the positions of A and B excitons and of the EIC emission line (I_2) in zero magnetic field.

impurity subsystem $\Delta_{e,h} \sim \langle S^z_{\mathrm{Mn}} \rangle_{H,T}$.[1,6] The magnitudes of the spin splittings in the conduction band and in the A and B valence subbands can be determined from an analysis of the magnitudes of the splitting of σ and π components of the A and B excitonic terms.[6,7] For saturating magnetic fields, these quantities are $\Delta_e = 7.5 \pm 0.5$ meV, $\Delta_h^A = 36.5 \pm 0.5$ meV, and $\Delta_h^B = 5 \pm 1$ meV. Differently polarized components are shifted symmetrically relative to their position at $H = 0$. The spectral distance between the D_0X recombination line and the lowest exciton term is essentially constant.

States with large radius in SMSS are characterized by the same carrier-impurity exchange constants as free electrons and holes. If Δ_e and Δ_h are the magnitudes of the spin splittings in the conduction band and in the A valence subband, then we can write the following expressions for the energies of the optically active exciton terms E_X^A and the energy of the neutral donor E_{D_0}:

$$E_X^A = E_X^0 \pm \frac{1}{2}(\Delta_e + \Delta_h), \tag{1}$$

$$E_{D_0} = E_{D_0}^0 \pm \frac{1}{2}\Delta_e, \tag{2}$$

where E_X^0 and $E_{D_0}^0$ are the energies of the A exciton and donor in zero magnetic field.

In the D_0X complex, electrons form a spin singlet. For this reason, the exchange field acts only on the hole, splitting the state of the complex into two states with energies

$$E_{D_0X} = E_{D_0X}^0 \pm \frac{1}{2}\Delta_h. \tag{3}$$

The selection rules in $\mathbf{H}\|\mathbf{C}_6$ geometry allow only two transitions between D_0X and D_0 states: from the ground state D_0X to the spin-excited state D_0 and from the spin-excited state D_0X to the ground state D_0. The energy of the emitted quantum of light in this case will be

$$\hbar\omega_{D_0X} = \hbar\omega_{D_0X}^0 \pm \frac{1}{2}(\Delta_e + \Delta_h), \tag{4}$$

where $\hbar\omega_{D_0X}^0$ is the RR energy of the D_0X complex at $H = 0$

$$\hbar\omega_{D_0X}^0 = E_{D_0X}^0 - E_{D_0}^0.$$

Since the transition from the ground state D_0X proceeds to the excited state of the donor, the difference between the spectral positions of the free and bound exciton lines does not coincide with the binding energy of EIC on the neutral donor. The binding energy of the exciton in D_0X (i.e., the energy necessary to separate D_0X into an exciton and a neutral donor in the ground state) can be written as

$$E_b = E_X + E_{D_0} - E_{D_0X} = E_{\mathrm{CB}}^0 - \Delta_e. \tag{5}$$

As the magnitude of the splitting of the conduction band increases, the binding energy of the exciton in D_0X decreases and vanishes for $\Delta_e = E_b^0$.

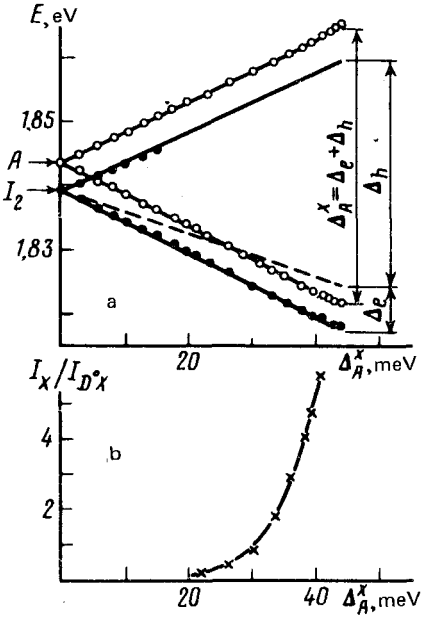

FIG. 3. (a) Position of the A term (○) and of the RR line of EIC (●) as a function of the magnitude of the A exciton splitting. The dashed line indicates the energy position of EIC. (b) Ratio of the emission intensities of free and bound excitons as a function of Δ_X^A.

The energy position of the RR line of EIC and the position of the excitonic term as a function of the magnitude of the splitting of the A exciton $\Delta_X^A = \Delta_e + \Delta_h \sim \langle S_{\mathrm{Mn}}^z \rangle_{H,T}$ is described by straight lines (Fig. 3a). If the magnitude of the spin splitting of the conduction band in saturating magnetic fields is known, it is possible to construct the dependence of the energy of D_0X on the function Δ_X^A (dashed line in Fig. 3a). It is evident that the emission line of free excitons in the RR spectrum of $Cd_{1-x}Mn_xSe$ (Fig. 3b) is excited in the region where the EIC and free exciton energies intersect, i.e., at a time when, according to our arguments, the binding energy of the exciton in D_0X vanishes.

Thus, in $Cd_{1-x}Mn_xSe$ in a magnetic field, the EIC state on the neutral donor becomes unstable relative to decay into a neutral donor and a free exciton. In this case, the impurity channel of radiative recombination is effectively suppressed and the emission lines of free excitons dominate the RR spectrum.

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