Luminescence of hot excitons and of excitons cooled by the electron-spin exchange energy in $Zn_{1-x}Mn_xSe$

V. G. Abramishvili, A. V. Komarov, S. M. Ryabchenko, and Yu. G. Semenov
Institute of Physics, Academy of Sciences of the Ukrainian SSR

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A line of an *LO*-phonon repetition of hot luminescence has been observed during resonant laser pumping of $Zn_{1-x}Mn_xSe$. In a magnetic field, a component splits off from this line. This component is shifted by the energy of the giant spin splitting of the conduction band. The effect is attributed to a fast relaxation of excitons due to an exchange scattering by spins of shallow donors.

There have been extremely few studies of the luminescence of magnetically mixed semiconductors during nearly resonant excitation. Some new effects might be expected in magnetically mixed semiconductors because of the specific features of the mechanisms for the momentum and spin scattering which stem from the exchange interaction of carriers with the magnetic subsystem. In this letter we are reporting a study in this direction for the magnetically mixed semiconductor $Zn_{1-x}Mn_xSe$ with $x = 0.009$.

The measurements were carried out at $T = 2$ K in magnetic fields $H \leqslant 35$ kOe with $\mathbf{k}\|\mathbf{H}\|\mathbf{z}$. The wave vectors $\mathbf{k}$ of the exciting light and of the light emitted backward ($-\mathbf{k}$) were both perpendicular to the cleavage plane of the sample. For excitation we used a helium-cadmium laser with an energy $E_L = 2.8075$ eV, which was 8 meV above the energy of the 1s-exciton transition at $H = 0$. The excitation and detection were carried out in circularly polarized light. We observed intense emission bands of exciton-impurity complexes and of donor acceptor pairs. We also observed an extremely narrow ($\Gamma \approx 0.6$ meV) and faint line which was shifted 31.5 meV down the energy scale from E_L (Fig. 1). At $H = 0$ the intensities of this line in σ^+ and σ^- light, I_p^+ and I_p^- are identical, regardless of the sign of the circular polarization of the excitation ($e_L = \sigma^+, \sigma^-$). In a field $H \neq 0$, I_p remains independent of e_L but acquires a polarization $\rho_p = (I_p^+ - I_p^-)/(I_p^+ + I_p^-)$, which reaches $\approx 80\%$ at $H_{\max} = 35$ kOe. In a magnetic field, an additional component splits off the long-wavelength side of this line. We denote the intensity of this additional component by I_{sp} (Fig. 1). This additional component is active essentially only in the σ^+ polarization. Figure 2 shows the magnetic-field dependence of the energies of these two lines. Line I_p is shifted with respect to the laser by an amount ΔE which is approximately equal to the energy of an *LO* phonon in ZnSe: $E_{LO} = 31$ meV (Ref. 1). Its position does not depend on H (Fig. 2). The shift of line I_{sp} with respect to I_p, on the other hand, agrees with the giant spin splitting of the conduction-electron states in $Zn_{1-x}Mn_xSe$ (Refs. 2–4): $G_{eM}(H,T) = x^* J_{eM} \langle S_M \rangle$, where x^* is the mole fraction of Mn^{2+} ions which are not bound in exchange pairs, J_{eM} is the exchange-interaction constant of the conduction electrons for the interaction with Mn^{2+} ions, $\langle S_M \rangle = S_M B_{S_M}(g_M \beta S_M H / k_B (T + T_0))$, is the average spin polarization of the Mn^{2+} ions

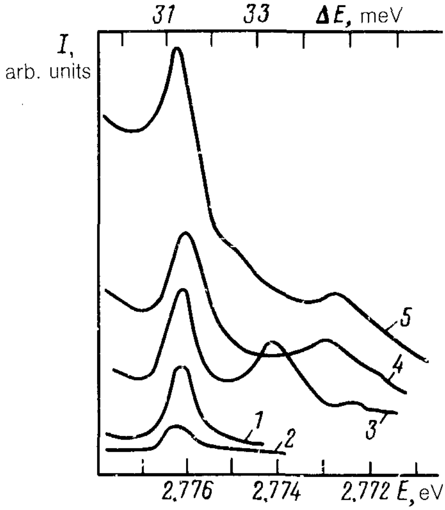

FIG. 1. Luminescence spectra of a $Zn_{1-x}Mn_xSe$ ($x = 0.009$) crystal in the region of the I_p and I_{sp} bands at $T = 2$ K (for an excitation polarization σ^-). 1—$H = 0$; 2,3—$H = 10.5$ kOe; 4—$H = 21.5$ kOe; 5—$H = 34$ kOe; 2—for the σ^- polarization of the emission; 3–5—for the σ^+ polarization of the emission. The upper energy scale shows the spectral shift with respect to the laser line, $\Delta E = E_L - E$.

with a spin $SM = 5/2$ which are not bound in exchange pairs, and T_0 is the effective correction to the temperature T for the impurity-impurity exchange interaction.

On the basis of its energy position, line I_p might be attributed to a Raman scattering by an LO phonon, and I_p might be regarded as Raman scattering by an LO phonon with a simultaneous flip of an electron spin (more probably, that of a shallow donor). A more detailed analysis shows, however, that these lines cannot be attributed to a Raman scattering. First, there is no dependence of I_p^+ or I_p^- on the sign of the circular polarization of the excitation (e_L), in contradiction of what we would need for Raman scattering.[5] Second, for I_{sp} we observe that the intensity (I_{sp}^-) correspond-

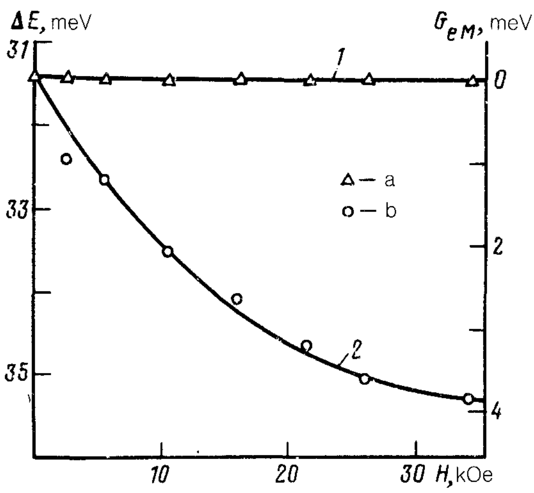

FIG. 2. Magnetic-field dependence $\Delta E(H)$ of the energy shifts of the I_p and I_{sp} bands with respect to the laser energy (scale at the left). The points are experimental. Δ—For the I_p band; O—for the I_{sp} band. Line 1 (drawn through the points)—H-independent position of the line I_p; line 2—Brillouin dependence of the quantity $E_{sp}(H) = E_p - G_{eM}(H)$, where $G_{eM}(H)$, was calculated with the values $x^* \approx 0.008$ and $T_0 = 1$ K, with $J_{eM} \approx 0.24$ meV (Refs. 2 and 3). The scale at the right is for $G_{eM}(H)$.

ing to the case $e_L = \sigma^-$ is greater than that (I_{sp}^+) corresponding to $e_L = \sigma^+$. From the standpoint of Raman scattering, this result would mean that processes involving a change in angular momentum $\Delta M = 2$ outweigh processes with $\Delta M = 0$. Such a situation is improbable. Finally, at $H \neq 0$ the exciton spin subbands experience a giant spin splitting, and the magnetic-field dependence of $E_L - E_{ex}$ (E_{ex} is the energy of the exciton active in the given polarization) becomes different for the different polarizations of the light. This circumstance should have had a corresponding effect on the intensities I_p and I_{sp} in the case of Raman scattering,[5] but we do not observe such an effect.

The results obtained here can apparently be attributed an LO-phonon repetition of the luminescence of hot excitons, with a partial energy relaxation of these excitons among the spins of shallow donors. During pumping at an energy exceeding the energy of an exciton resonance by an amount $E_L - E_{ex} < E_{LO}$, "hot" excitons (with an energy $E_{ex} = E_L$) apper in the crystal. The time scale of the energy relaxation of these excitons among acoustic phonons may be substantially longer than the time scale of the relaxation of the exciton momentum which results from scattering by potential fluctuations in the solid solution of the semiconductor. The angular momentum of a hole in the degenerate Γ_8 valence band, which is associated with the momentum, and thus the angular momentum of the exciton "forget" the polarization of the excitation over the lifetime of the hot excitons. An additional mechanism for the loss of the polarization memory might be an exchange scattering of the carriers making up the exciton by the spins of Mn^{2+} ions. The role played by the magnetic field, which is responsible for the giant spin splitting of the exciton dispersion branches, reduces to one of causing a redistribution of the densities of exciton states which is of such a nature that the exciton branch active in the σ^+ polarization is filled to a greater degree as a result of fast elastic-scattering processes. As a result, the hot-exciton luminescence and also its LO-phonon repetition with an energy $E_L - E_{LO}$ lose the polarization of the excitation at $H = 0$, the polarization $\rho_p > 0$ becomes independent of e_L at $H \neq 0$, and ρ_p increases with H. In addition to other fast processes, we should take into account the exchange scattering by spins of shallow donors, whose cross section should be ≈ 4 orders of magnitude larger than the cross section for exchange scattering by Mn^{2+}. As a result, at donor concentrations $\gtrsim 10^{16}\ cm^{-3}$ a peak will appear in the hot-exciton distribution, shifted from the original energy by the giant spin splitting of the electron of a shallow donor.

The particular features of the dependence of $I_{sp}^+(e_L)$ on the polarization of the excitation in a field $H \neq 0$ can be explained by taking into account the role played by inelastic spin-dependent scattering from the upper polariton branch to the lower branch.

In summary, this study has yielded the first observation of a hot luminescence in a magnetically mixed semiconductor under conditions close to but nevertheless distinguishable from (on the basis of polarization characteristics) Raman scattering. This study has yielded the first observation of a relaxation of hot excitons through the spin flip of a shallow donor, as a consequence of the exchange scattering of an exciton by the latter. A structural feature associated with this process has been observed in the distribution of hot excitons.

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