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Anisotropy of magnetic polarons bound to acceptors in $Cd_{1-x}Mn_xSe$

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Time-resolved donor-acceptor luminescence provides the main parameters of magnetic polarons bound to acceptors in $Cd_{1-x}Mn_xSe$. Time-resolved polarization of this emission with $\mathbf{H} \| \mathbf{c}$ in the Faraday geometry reveals the freezing of the polaron orientation at low temperature. This is related to the gyromagnetic factor $g_\perp = 0$ for the hole in wurtzite crystals, leading to a bistable magnetic polaron.

Among the properties of semimagnetic semiconductors,[1] one of the most noticeable is probably the formation of magnetic polarons bound to donors (D^0-BMP)[2,3] or acceptors (A^0-BMP),[4] caused by the exchange interaction between weakly bound carriers and the magnetic moments of Mn^{2+} ions. Up to now, BMP's were studied in cases where the exchange integrals (denoted usually $N_0\beta$ for free holes and $N_0\alpha$ for free electrons) were isotropic: Thus, these BMP's were free to orient their total magnetic moment in any direction. In wurtzite crystal, the top of the valence band is of Γ_9 symmetry, the gyromagnetic ratio vanishes for a magnetic field $\mathbf{H} \perp \mathbf{c}$ ($g_\perp = 0$),[5] and that property is true also for the exchange integral ($N_0\beta_\perp = 0$). As a consequence, A^0-BMP's in CdMnSe should have a strong tendency to align their magnetic moment parallel or antiparallel to the c axis. In a previous work, Heiman *et al.*[6] studied the polarization of donor-acceptor (D-A) luminescence in CdMnSe in the Faraday geometry ($\mathbf{H} \| \mathbf{c}$) under dc conditions. They concluded that A^0-BMP's did not have time to form below 10 K; a conclusion rather surprising considering the long lifetime of D-A emission.[7]

In this Rapid Communication, we present a time-resolved study of D-A luminescence in $Cd_{1-x}Mn_xSe$ which allows, from the shift of the band as a function of time and temperature T, to extract the exchange contribution $E_p(T)$ to the binding energy of the acceptor. With a magnetic field $\mathbf{H} \| \mathbf{c}$ applied, the time evolution of the circular polarization P_c,[8] which *increases* with time delay, gives evidence of the bistable character of A^0-BMP's at low T.

The experiments are done on single crystals of $Cd_{0.95}Mn_{0.05}Se$ grown at the Institute of Physics of the Polish Academy of Sciences. The samples are analogous to those used for Raman spin-flip (RSF) experiments on D^0-BMP's.[2] The excitation is provided by a dye laser modulated by an acousto-optic deflector (pulse width 200 ns, frequency 50 khz, peak power 10 mW). The luminescence is analyzed by a double-grating monochromator and processed in the so-called "single photon counting" mode; a microcomputer programmed as a multichannel analyzer controls the data acquisition. Time-resolved spectra from 13 000 to 15 000 cm^{-1} with 10 cm^{-1} resolution were obtained during one hour of data accumulation. The precise line position and linewidth were obtained from calculations of the first and second moments.

Figure 1 shows the spectrum emitted at 4.8 K at different time delays. The D-A nature of the 14 000 cm^{-1} band is already evidenced by the shift of the band with delay. The line shape is somewhat broader at early time, but stabilizes after about 0.5 μs; this is why we present quantitative analysis only for delay larger than 0.5 μs. Let us recall that the energy of a photon emitted by a D-A pair at separation $R_{D\text{-}A}$ is given by

$$h\nu = E_G(T) - E_D - [E_A + E_p(T)] + e^2/KR_{D\text{-}A} \quad , \tag{1}$$

where $E_G(T)$ is the band gap, E_D and E_A the binding energy of the donor and the acceptor, and $e^2/KR_{D\text{-}A}$ the Coulomb interaction. Figure 2 gives the line position as a function of time delay at different temperatures. The time evolution, which depends only weakly on temperature, reflects the increase of $\langle R_{D\text{-}A} \rangle$ (from about 120 to 300 Å). The shift as a function of T reflects the evolution of $E_p(T)$, the polaron energy, which has been plotted in Fig. 3. To evaluate the main parameters of the A^0-BMP, we use the so-called muffin-tin model,[9] where the hole is coupled equally to N spins of $S = \frac{5}{2}$. In this approximation, the total energy is

$$E = \beta' \sigma M_z / 2\Omega + g\mu_B H M_z + A_1 M^2 \quad , \tag{2}$$

where M is the magnetization, M_z its component along the c axis, H the magnitude of the applied magnetic field parallel to $\mathbf{c}$, $N_0\beta'$ the exchange integral for the acceptor, Ω the volume of the muffin tin, and $\sigma = \pm 1$ according to the two

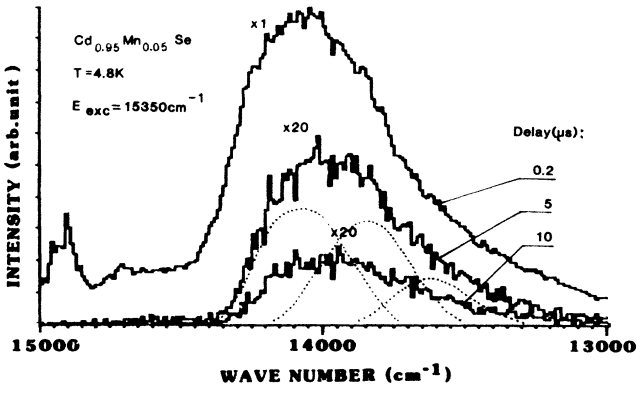

FIG. 1. Luminescence spectrum at different time delays (0.2, 5, 10 μs). The dotted curves suggest, for the 5 μs spectrum, a decomposition into a no phonon line and LO phonon replicas ($h\nu_{LO} \sim 26$ meV). The full width at half maximum of the no phonon line is about 46 meV.

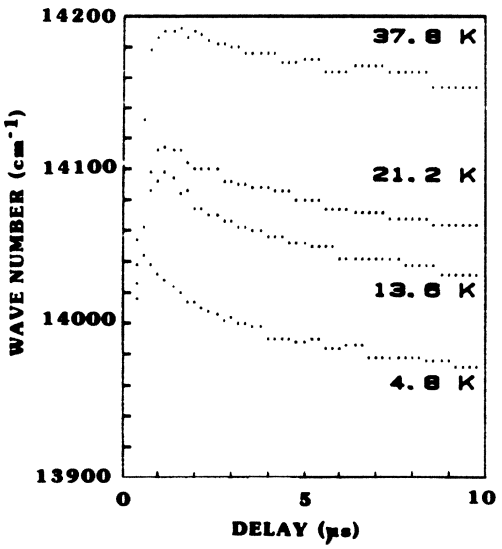

FIG. 2. Time evolution of the D-A line position at four different temperatures. The temperature dependence of E_G has been taken into account in order to display the temperature variation of $E_p(T)$.

possible hole states. The last term is an antiferromagnetic contribution, where $A_1 = 4kT_0/3N(S+1)S$. $E_p(T)$ is obtained as a thermal average of the first term in Eq. (2), which can be performed exactly. A good fit of $E_p(T)$, as shown on Fig. 3, is obtained by taking $N = 10$, the radius of the polaron 13.5 Å,[10] and $N_0\beta' = -0.8$ eV, a value lower than the free-hole value, $N_0\beta = -1.11$ eV,[11] because a substantial mixing between A and B holes occurs in the acceptor wave function,[12] the A-B splitting being small with respect to E_A. The polaron energy $E_p(T)$ is larger than in $Cd_{1-x}Mn_xTe$[4] because β' is larger and the Bohr radius smaller [$E_p(0) = 50$ meV]. Notice that a theoretical model is needed to place the base line in Fig. 3 and to determine E_A which is found equal to 100 ± 5 meV. It was found that Li and Na give an acceptor level with $E_A = 109 \pm 6$ meV in CdSe.[13]

Time-resolved measurements of P_c were performed in a superconducting magnet up to 6 T, in the Faraday geometry. If the acceptor retains pure Γ_9 symmetry, P_c is given by

$$P_c = (P_e + P_h)/(1 + P_e P_h) \ , \tag{3}$$

where P_e and P_h are the donor and acceptor polarizations. Most of the data were taken at the peak of the D-A band; a few spectroscopic data show that P_c decreases slowly with decreasing wave number, a feature that might be related to participation of LO phonon replicas. The remarkable point is the *increase* of P_c with time delay. This is observed only for H not too large, away from saturation. Figure 4 shows the time evolution of P_c at a constant H/T value, at several temperatures. One can clearly see that the rate of change of P_c becomes very slow at low temperature. Such a behavior can be easily explained by Eq. (2): When $H = 0$, the total A^0-BMP energy presents two equivalent minima for $M_z = \pm NS$ separated by a saddle point at $M = 0$. Since the polaron involves a rather large number of particles, we assume that tunneling may be neglected; hence, transfer from one minimum to the other requires a thermal activation over a potential barrier of the order of $E_p(0)$. This explains why the time to reach equilibrium between the two states split by $2g\mu_B HNS$ becomes long at low T. A thorough analysis of P_c is certainly beyond the scope of this paper. We would like to discuss two points.

(i) How to extract P_h from the measurements of P_c? The donor polarization P_e is well known from RSF experiments and is close to that of the free electron if $H \geq 0.1$ T; so it can be easily calculated. If it is introduced in Eq. (3), one finds a value of P_c already larger than the experimental one, even if $P_h = 0$. In particular, the value of P_c at saturation, P_{sat}, is only 75–80%. We think that the hole in the A^0-BMP no longer has a pure Γ_9 symmetry since it is subjected to perturbations which do not possess axial symmetry: The magnetic moment of A^0-BMP has a large component along the c axis, but due to magnetic fluctuations, it has a nonzero transverse component; in addition, the acceptor is perturbed by the random substitution of a few Mn atoms inside its orbit. We present a phenomenological model with one fitting parameter δ. Equation (1) of Ref. 11 suggests that, for an oblique perturbation, mixing occurs mainly

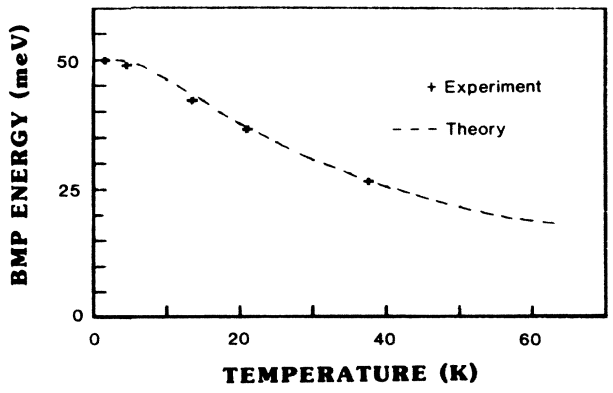

FIG. 3. Exchange contribution to A^0BMP energy $E_p(T)$ has a function of T. $\mp$ are experimental data. The dashed line is the theory.

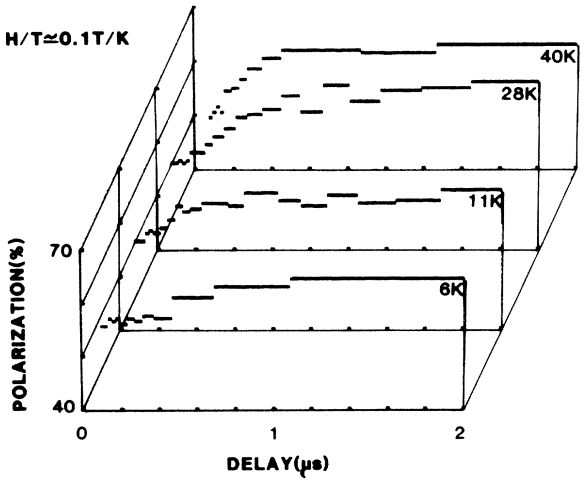

FIG. 4. Time evolution of the circular polarization P_c at different temperatures, for a constant ratio $H/T \sim 0.1$ T K^{-1}.

between $|A,\frac{3}{2}\rangle$ and $|B,\frac{1}{2}\rangle$ holes. So we assume a hole state in the BMP of the following form: $|h+\rangle = (1-\delta^2)^{1/2} \times |A,\frac{3}{2}\rangle + \delta|B,\frac{1}{2}\rangle$ and $|h-\rangle$ its transform by time reversal. Then the new formula for P_c is

$$P_c = (GP_e + P_h)/(1 + GP_eP_h) \quad , \tag{4}$$

where $G = (3-4\delta^2)/(3-2\delta^2)$. Unfortunately, Eq. (4) implies a saturation $P_{c\,\mathrm{sat}} = 1$, in contrast with experiment. We have to assume some kind of depolarization and define $P_c' = P_c/P_{c\,\mathrm{sat}}$. Then, P_h can be obtained from Eq. (4), where P_c' is the experimental value and P_e the calculated one,

$$P_h = (P_c' - GP_e)/(1 - GP_c'P_e) \quad . \tag{5}$$

That procedure gives satisfying results at least for $T \geq 5$ K,[14] assuming δ^2 of the order of 0.4. On Fig. 5, as a function of H, we compare the values of $P_h(2)$ at a delay of 2 μs with the thermodynamic equilibrium $P_{h,\mathrm{th}}$ obtained by an appropriate average on Eq. (2). The values of $P_h(0)$ at zero delay are compared to the following model: Our sample is n type, so A^0 is photocreated when the field H is already present. The N spins in the box around A^- undergo magnetic fluctuations and one can readily calculate $P_{M_z}(H,T)$, the rate of "magnetic polarization." Figure 5 shows that, to a good approximation, $P_h(0) = P_{M_z}$. This means that if at the time of the hole capture, M_z points towards a given direction, then A^0-BMP will develop its magnetization towards the same direction, independent of the spin polarization of the captured hole.[15] $P_h(2)$ is found to be smaller than $P_{h,\mathrm{th}}$ and the discrepancy seems to increase at low T. This is consistent with the model of A^0-BMP orientation freezing.

(ii) How to justify the order of magnitude of the time constant of P_c as a function of T? The rate of transfer U from one valley to the other is proportional to the probability of reaching the saddle point, assuming the polaron is in a given valley. With the model leading to Eq. (2), U is thermally activated by an energy $E_{ac} = 42$ meV at $H = 0$. Such a value of E_{ac} would probably induce a rather abrupt change in the P_c time constant at a temperature higher than observed. In fact, the property $g_\perp = 0$ for the hole is valid only to first order, i.e., for small transverse field. For large transverse magnetization, a type-A hole can gain exchange energy,[11] so that the saddle point does not occur at $M = 0$ but rather at $M = NS$, $M_z = 0$, with a substantial reduction of E_{ac}, maybe by a factor of 2. In addition, since the mean number of spins in the A^0-BMP is 10, N should fluctuate from 6 to 14, inducing a broad distribution of E_{ac} values. These two facts justify probably the temperature range (10–40 K), where the P_c time constant is in the μs range.

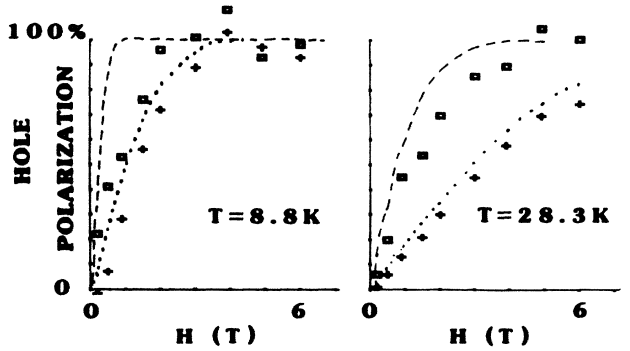

FIG. 5. Initial A^0BMP polarization P_h (○) (+) compared to calculated P_{M_z} (dotted curve) and final A^0BMP polarization $P_h(2)$ (□) compared to the calculated value at equilibrium $P_{h,\mathrm{th}}$ (dashed curve), at two temperatures.

To conclude, we have shown that, in wurtzite semimagnetic semiconductors (SMSC's), despite the fact that Mn^{+2} ions of S-like electronic configuration have essentially no anisotropy, the strong anisotropy of the Γ_9 hole is transferred to A^0-BMP. If one could grow p-type $Cd_{1-x}Mn_xSe$, the component of magnetization related to A^0BMP should exhibit magnetocrystalline anisotropy and hysteresis at low T. More theoretical studies of acceptors in wurtzite SMCS's are needed in order to bring interpretation on a more quantitative basis.

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[15]A somewhat different situation, namely, the direct creation of localized excitons by polarized light (site selection) and subsequent development of a magnetic polaron was considered by J. Warnock, R. N. Kershaw, D. Ridgely, K. Dwight, A. Wold, and R. R. Galazka, J. Lumin. **34**, 25 (1985).