Crystal-field model for acceptor-associated bound magnetic polarons in wurtzite semiconductors

A. K. Bhattacharjee
Laboratoire de Physique des Solides, Bâtiment 510, Université Paris-Sud, Centre d'Orsay, 91405 Orsay, France
(Received 21 January 1987)

The effects of coupling between the A and B valence-band states in an acceptor-associated bound magnetic polaron (A^0-BMP) in hexagonal crystals such as $Cd_{1-x}Mn_xSe$ are studied within a uniaxial model. The effect is found to be small for both the average BMP energy and the equilibrium hole polarization. However, the average excitation energy of the B-like hole states is reduced by an order of magnitude at low temperatures. The resulting spin-lattice relaxation time of the hole, within the Orbach framework, accounts for the time evolution of the hole polarization, inferred from time-resolved luminescence experiments.

A spherical approximation[1,2] has proven adequate for an acceptor-associated bound magnetic polaron (A^0-BMP) in cubic systems like $Cd_{1-x}Mn_xTe$, where the top of the valence band is a Γ_8 quartet. But, in wurtzite crystals like $Cd_{1-x}Mn_xSe$ the hexagonal crystal field leads to a substantial splitting between the Γ_9 and Γ_7 doublets. The ground state of a shallow acceptor is then associated with the upper band A (Γ_9). Theoretically the Ising model, with the Mn spins treated classically, has been used[3,4] to treat the corresponding A^0-BMP. This, of course, neglects any mixing of the B band (Γ_7) states through the hole-Mn exchange interaction. However, in $Cd_{0.95}Mn_{0.05}Se$ at 2 K the BMP energy is 50 meV.[4] On the other hand, the energy separation between the A and B bands is 26 meV. It is slightly less (23 meV) for the hydrogenic $1s$ states associated with them.[5] Thus, the A-B mixing is expected to be non-negligible.

In the following, we present a simple model for A^0-BMP, which incorporates this mixing. We add a uniaxial crystal-field term to the spherical Heisenberg model, previously used for cubic crystals. The bound hole is treated as a particle of total angular momentum $j=\frac{3}{2}$. The A-band associated ground doublet is represented by $j_z=\pm\frac{3}{2}$, and the B-band associated excited one by $j_z=\pm\frac{1}{2}$. The splitting between them is represented by the uniaxial term $-Dj_z^2$.

Within a finite-radius constant-coupling approximation[6] for the hole-Mn exchange, the Hamiltonian is then diagonalized exactly and the partition function calculated. This yields good fits of the BMP energy[4] as a function of temperature, and the equilibrium hole polarization[3] as a function of applied field. But, a more interesting result is obtained from the zero-field equilibrium population of the $j_z=\pm\frac{3}{2}$ and $j_z=\pm\frac{1}{2}$ states. The ratio yields the average excitation energy δ of the B-like hole states. At low temperatures (~ 5 K), δ is an order of magnitude smaller than the crystal-field (CF) splitting $2D$. Within the framework of a thermally activated Orbach process, we then calculate the spin-lattice relaxation time τ of the hole. The order of magnitude of τ as well as its temperature dependence are consistent with time-resolved polarization measurements.[4,7,8]

In the spherical approximation, the exchange interaction between a bound hole and the Mn^{2+} ions is represented by the Heisenberg Hamiltonian

$$H_{ex}=-J\mathbf{j}\cdot\sum_i b_i\mathbf{S}_i \ . \tag{1}$$

Here, $\mathbf{S}_i$ denotes the spin ($S=\frac{5}{2}$) of the Mn ion situated at $\mathbf{R}_i$, and $b_i=|\phi(\mathbf{R}_i)|^2$, where

$$\phi(\mathbf{r})=(\pi a_B^3)^{-1/2}\exp(-r/a_B)$$

is the hydrogenic envelope function of the acceptor ground state.

To this, for wurtzite crystals, we add

$$H_{CF}=-D(j_z^2-\tfrac{9}{4}) \ , \tag{2}$$

where z is along the c axis. If a magnetic field B is applied in the same direction, we have also the Zeeman term

$$H_Z=-\mu_B g_{Mn}B\sum_i S_{iz}-\mu_B g_h B j_z \ . \tag{3}$$

An exactly soluble quantum-mechanical model is obtained by making the following approximation:

$$b_i=\begin{cases}\dfrac{1}{V}, & R_i\le R_c\\ 0, & R_i>R_c,\end{cases} \tag{4}$$

where R_c is the effective polaron radius and $V=(4\pi/3)R_c^3$. According to Ref. 6, $R_c=1.84a_B$. The effective number of Mn ions in the BMP is $N\simeq N_0Vx$, where N_0 is the number of cation sites per unit volume. H_{ex} is thus replaced by

$$H_0=-(J/V)\mathbf{j}\cdot\boldsymbol{\sigma} \ , \tag{5}$$

where

$$\boldsymbol{\sigma}\equiv\sum_{i=1}^{N}\mathbf{S}_i \ . \tag{6}$$

The Hamiltonian

$$H=H_0+H_{CF}+H_Z \tag{7}$$

can then be diagonalized exactly, by noting that σ and $M=\sigma_z+j_z$ are good quantum numbers. Here, $\sigma=NS$, $NS-1$, . . ., 0 (assuming even N). The energy levels $\varepsilon_{\sigma Ml}$ are obtained by diagonalizing H in the subspace

$$\{\,|\,\sigma,\sigma_z=M-m\,\rangle\,|\,j,j_z=m\,\rangle\,\}\ .$$

Clearly, there are 1, 2, 3, or 4 values of l, depending on σ and M. The partition function is

$$Z=\sum_{\sigma=0}^{NS}\sum_{M=-\sigma-3/2}^{\sigma+3/2}\sum_{l}\zeta(\sigma,M,l)\ , \tag{8}$$

where

$$\zeta(\sigma,M,l)=\omega(\sigma)\exp(-\varepsilon_{\sigma Ml}/k_BT)\ . \tag{9}$$

Here

$$\omega(\sigma)=\Omega(\sigma)-\Omega(\sigma+1) \tag{10}$$

with $\Omega(\mu)$ being given by[9] the coefficient of X^{μ} in $(X^S+X^{S-1}+\cdots+X^{-S})^N$. The equilibrium population of the $j_z=m$ hole state is given by

$$n_m=\sum_{\sigma}\sum_{M}\sum_{l}\zeta(\sigma,M,l)\,|\,a^m_{\sigma Ml}\,|^2/Z\ , \tag{11}$$

where

$$a^m_{\sigma Ml}\equiv\langle\,\sigma Ml\,|\,\sigma,\sigma_z=M-m;j,j_z=m\,\rangle\ . \tag{12}$$

In zero field, $n_m=n_{-m}$, and

$$\delta=-k_BT\ln(n_{1/2}/n_{3/2}) \tag{13}$$

is the average excitation energy of the B-like hole states. In an applied field, the degree of circular polarization of donor-acceptor pair (DAP) luminescence is

$$P_c=\frac{3(n_{-3/2}\nu_{\downarrow}-n_{3/2}\nu_{\uparrow})+(n_{-1/2}\nu_{\uparrow}-n_{1/2}\nu_{\downarrow})}{3(n_{-3/2}\nu_{\downarrow}+n_{3/2}\nu_{\uparrow})+(n_{-1/2}\nu_{\uparrow}+n_{1/2}\nu_{\downarrow})}\ , \tag{14}$$

where $\nu_{\uparrow}$ and $\nu_{\downarrow}$ represent the population of spin-up and spin-down electron states, respectively. Thermal equilibrium values of $\nu_{\uparrow}$ and $\nu_{\downarrow}$ can be estimated from the conduction-band spin splitting given by[10]

$$\Delta E_c=\bar{x}N_0\alpha SB_S\left[\frac{Sg_{\mathrm{Mn}}\mu_BB}{k_B(T+T_0)}\right]+\mu_Bg_eB\ . \tag{15}$$

Then

$$\nu_{\uparrow}/\nu_{\downarrow}=\exp(-\Delta E_c/k_BT)\ . \tag{16}$$

The relevant parameters for $Cd_{0.95}Mn_{0.05}Se$ are[11] $g_e=0.5$ and $\bar{x}N_0\alpha=7.6$ meV. Also, $T_0=1.5$ K (Ref. 12) and $g_{\mathrm{Mn}}=2$. Here, we have neglected the relatively small polaron effect on the donor states.

Let us now present some of our results for $Cd_{0.95}Mn_{0.05}Se$. The acceptor binding energy in CdSe is estimated 100 meV.[4] From the measured[13] static dielectric constants (average $=8.92$), we obtain $a_B=8$ Å. The known lattice constants $a=4.309$ Å and $c=7.021$ Å give $N_0=0.017\,72$ (Å)$^{-3}$. Thus the effective polaron volume[6] $V=25.93\,a_B^3$ contains $N=12$. Let us recall[5] that $D=11.5$ meV. In Fig. 1, the upper curve shows the resulting zero-field polaron binding energy $E\equiv-\langle\varepsilon\rangle$ as a function of temperature. Note that an excellent agreement is obtained with the experimental data of Ref. 4. The only free parameter is J, which equals $\beta/3$ in the usual notation. The theoretical curve corresponds to $N_0\beta=0.81$ eV, which is 73% of the free-hole value 1.11 eV.[14] This reduction factor for bound hole is about the same as that predicted[15] for $Cd_{1-x}Mn_xTe$. In Fig. 1, we also present δ as a function of T. Note that δ is very small at low temperatures, it increases with T as the polaron binding decreases. At high T (not shown in the figure) δ approaches $2D$ asymptotically.

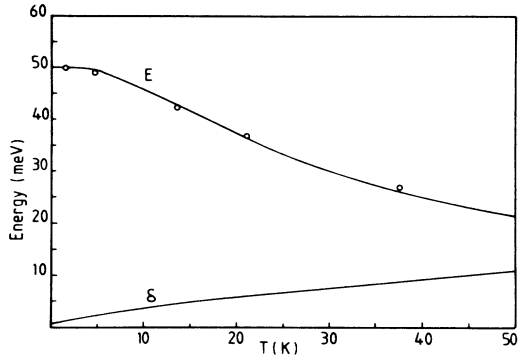

FIG. 1. The upper curve shows theoretical polaron binding energy E as a function of temperature in $Cd_{0.95}Mn_{0.05}Se$. The circles represent experimental data from Ref. 4. The lower curve shows the average excitation energy δ of the B-like hole states.

Figure 2 presents our results for equilibrium polarization as a function of applied field at different temperatures. The solid curves show the hole polarization $P_h\equiv-\frac{2}{3}\langle j_z\rangle$, while the dashed curves correspond to the DAP polarization P_c from Eq. (14). All the curves have been obtained by multiplying the calculated values by 0.8, the observed saturation value. Experimental DAP polari-

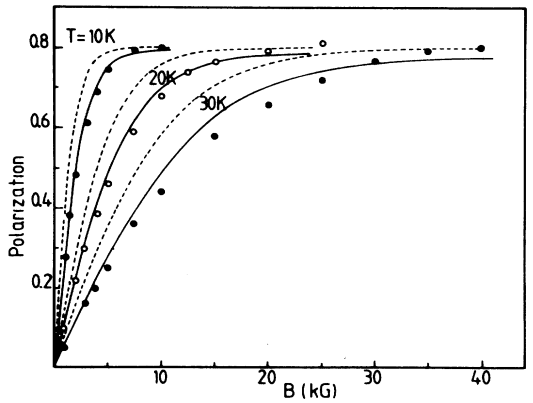

FIG. 2. Theoretical curves for equilibrium polarization in $Cd_{0.95}Mn_{0.05}Se$, scaled to the saturation value 0.8. The solid curves show the hole polarization P_h, while the dashed ones show the DAP polarization P_c. The circles represent experimental data from Ref. 3.

zation data from Ref. 3 are presented for comparison. It is interesting to observe that experimental data show agreement with P_h, rather than P_c curves. In fact, in Ref. 3, the electronic polarization was neglected and experimental data were shown to fit P_h, calculated in the Ising approximation. Thus, our theoretical P_h curves are in agreement with those of Ref. 3. On the other hand, the experimental DAP polarization lying close to P_h, would seem to indicate that the electron spin distribution does not reach lattice thermal equilibrium before recombination. Such an effect was previously reported[16] in $Cd_{1-x}Mn_xTe$. It is, however, surprising in a n-type material.

Let us mention that we have studied the D dependence of both E and polarization (P_c or P_h). As D increases from 0, E at a finite temperature decreases and the low-field polarization increases. However, for $D > 10$ meV, this effect saturates, i.e., E and P remain unchanged with increasing D in the temperature range of interest $T \leq 50$ K. This shows that the Ising approximation used in Refs. 3 and 4 is adequate for these equilibrium properties in $Cd_{1-x}Mn_xSe$.

The most interesting aspect of the present model is that it provides a framework for discussing time-resolved polarization measurements. The ground state of A^0-BMP in zero field is doubly degenerate: $M = \pm(NS + \frac{3}{2})$, corresponding to orientation parallel or antiparallel to the c axis. The orientational relaxation time is expected to be long compared to that in cubic $Cd_{1-x}Mn_xTe$, because direct $+\frac{3}{2} \leftrightarrow -\frac{3}{2}$ hole transitions are forbidden and there is a finite activation energy for relaxation to proceed via $j_z = \pm\frac{1}{2}$ states. We estimate the spin-lattice relaxation time τ of the hole by applying the Orbach formula[17]

$$\frac{1}{\tau} = C\left[\frac{\delta}{k_B}\right]^3 / (e^{\delta/k_BT} - 1) \tag{17}$$

with δ given by the average excitation energy of the $j_z = \pm\frac{1}{2}$ states, discussed above. In this picture, the polaron formation time ($\sim 10^{-9}$ sec, according to Ref. 18) is assumed to be much shorter than τ. Indeed, we shall see that $\tau \sim 10^{-6}$ sec. On the other hand, direct spin-lattice relaxation time of individual Mn spins is much longer[19] ($\sim 10^{-4}$ sec). Thus, τ plausibly characterizes the time evolution of the BMP orientation. Note that δ at low temperatures is much smaller than the Debye temperature of CdSe [181 K (Ref. 20)]. This is consistent with the two-phonon process implied in Eq. (17), with

$$C = \frac{3}{2\pi\hbar^4\rho v^5}(k_B)^3 |V_1|^2 , \tag{18}$$

where ρ is the density and v is the velocity of sound. Assuming $V_1 \simeq \frac{1}{3}(2D)$ for the coupling matrix element, and using ρ and average v from Ref. 20, we obtain $C = 2.8 \times 10^4$ sec^{-1}. Since this is only an order of magnitude estimate, we take $C = 10^4$ sec^{-1}. The resulting τ as a function of temperature in $Cd_{0.95}Mn_{0.05}Se$ is shown in Fig. 3. It is in good agreement with time-resolved DAP

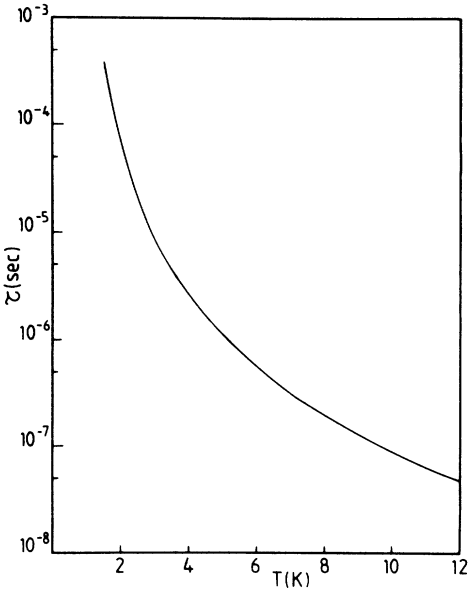

FIG. 3. Spin-lattice relaxation time τ of the hole (in zero field) as a function of temperature.

polarization data of Scalbert *et al.*[4,7,8] They reported that[4] at 6 K (with $B = 6$ kG) the time to reach the equilibrium value of polarization was about 1 μsec. The characteristic time was also found to decrease with increasing T. A more direct comparison is provided by their zero-field optical pumping data.[7,8] At 1.7 K a polarization of 8% was obtained that remained stable during 5 μsec, indicating a longer relaxation time, in agreement with the calculated τ. With increasing temperature, the polarization was found to decrease rapidly, almost disappearing at 10 K. This is also consistent with our τ curve: for $T \geq 10$ K, $\tau < 10^{-7}$ sec, which is apparently shorter than the time scale of the experiment.

To summarize, we have developed a uniaxial crystal-field model for A^0-BMP in wurtzite semiconductors. It incorporates the B-band mixing. We obtain good fits of both the BMP energy as a function of temperature and the equilibrium hole polarization as a function of applied field in $Cd_{0.95}Mn_{0.05}Se$. The effect of the B-band states is small for these equilibrium properties. On the other hand, the polaron coupling drastically reduces the average excitation energy δ of the B-like hole states at low temperatures. By using δ in the two-level Orbach formula, we estimate the hole spin-lattice relaxation time τ. Both the order of magnitude and the temperature dependence of τ are found to be in good agreement with the relaxation time, inferred from time-resolved DAP polarization data.

I wish to thank C. Benoit à la Guillaume, D. Scalbert, and J. Cernogora for numerous discussions.

[1]A. K. Bhattacharjee, R. Planel, and C. Benoit à la Guillaume, in *Proceedings of the 17th International Conference on the Physics of Semiconductors, San Francisco, 1984,* edited by J. D. Chadi and W. A. Harrison (Springer-Verlag, New York, 1985), p. 1431.

[2]J. Warnock and P. A. Wolff, Phys. Rev. B **31**, 6579 (1985).

[3]D. Heiman, J. Warnock, P. A. Wolff, R. Kershaw, D. Ridgley, K. Dwight, and A. Wold, Solid State Commun. **52**, 909 (1984).

[4]D. Scalbert, M. Nawrocki, C. Benoit à la Guillaume, and J. Cernogora, Phys. Rev. B **33**, 4418 (1986).

[5]P. Y. Yu and C. Hermann, Phys. Rev. B **23**, 4097 (1981).

[6]S. M. Ryabchenko and Yu. G. Semenov, Zh. Eksp. Teor. Fiz. **84**, 1419 (1983) [Sov. Phys.—JETP **57**, 825 (1983)].

[7]D. Scalbert, M. Nawrocki, C. Benoit à la Guillaume, and J. Cernogora, Proceedings of the 18th International Conference on the Physics of Semiconductors, Stockholm, 1986 (unpublished).

[8]D. Scalbert, Doctoral thesis, Université Paris VII, 1986.

[9]J. H. Van Vleck, *The Theory of Electric and Magnetic Susceptibilities* (Oxford Univerisity Press, Oxford, 1932), p. 324.

[10]J. A. Gaj, R. Planel, and G. Fishman, Solid State Commun. **29**, 435 (1979).

[11]D. Heiman, P. A. Wolff, and J. Warnock, Phys. Rev. B **27**, 4848 (1983).

[12]D. Heiman, Y. Shapira, S. Foner, B. Khazai, R. Kershaw, K. Dwight, and A. Wold, Phys. Rev. B **29**, 5634 (1984).

[13]D. Berlincourt, H. Jaffe, and L. R. Shiozawa, Phys. Rev. **129**, 1009 (1963).

[14]R. L. Aggarwal, S. N. Jasperson, J. Stankiewicz, Y. Shapira, S. Foner, B. Khazai, and A. Wold, Phys. Rev. B **28**, 6907 (1983).

[15]J. Mycielski and C. Rigaux, J. Phys. (Paris) **44**, 1041 (1983).

[16]A. V. Komarov, S. M. Ryabchenko, O. V. Terletskii, R. D. Ivanchuk, and A. V. Savitskii, Fiz. Tekh. Poluprovodn. **14**, 17 (1980) [(Sov. Phys. Semicond. **14**, 9 (1980)].

[17]See, for example, A. Abragram and B. Bleaney, *Electron Paramagnetic Resonance of Transition Ions* (Clarendon, Oxford, 1970), p. 561.

[18]A. V. Nurmikko, J. Lumin. **30**, 355 (1985).

[19]H. Krenn, W. Zawadzki and G. Bauer, Phys. Rev. Lett. **55**, 1510 (1985).

[20]C. F. Cline, H. L. Dunegan and G. W. Henderson, J. Appl. Phys. **38**, 1944 (1967).