Anticrossing of Raman Lines in $Cd_{1-x}Fe_xSe$: Van Vleck–Type Bound Magnetic Polaron

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Anticrossing of two Raman lines, that of a donor-electron spin flip and that of an intra-Fe^{++}-ion excitation, has been observed in $Cd_{1-x}Fe_xSe$, a Van Vleck–type semimagnetic semiconductor. A new model of a bound magnetic polaron (BMP) is reported, which accounts for the experimental data. At zero magnetic field, this BMP is characterized by a finite local spin polarization at its center, $\langle S^x\rangle = 0.06$, and by an exchange-energy shift of its ground state of $\Delta E_p = -0.26\ \mathrm{cm}^{-1}$ for $x = 0.018$, despite the fact that the spin-flip energy of the donor electron is strictly zero.

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Semimagnetic semiconductors (SMSC), where dilute magnetic ions (usually Mn^{++} ions) are randomly distributed in the host matrix, have been extensively investigated, due to dramatic effects of the exchange interaction between the charge carriers and the localized spins on the physical properties.[1] In particular, the charge carrier in a bound state interacts with the neighboring localized spins to form a bound magnetic polaron (BMP), evidenced by a nonvanishing spin-flip energy in zero magnetic field[2] and an increase of the binding energy.[3] Adequate theoretical models have been proposed[4,5] to describe the bound magnetic polaron in SMSC's containing paramagnetic Mn^{++} ions.

Much interest has recently been attracted by SMSC's containing Fe^{++} ions incorporated in II-VI semiconductor matrices[6] such as $Zn_{1-x}Fe_xSe$, $Zn_{1-x}Fe_xTe$, or $Cd_{1-x}Fe_xSe$. The Fe^{++} ion possesses in these alloys a nonmagnetic ground state and exhibits Van Vleck paramagnetism. This fact, related to the presence of a nonvanishing orbital momentum in the $3d^6$ configuration of the Fe^{++} ion ($L=2$, $S=2$), allows us to expect new properties compared to SMSC's containing Mn^{++} ions ($3d^5$ configuration, $L=0$, $S=\frac{5}{2}$). In particular, Heiman *et al.*[7] conclude that the BMP does not exist in $Cd_{1-x}Fe_xSe$, on the basis of a Raman scattering study showing that the spin-flip energy vanishes in the zero-field limit.

In this Letter, we address the question of the existence of the BMP in SMSC's containing Van Vleck ions, such as Fe^{++}. The two fundamental features of the BMP are a lowering ΔE_p of its ground-state energy due to carrier-ion exchange and nonvanishing local spin polarization $\langle S^x\rangle$. We show that the Raman scattering results of Ref. 7 are not in contradiction with either of these features. One particularity of the Fe^{++} ion is the nondegeneracy of its ground state. As a consequence, a system of N ions and a conduction electron has a doubly degenerate (electron spin) ground state. This Kramers degeneracy cannot be lifted by exchange alone; hence the spin-flip energy is strictly equal to zero at zero magnetic field. This does not, however, prevent the existence of the BMP. The exchange coupling between the donor electron and the Fe^{++} ions generates a spin polarization of these ions. However, it is not possible to flip the electron spin independently from the Fe^{++} spin polarization (which results from a quantum-mechanical mixing), contrary to the case of Mn^{++}-based BMP (where the polarization results from a statistical average over preexisting moments). The exchange also causes an energy shift which could hardly be seen directly in a Raman experiment for two reasons: It is approximately the same for the ground state and for the low-lying excited states (the partners for the Raman transition) and furthermore, it is small (reduced by an energy denominator).

We shall see that it is possible to increase dramatically the effect of this interaction by bringing the interacting levels closer together with the help of a magnetic field. It is then possible to measure this coupling in a Raman scattering experiment by the observation of the anticrossing of two Raman transitions, namely electron spin flip and Fe^{++}-ion exchange. It is the purpose of the present work to report the observation of such an anticrossing in $Cd_{1-x}Fe_xSe$ from which we infer the existence of the BMP. The two parameters ΔE_p and $\langle S^x\rangle$ which define the BMP are also estimated.

The experiments were performed on monocrystals of $Cd_{1-x}Fe_xSe$ grown by a modified Bridgman method with Fe concentration $x=0.018$ and $x=0.034$ checked by microprobe analysis. Fluctuations of the composition do not exceed 5% of the mean value. The samples were immersed in superfluid helium and the Raman scattering was studied in the backscattering configuration on a cleaved face containing the c axis, using about 10 mW of dye-laser light resonant on the bound exciton.[8] The magnetic field was applied perpendicularly to the c axis along the direction of light propagation (the field also causes some tuning of the resonance).

Figure 1 shows the Raman spectra for the resonance on the bound exciton without magnetic field and for magnetic fields in the region of the anticrossing between

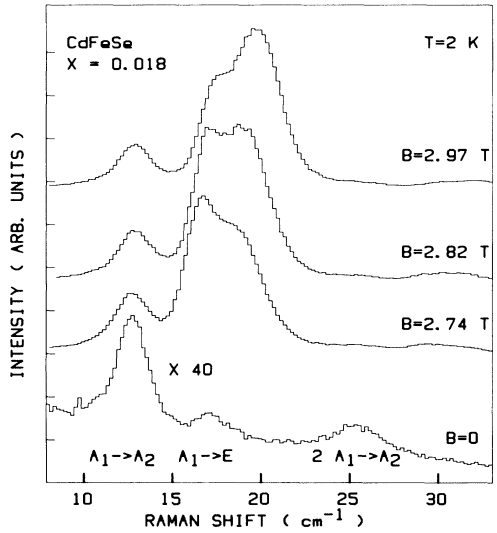

FIG. 1. Examples of Raman spectra of $Cd_{0.982}Fe_{0.018}Se$ at 2 K and magnetic field indicated ($\mathbf{B}\perp\mathbf{c}$). Laser wave number was 14840 cm^{-1}. Relative intensities change because of the mixing of wave functions of the transition final states.

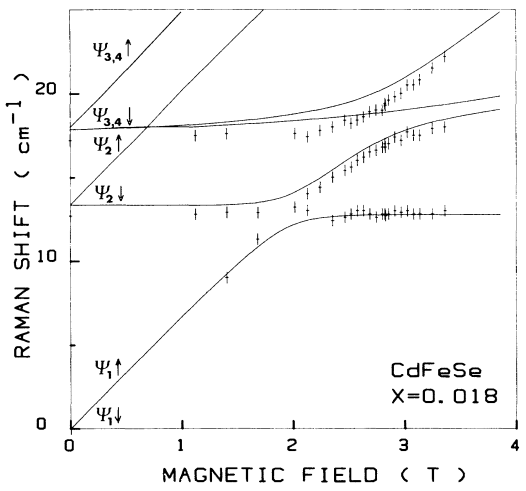

FIG. 2. Calculated (solid lines) and experimental (crosses) values of Raman shifts in $Cd_{0.982}Fe_{0.018}Se$ vs magnetic field $\mathbf{B}\perp\mathbf{c}$. The lowest line originating from the E level couples weakly to the spin-flip line and is not observed in the experiment.

the spin-flip (SF) line and the $A_1 \rightarrow E$ line. The three lines observed in zero magnetic field correspond, respectively, to $A_1 \rightarrow A_2$ (13 cm^{-1}), $A_1 \rightarrow E$ (17.6 cm^{-1}), and two $A_1 \rightarrow A_2$ (26 cm^{-1}) intra-Fe^{++}-ion transitions, A_1 being the ground state of the Fe^{++} ion. However, it has been shown[8] that, for small x, the $A_1 \rightarrow E$ transition is not resonant on the type-A exciton and should not be observed in these resonant conditions. Presumably the Fe-Fe interaction makes the $A_1 \rightarrow E$ transition Raman active; in addition, selection rules can be changed under the action of a transverse magnetic field B. The Raman spectra with applied magnetic fields in Fig. 1 clearly evidence the existence of the anticrossing effect. The distance between the two components, estimated by comparison of the experimental line shape with two overlapping Gaussians, is 2.2 ± 0.2 cm^{-1}. The resulting positions of the levels as a function of B are compared with theory in Fig. 2.

On the other hand, for the free-exciton resonance, the variation of the $A_1 \rightarrow E$ energy versus B does not show any anomaly, which demonstrates that the $A_1 \rightarrow E$ line observed in these conditions originates from Fe^{++} ions situated mainly outside the neutral donors. The model also predicts an anticrossing between the SF line and the $A_1 \rightarrow A_2$ line for $\mathbf{B}\perp\mathbf{c}$ but smaller than the previous one (see below). Our results are not in disagreement with this theoretical prediction since a broadening of the SF line is observed at the crossing point. From this broadening, the estimate of the coupling energy is 1.2 ± 0.2 cm^{-1} (however, the splitting is too small compared to the linewidth to resolve the two components).

A similar anticrossing has been observed for an $x = 0.034$ sample. In this case, however, the large width of the Raman lines did not allow us to measure precisely the coupling energy.

For the theoretical model, we consider an electron of spin s localized at a donor site (hydrogenic envelope wave function Ψ_e) interacting with Fe^{++} ions of spins S_i which occupy cation sites R_i in the wurtzite lattice of CdSe. States of Fe^{++} in CdSe have been calculated in Ref. 9; in this work, we use an independent calculation.[10] We start from iron-ion wave functions $\phi_j(i)$ at site R_i in a magnetic field ($j = 1, \ldots, 25$) and treat in perturbation the electron-Fe^{++} exchange, assumed to be of the Heisenberg form:

$$H = -\alpha \sum_i |\Psi_e(R_i)|^2 \mathbf{S}_i \cdot \mathbf{s} = \sum_i c_i h_i , \qquad (1)$$

where α is the conduction-electron–Fe^{++}-ion exchange integral,

$$c_i = -\alpha |\Psi_e(R_i)|^2 \text{ and } h_i = \mathbf{S}_i \cdot \mathbf{s} .$$

The doubly degenerate ground state of the unperturbed system will be $\Psi_{1\sigma} = \Psi_1 \chi_\sigma$, where $\Psi_1 = \prod_i \phi_1(i)$ describes all the ions in their ground state ϕ_1 and $\sigma = \uparrow$ or $\downarrow$ indicates the electron-spin eigenstates of the spinor χ_σ. Note that the quantization axis for the electron spin is along the magnetic field, defined as the x axis, perpendicular to the c axis which corresponds to the z axis in the reference system used to make explicit the wave functions ϕ_j. According to Eq. (1),

$$H|\Psi_{1\sigma}\rangle = \sum_{j\sigma'} \langle \phi_j(i)\chi_{\sigma'}| h_i |\phi_1(i)\chi_\sigma\rangle \sum_i c_i |\Psi_{1\sigma'}\phi_j(i)/\phi_1(i)\rangle . \qquad (2)$$

Note that the bra-ket in Eq. (2) does not depend on i. To first order, the only normalized excited states (involving one Fe^{++} ion in the jth excited state) coupled to the ground state by the exchange H are thus

$$\Psi_{j\sigma}=\left(\sum_n c_n^2\right)^{-1/2}\sum_i c_i\Psi_{1\sigma}\phi_j(i)/\phi_1(i)\,.$$

In the same way, the excited states coupled to $\Psi_{j\sigma}$ to second-order approximation can be derived from the expansion of $H\,|\,\Psi_{j\sigma}\rangle$. This expansion involves new excited states:

$$\Psi_{jk\sigma}=\sum_{i\neq g}G_{ig}\Psi_{1\sigma}\phi_j(i)\phi_k(g)/\phi_1(i)\phi_1(g)\,,$$

where

$$G_{ig}=c_ic_g\left(\sum_{n\neq m}c_n^2c_m^2\right)^{-1/2},\quad \text{for } j\neq k\,,$$

or

$$G_{ig}=\tfrac{1}{2}c_ic_g\left(\sum_{n>m}c_n^2c_m^2\right)^{-1/2},\quad \text{for } j=k\,.$$

It also involves some one-ion excited states orthogonal to the $\Psi_{j\sigma}$'s, which we neglect due to their weak coupling with the states we have made explicit above.

To first-order perturbation, the diagonal matrix elements for the ground state will be

$$\langle\Psi_1\uparrow\,|\,H\,|\,\Psi_1\uparrow\rangle=\tfrac{1}{2}E_{SF}=-\tfrac{1}{2}N_0x\alpha\langle\phi_1\,|\,S^x\,|\,\phi_1\rangle$$
$$=-\langle\Psi_1\downarrow\,|\,H\,|\,\Psi_1\downarrow\rangle\,,\qquad(3)$$

where N_0 is the number of unit cells per unit volume and E_{SF} is the spin-flip energy. Equation (3) holds to a good approximation also for the excited states. In the low-field limit, the energy of Eq. (3) is proportional to the magnetic field (see Fig. 2), which corresponds to the fact that $\langle S^x\rangle\propto B$. It is thus natural to define an effective electron g factor, temperature independent within our approximation, equal to $g_{\rm eff}^{\perp}=N_0x\alpha\langle S^x\rangle/\mu_BB$. Equation (3) takes the form of the usual mean-field expression as in the canonical SMSC's with magnetic ions such as Mn^{++}. However, for Mn^{++} ions, $\langle S^x\rangle$ is a thermal average and thus depends on temperature. For Fe^{++}, $\langle S^x\rangle$ denotes a simple expectation value for the ion ground state. A second difference lies in the fact that for an Mn^{++} ion ($L=0$), $\langle S^x\rangle$ is the magnetization. Because of the presence of the orbital momentum of the Fe^{++} ion, the total magnetization of $Cd_{1-x}Fe_xSe$ will be greater by a factor λ than its part originating from the spin. This factor has been estimated by Twardowski[11] as $\lambda=1.115$ for cubic $Zn_{1-x}Fe_xSe$. Using wave functions calculated in Ref. 10 we find $\lambda=1.125$, in reasonable agreement with Ref. 11. In the numerical calculation that follows, we neglect the presence of the orbital momentum. Note that to first-order approximation, the deformation of the local spin polarization in the vicinity of the electron is not taken into account. The magnetic polaron effect comes from the second-order terms.

The second-order correction comes from the off-diagonal matrix elements which are much smaller than the diagonal ones,

$$\langle\Psi_{1\sigma}\,|\,H\,|\,\Psi_{j\sigma'}\rangle=\left(\sum_n c_n^2\right)^{1/2}\langle\phi_{1\sigma}\,|\,h\,|\,\phi_{j\sigma'}\rangle$$
$$=\frac{N_0\alpha x}{N^{1/2}}\langle\phi_{1\sigma}\,|\,h\,|\,\phi_{j\sigma'}\rangle\,,$$

since they are reduced by the square root of the number N of Fe^{++} ions contained in a volume of $8\pi a^3$, where a is the effective Bohr radius. This number sets the scale for an equivalence between this model and that of a muffin-tin wave function; under the approximations we make here the two models are equivalent. The elements of the type $\langle\Psi_{1\sigma}\,|\,H\,|\,\Psi_{j\sigma'}\rangle$ and $\langle\Psi_{j\sigma}\,|\,H\,|\,\Psi_{jk\sigma'}\rangle$ are of comparable magnitude, whereas elements $\langle\Psi_{j\sigma}\,|\,H\,|\,\Psi_{k\sigma'}\rangle$, being much smaller, have been neglected. Higher-order Fe^{++} excitations have been also neglected. In an explicit calculation we find that the exchange shift without magnetic field is, to a good approximation, the same for the ground state Ψ_1 as for the excited states Ψ_j (since N is large enough).

This shift, which is a fundamental magnetic-polaron feature, is equal to

$$\Delta E_p=-\sum_{j\neq1,\sigma'}|\langle\Psi_{1\sigma}\,|\,H\,|\,\Psi_{j\sigma'}\rangle|^2/(E_j-E_1)\,.$$

It disappears in the limit of an infinitely extended wave function (in contrast with the mean-field diagonal term).

The second fundamental feature of the magnetic polaron, a nonvanishing local Fe spin polarization without magnetic field, can be calculated as the expectation value of the S^x operator as a function of the distance from the polaron center. For this calculation we apply an infinitesimal magnetic field B; i.e., we take the limit $B\to0$ and $T\to0$ while B/T remains constant and large enough to obtain full electron-spin polarization. A straightforward calculation yields for $\mathbf{B}\perp\mathbf{c}$

$$\langle S^x\rangle(r)=\alpha\,|\,\Psi(r)\,|^2\sum_j|\langle\phi_1\,|\,S^x\,|\,\phi_j\rangle|^2/(E_j-E_1)\,,$$

which at the center of the polaron ($r=0$) gives $\langle S^x\rangle=0.06$. It is interesting to note that the obtained value of $\langle S^x\rangle$ depends on the direction of the infinitesimal magnetic field (reflecting the magnetic anisotropy of the material), while ΔE_p does not.

Results of a simplified numerical calculation, involving the six lowest Fe^{++} states and neglecting two-excitation states are shown in Fig. 2. Anticrossing can be observed between $\Psi_1\uparrow$ and $\Psi_2\downarrow$ and between $\Psi_1\uparrow$ and $\Psi_4\downarrow$ states. The splitting at the crossing points is a measure of the off-diagonal matrix elements. The experimental results, also shown in Fig. 2, are in a reasonable agreement with the calculated curves. We used the following parameter values: $x=0.018$ from a microprobe measurement, $N_0\alpha=0.25$ eV (the value of Ref. 7 multiplied by the coefficient λ to take into account the ratio between the

magnetization and $\langle S^x \rangle$), and $a = 39$ Å, using the data of Ref. 12. Note that no adjustable parameters have been used. The main discrepancy (theoretical levels issuing from A_2 and E higher than the experimental points) comes from the neglect of two-excitation states $\Psi_{jk\sigma}$.

When limiting ourselves to a single pair of interacting states, for example, $\Psi_1\uparrow$ and $\Psi_4\downarrow$ (transitions from the ground state $\Psi_1\downarrow$), we obtain an approximate analytic result for the Raman shift E_R:

$$E_R = \frac{E_{14}+E_{SF}}{2} \pm \left[\left(\frac{E_{14}-E_{SF}}{2} - \frac{V_0^2}{E_{14}} \right)^2 + V^2 \right]^{1/2},$$

where $E_{14} = E_4 - E_1$ and the off-diagonal matrix element V consists of the following two parts: the zero-field part V_0, which contributes to the polaron shift of the ground-state energy without a magnetic field (about $\frac{2}{3}$ of the total value) and the field-dependent part V_1 (a second-order term coming mainly from the Ψ_2 state). For the anticrossing between $\Psi_1\uparrow$ and $\Psi_2\downarrow$ states, $V_0 = 0$; hence the whole effect comes from the field-dependent part V_1, which explains why it is small.

Using the parameters described above, we find $g_{\text{eff}}^{\perp} = 14.5$. For the polaron shift of the zero-field ground state, we find $\Delta E_p = -0.26\ \text{cm}^{-1}$, and for the local spin polarization at the center of the polaron ($r = 0$), $\langle S^x \rangle = 0.06$. Note that these values of ΔE_p and $\langle S^x \rangle$ are relevant at $T = 2$ K, though $\Delta E_p < kT$, since the first excited state of the BMP is near 13 cm^{-1}.

In conclusion, the observed anticrossing of the Fe^{++} levels with donor spin-flip excitation under the application of a magnetic field proves the existence of a Van Vleck BMP, induced by off-diagonal exchange matrix elements. This new type of BMP is thus a quantum effect. This is in contrast with usual BMP's in Mn-based SMSC where thermodynamical aspects are crucial. In particular, at $B = 0$, it is in a pure quantum state at low temperature where only the doublet ground state is populated. One outstanding manifestation of the quantum nature of the BMP in Van Vleck SMSC is that, at $B = 0$, the spin-flip energy of the BMP electron is strictly zero, a feature which has no classical analog and is beyond the scope of previous models: It illustrates that the exchange interaction and the BMP effect cannot be treated in terms of an effective molecular field.

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