Nonmagnetic Ground State of Fe^{2+} in CdSe: Absence of Bound Magnetic Polaron

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Donor electrons in (Cd,Fe)Se show no bound magnetic polaron effects in the spin-flip light-scattering spectra, that are usually observed in manganese-based materials. The absence of thermal magnetic fluctuations demonstrates that the ground state of the Fe^{2+} ion has *no permanent magnetic moment*—a feature of Van Vleck ions. The spin-flip linewidth is accounted for by consideration of compositional alloy fluctuations. A sizable magnetic anisotropy produces a similar optical anisotropy.

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Dilute magnetic semiconductors (DMS) containing ions with permanent magnetic moments, such as in (Cd,Mn)Te, have been widely studied and are reasonably well understood.[1,2] On the other hand, DMS with magnetic ions possessing only *field-induced moments* in the ground state (e.g., Fe^{2+}) have been studied only recently.[3-7] The latter class of DMS are expected to produce totally new effects. One characteristic signature of the magnetically inactive singlet ground state of the Fe^{2+} is Van Vleck paramagnetism—a temperature-independent susceptibility at low temperatures. Such a behavior was observed well below 10 K in (Zn,Fe)Se,[4,7] (Hg,Fe)Se,[5] and (Cd,Fe)Se.[5,6] In this Letter we show a novel manifestation of the singlet ground state of Fe^{2+} in the spin-flip Raman-scattering (SFRS) spectrum of donor electrons in (Cd,Fe)Se. These effects, which probe the magnetism on a microscopic scale of $\simeq 40$ Å, are more striking than the observed weak temperature dependence of the macroscopic susceptibility at low T, since the latter can also be produced by strong antiferromagnetic interactions.

The s-d exchange interaction in DMS, between semiconductor carriers and magnetic ions, causes the SFRS from donor electrons to have unique features not found in nonmagnetic semiconductors. Among these are large Zeeman splitting and linewidth, and a sizable splitting even at zero applied magnetic field B. It has been established, both experimentally[8-12] and theoretically,[9,13-15] that the Zeeman splitting of the donor electron at low temperatures is proportional to the instantaneous value of magnetization within the donor orbit, $\mathbf{M}_{\text{Local}}$. The complex consisting of the donor electron and the spins of the magnetic ions within its orbit is known as a bound magnetic polaron (BMP).

Some of the unusual properties of donor BMP are attributed to large fluctuations in $\mathbf{M}_{\text{Local}}$. For ions with permanent moments there are two types of fluctuations: (1) variations of $\mathbf{M}_{\text{Local}}$ with time, due to *stochastic thermal fluctuations* of the net spin within the orbit of a given donor and (2) variations from donor to donor, due to *compositional alloy fluctuations* in the number of spins within the donor's orbit.[9,13-15] The stochastic fluctuations are most important at zero and low fields. Specifically, they give rise to a nonzero average magnitude $\langle |\mathbf{M}_{\text{Local}}| \rangle$ at $B=0$, which results in a finite SFRS energy at $B=0$. They are also the dominant cause of the SFRS linewidth at zero and low B. The compositional fluctuations, on the other hand, are the dominant cause of the linewidth at high fields.

Novel features are expected when the magnetic ions possess no permanent moment, but only field-induced moments. First, since $\mathbf{M}_{\text{Local}}=0$ at $B=0$ there should be no splitting (no linewidth) at zero field. Second, the linewidth should be predominantly due to compositional fluctuations. The primary aim of this Letter is to contrast these unique features of (Cd,Fe)Se SFRS with that of (Cd,Mn)Se. The first observations of SFRS in (Cd,Fe)Se were made by Suh *et al.*, but they did not address these features.[16]

Van Vleck paramagnetism arises when the local environment of a magnetic ion produces a magnetically inactive singlet ground state. In a tetrahedrally bonded crystal the $Fe^{2+}(3d^6)$ free-ion energy levels are split by crystal-field and spin-orbit coupling.[7,17] The lowest levels have separations on the order of a few millielectronvolts, so that at liquid-helium temperatures only the ground state is significantly populated. It is a singlet with no permanent magnetic moment. In an applied magnetic field **B** the ground state develops a moment due to an admixture of wave functions from excited states. The induced magnetic moment of the ground state along the **B** direction, in second-order perturbation theory, is[18]

$$\mu_0=\sum_n 4|\mu_{0n}|^2 B/(E_n-E_0), \qquad (1)$$

where μ_{0n} is a matrix element of the magnetic-moment operator between the ground state and the nth level. Most of the admixture comes from the lowest levels because of the energy denominator. In the wurtzite structure these levels are further split by the trigonal crystal field. This results in a variation of the susceptibility with field direction (magnetic anisotropy).

Spin-flip light scattering from donor electrons was measured from samples of $Cd_{1-x}Fe_xSe$ with $x=0.006$ and 0.04, grown by the Bridgman method. The x values were determined from the energy of the exciton photoluminescence with use of $E(x)=1820.8+1480x$ meV, from Ref. 3 and our own measurements. Sample cooling was provided by immersion in the liquid and the cw laser intensity was kept below 1 W/cm^2. Scattered light was collected with $f/6$ optics and analyzed with a 0.85-m double-grating spectrometer.

Figure 1 displays spin-flip Raman spectra as a function of B for (Cd,Fe)Se, and a comparable Mn-based material. They show remarkable differences—the Mn alloy has a sizable shift at $B=0$ and a 10 times larger linewidth; both are features of BMP fluctuations. Figure 2 exhibits the positions of the spectral peaks, ΔE, for both materials plotted as a function of magnetization M. (We use M instead of B to account for the differences in susceptibility, 0.50 emu/g-T for Fe and 2.0 emu/g-T for Mn.) In (Cd,Fe)Se the energy shift of the spin-flip line varies linearly with B (and M) and extrapolates to zero, whereas in (Cd,Mn)Se there is a large energy shift as $B\rightarrow 0$. The additional low-field splitting associated with Mn^{2+} ions has also been observed in (Cd,Mn)S[12,19] and (Zn,Mn)Se.[20] We attribute the negligible low-field splitting in the Fe-based material to lack of a permanent moment in the ground state of the Fe^{2+} ion. This difference is shown schematically in Fig. 1. The moments of the Fe^{2+} ions grow with increasing field, while the larger moments of the Mn^{2+} ions gradually align to increase their z component, but with a large component *not* parallel to **B**. Because the ion moments are large, significant alignment occurs when the magnetic energy becomes comparable to the thermal energy, i.e., $5\mu_B B \sim k_B T$. As a result, the slope of ΔE vs B for the Mn material varies considerably with temperature.[8-10] In contast, the Fe material showed no variation between $T=1.7$ and 4.2 K—a characteristic of Van Vleck paramagnetism. An alternative interpretation of the linear-B behavior and small linewidths in (Cd,Fe)Se might be attributed to delocalization of donor electrons, as observed in heavily doped (Cd,Mn)S.[12] However,

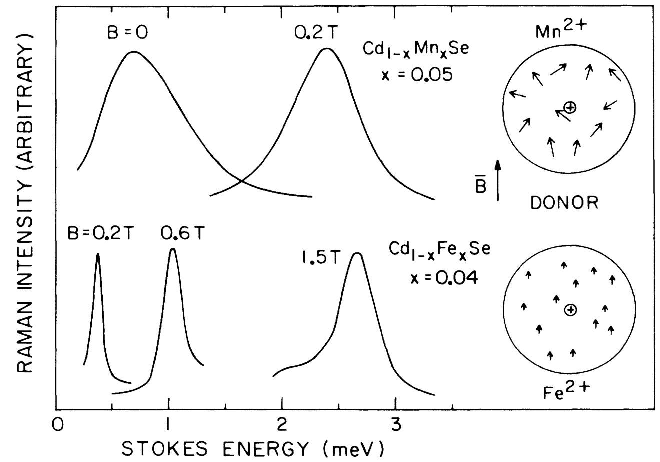

FIG. 1. Spin-flip Raman spectra of Fe- and Mn-doped CdSe for various magnetic fields B at temperature $T=1.9$ K and laser energy 1832 meV. On the right-hand side is an illustration of the spins within the hydrogenic donor orbit at low fields.

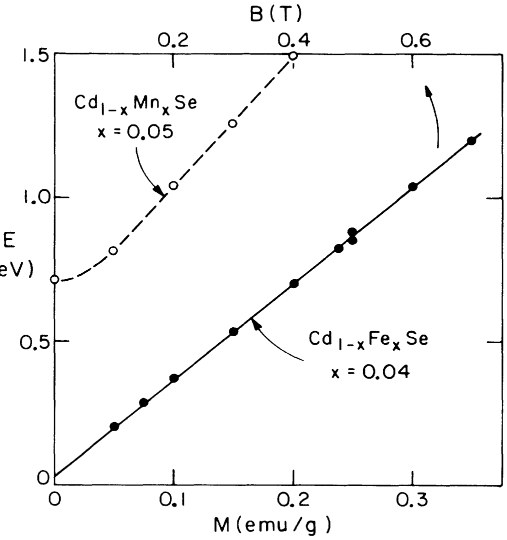

FIG. 2. Energy of the spin-flip Raman peak ΔE as a function of magnetization M for donor electrons in Fe-doped (filled circles) and Mn-doped (open circles) CdSe at temperature $T=1.9$ K. The larger ΔE for the Mn alloy results from the finite, instantaneous total moment of Mn ions within the donor BMP. The lines were drawn to aid the eye. The magnetic field scale B is for the Fe material only, and should be divided by 4 for the Mn material.

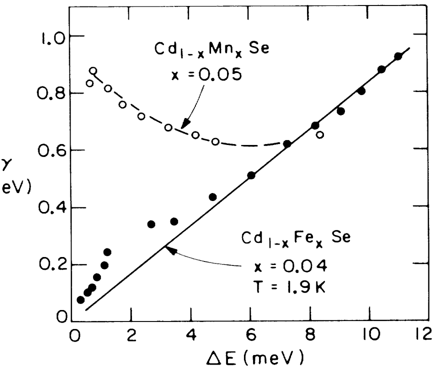

FIG. 3. Full width at half-maximum height γ vs peak energy ΔE for the spin-flip Raman spectra in Fe-doped (filled circles) and Mn-doped (open circles) CdSe at temperature $T=1.9$ K. The solid line represents compositional alloy fluctuations, due to variations in the number of magnetic ions from donor to donor, given by Eq. (2). The dashed line is drawn for aesthetic reasons. The instrumental resolution, less than $\frac{1}{3}$ of the linewidth, has been subtracted in quadrature.

delocalization is not occurring in the present case, as discussed below.

The full width at half-maximum height, γ, of the Gaussian-like spectral profile is plotted as a function of ΔE in Fig. 3. Again there is a large constrast between the two materials at low ΔE (small B). The Mn compound has a large γ, as a result of stochastic magnetic fluctuations in the local moment within the donor, determined by the root mean square fluctuation of $|\mathbf{M}_{\text{Local}}|$ about its mean value. The linewidth of the Fe alloy is an order of magnitude smaller at low ΔE. This remarkable difference is further evidence that the ground state of the Fe^{2+} ion does not have a permanent moment.

In the Fe alloy γ is linear in ΔE, with γ varying by an order of magnitude, from 0.07 to 0.92 meV. This dependence arises from compositional alloy fluctuations —*there is a different number of Fe^{2+} ions within each donor*, so that $\langle|\mathbf{M}_{\text{Local}}|\rangle$ varies from donor to donor. If N is the average effective number of magnetically active Fe^{2+} ions within the hydrogenic donor orbit, then a normal distribution of fluctuations about N leads to fluctuations in $\langle|\mathbf{M}_{\text{Local}}|\rangle$ and hence to the observed Gaussian spectrum. The linewidth is[21]

$$\gamma=\left[\frac{8\ln 2}{N}\right]^{1/2}\frac{\partial\bar{x}}{\partial x}\frac{x}{\bar{x}}\Delta E, \tag{2}$$

where $\bar{x}$ is the effective x value.[9,22] For $x=0.04$, the concentration of magnetic ions which contribute to $\langle|\mathbf{M}_{\text{Local}}|\rangle$ is $\bar{x}=0.026$ and $\partial\bar{x}/\partial x=0.35$.[4,22] We then match the measured slope $\gamma/\Delta E=0.092$ in Fig. 3, using $N=200$. Thus it is clear that the electrons giving rise to the observed spin-flip scattering are well localized in donor orbits.

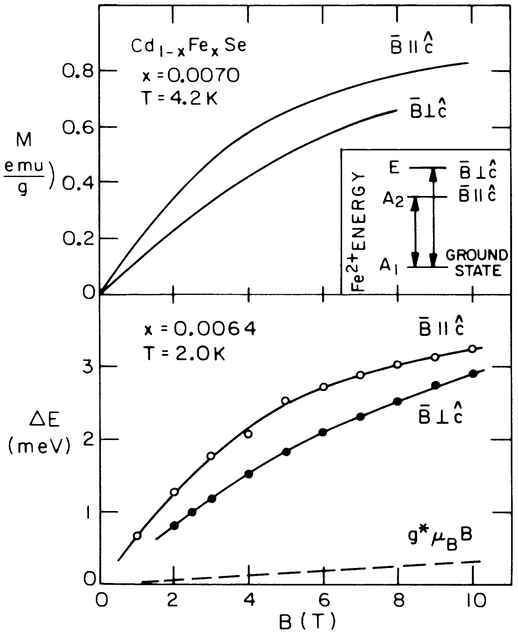

FIG. 4. Anisotropy in magnetization M and spin-flip Raman shift ΔE vs applied magnetic field B for (Cd,Fe)Se. Measurements revealed almost no temperature dependence below $T=4.2$ K. Solid lines were drawn through the optical data for clarity. The dashed line shows the background Zeeman splitting for pure CdSe. Inset: The three lowest energy levels for the Fe^{2+} ions, where A and E denote singlet and doublet states having the admixture selection rules indicated by arrows.

Magnetic anisotropy in (Cd,Fe)Se was discovered in the optical spin splittings and the magnetization, displayed in Fig. 4. No anisotropy has been observed in Mn-based materials. Both ΔE and M are largest when $\mathbf{B}$ is applied parallel to the hexagonal c axis. The largest percentage difference occurs at low field where the susceptibility ratio is $\chi_\perp/\chi_\parallel=0.6$. The anisotropy arises from the additional axial crystal-field splitting of the triply degenerate first excited state of the Fe^{2+} ion in the wurtzite structure. The inset shows the A_1 singlet ground state, and the A_2 singlet and E doubly degenerate excited states. Although these levels have been identified in wurtzite crystals in Ref. 7, no anisotropy was reported for (Cd,Fe)Se. The reason is that the crystals used in Ref. 7 were cubic (zinc blende), whereas the Bridgman-grown crystals in the present work had the wurtzite structure. When $\mathbf{B}$ is parallel to the c axis, selection rules allow mixing of the A_2 level with the A_1 ground state, and the smaller energy denominator of Eq. (1) gives a larger induced moment.[7] Eventually at very high fields, the field-dependent shifts of the energy levels become larger than their splittings, and the anisotropy decreases.

The shift ΔE was found to be proportional to M in (Cd,Fe)Se, through the s-d exchange energy αN_0. To extract the magnitude of αN_0 we used the assumption of

Ref. 4, that the s-d interaction has the same form as for Mn-based materials. This gives $\alpha N_0=(2\mu_B A/W)(\Delta E - g^*\mu_B B)/M$, where M is moment per gram, μ_B the Bohr magneton, A Avogadro's number, W the molecular weight, and $|g^*|=0.54$ from our measurement on pure CdSe. We find $\alpha N_0=225\pm 5$ meV, independent of the field direction and x value between $x=0.006$ and 0.04 . This is somewhat smaller than 260 meV obtained in (Cd,Mn)Se.[23]

It is remarkable that the fluctuation effects observed here for weakly localized electrons are even more pronounced for strongly localized holes. This work can naturally be extended to hole localization in acceptors and excitons. The absence of fluctuations in Fe-based materials should have a significant influence on acceptor-BMP, exciton-BMP formation, and spin-polarized optical pumping.

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