Electric-Dipole Spin Resonance of Bound Electronic States in $\mathrm{Cd}_{1-x}\mathrm{Mn}_x$ Se

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(Received 24 June 1982)

The observation of strong electric-dipole spin resonance of donor electrons in $\mathrm{Cd}_{1-x}\mathrm{Mn}_x\mathrm{Se}$ in far-infrared magnetotransmission experiments is reported. The resonance is shown to be allowed through corrections to the effective-mass Hamiltonian due to the uniaxial and acentric crystal structure, and constitutes a powerful new tool for the study of diluted magnetic semiconductors with uniaxial symmetry.

PACS numbers: 78.20.Ls, 75.20.Ck, 75.30.Et, 78.50.Ge

We report the first observation of the electric-dipole spin-resonance (EDSR) transition of donors in $\mathrm{Cd}_{1-x}\mathrm{Mn}_x\mathrm{Se}$ in far-infrared magnetotransmission experiments. There are two reasons why this spin-flip transition is of interest. First, $\mathrm{Cd}_{1-x}\mathrm{Mn}_x\mathrm{Se}$ is a diluted magnetic semiconductor in which the Zeeman splitting of the 1s donor level is dramatically enhanced by the exchange interaction between the localized magnetic moments (in this case Mn^{++}) and band electrons.[1] This Zeeman splitting can be described by an effective g factor which, besides being extremely large, is temperature and magnetic field dependent, as has been demonstrated by spin-flip Raman scattering experiments in $\mathrm{Cd}_{1-x}\mathrm{Mn}_x\mathrm{Se}$ reported by Nawrocki *et al.*[2] The Raman work has also shown that in this material the Zeeman splitting of donor states does not vanish at zero magnetic field because of the existence of the bound magnetic polaron.

Secondly, direct (one-photon) transitions between two spin states of the 1s ground level of the donor are normally forbidden by electric-dipole selection rules.[3] However, in pyroelectric crystals (uniaxial crystals without inversion symmetry such as CdS, CdSe, or $\mathrm{Cd}_{1-x}\mathrm{Mn}_x\mathrm{Se}$) in the presence of spin-orbit interaction, electron states are described by a Hamiltonian which contains a term[4]

$$H' = \lambda[\hat{c}\cdot(\vec{s}\times\vec{k})], \tag{1}$$

where $\hat{c}$ is the unit vector along the c axis, $\vec{s}$ and $\vec{k}$ are the spin and momentum operator of the electron, respectively, and λ is a constant. This term, regarded as a perturbation, mixes states of different orbital angular momentum with respect to the $\hat{c}$ axis, but conserves total (orbital plus spin) angular momentum about that axis. Thus, the perturbed conduction-band states in such acentric uniaxial crystals contain a mixture of up and down spin, thereby permitting EDSR transitions. The resulting absorption provides a direct means of determining λ.

In discussing EDSR for $\mathrm{Cd}_{1-x}\mathrm{Mn}_x\mathrm{Se}$, we will assume that the electrons in question are bound in donor states. We calculate ground-state wave functions by using first-order perturbation theory, with H' of Eq. (1) as the perturbing Hamiltonian. It is convenient to perform the calculation for two distinct geometries, $\vec{B}\perp\hat{c}$ and $\vec{B}\parallel\hat{c}$, where $\vec{B}$ is the dc magnetic field. For example, for $\vec{B}\perp\hat{c}$ (and $\vec{B}\parallel\hat{z}$ and $\hat{c}\parallel\hat{x}$), perturbation theory gives the first-order wave functions of $1s\uparrow$ and $1s\downarrow$ states in the form

$$\Psi_{1s\uparrow} \cong \left(1+\frac{i\lambda m^*}{2\hbar^2}y\right)|1s\uparrow\rangle + \frac{\lambda m^*}{2\hbar^2}\frac{\Delta E}{\Delta E-\hbar\omega_s}z|1s\downarrow\rangle, \tag{2}$$

$$\Psi_{1s\downarrow} \cong \left(1-\frac{i\lambda m^*}{2\hbar^2}y\right)|1s\downarrow\rangle - \frac{\lambda m^*}{2\hbar^2}\frac{\Delta E}{\Delta E+\hbar\omega_s}z|1s\uparrow\rangle, \tag{3}$$

where $|1s\rangle$ is the unperturbed donor ground state and $\hbar\omega_s$ is the spin-flip energy. The sum over states for the perturbed wave functions has been reduced to the above form (exact at $B=0$) by using the relation between the momentum and position matrix elements. $\Delta E = E_x - E_{1s}$ is the excitation energy between the 1s ground state and the excited donor states of higher angular momentum. Equations (2) and (3) are also exact when ΔE is constant which is a reasonable approximation because all excited states lie rather close to each other compared to the 1s level. In this formulation we also assume that the spin splitting for all donor levels is approximately the same. The EDSR matrix element obtained with Eqs. (2) and

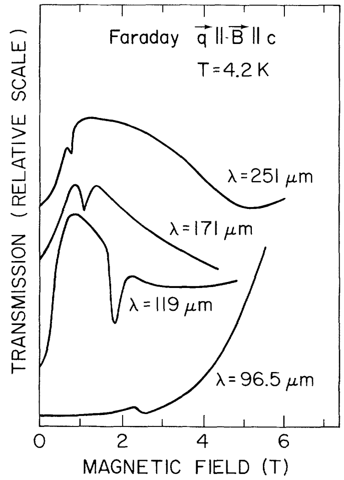

FIG. 1. Magnetotransmission of $Cd_{0.9}Mn_{0.1}Se$ in the Faraday geometry at 4 K for different frequencies.

(3) has the form

$$\langle\psi_{1s}|z|\psi_{1s\uparrow}\rangle \cong \frac{\lambda m^* a_0^{*2}}{\hbar^2}\,\frac{\Delta E\hbar\omega_s}{(\Delta E)^2-(\hbar\omega_s)^2}\,, \tag{4}$$

where a_0^* is the effective Bohr radius. The matrix element has only a z component, i.e., it is excited by the electric field component parallel to $\vec{B}$.

A similar calculation for $\vec{B}\parallel\hat{c}$ leads to an identical matrix element (except for $\sqrt{2}$), which now corresponds to excitation by one circular polarization (in the x-y plane) of the incident electric field. For the opposite circular polarization, and for the linear polarization $\vec{E}\parallel\vec{B}$, the EDSR matrix element vanishes.

Our experiments were performed on $Cd_{0.9}Mn_{0.1}$-Se crystals grown by the Bridgman method. Transport measurements on a specimen adjacent to those used in the far-ir experiments show the material to be n type, with an electron density of $1.4\times10^{16}/cm^3$ and a mobility of 1600 cm^2/V s at 77 K.[5] At 2 K the sample resistivity goes up to $\sim10^5$ Ω cm and shows a negative magnetoresistance[6] similar to that previously observed.[7]

Magnetotransmission spectra observed at 4.2 K for several discrete wavelengths are presented in Fig. 1, showing a single well-defined EDSR line superimposed on a slowly varying background. The background, which is not directly relevant to the EDSR, will be discussed elsewhere. The EDSR positions are in excellent agreement with the energies of the spin-flip Raman lines observed by Heiman[5] on samples from the same $Cd_{1-x}Mn_xSe$ ingot, and, like the Raman data, extrapolate to a finite energy at $B=0$, because of the existence of the bound magnetic polaron, as already established by Nawrocki *et al.*[2]

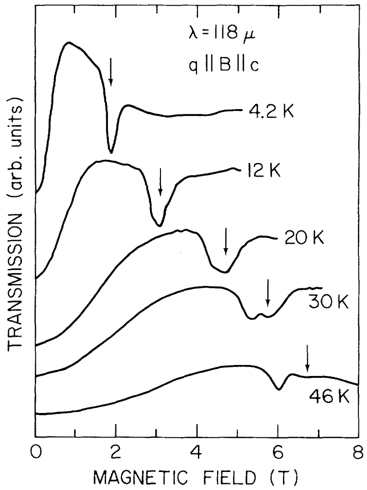

FIG. 2. Magnetotransmission of $Cd_{0.9}Mn_{0.1}Se$ in the Faraday configuration at different temperatures. The arrow marks the EDSR at low temperatures. At high temperatures ($T>10$ K), the line splits and the arrow marks the peak associated with the low-field EDSR by continuity.

Selection rules for EDSR were determined by transmission of polarized far-ir radiation in various configurations through oriented single-crystal slabs with the c axis either normal to the face or in the plane of the sample. The results obtained with linearly polarized far-ir radiation can be summarized in a single statement: The EDSR transition occurs only when

$$(\vec{E}\times\hat{c})\times\vec{B}\neq 0. \tag{5}$$

It is easy to show that Eq. (5) follows from the form of the Hamiltonian, Eq. (1). We also measured magnetotransmission of circular polarization in the Faraday geometry using samples cut with the c axis normal to the face. In this case EDSR is observed for the same sense of circular polarization that couples to cyclotron resonance of *electrons*, and not for the opposite sense. Thus the sign of the g factor for the conduction band of $Cd_{1-x}Mn_xSe$ is *positive*. This measurement also determines the sign of the exchange constant α which governs the exchange interaction in the Γ_6 conduction band in diluted magnetic semiconductors.[1]

A further important feature of EDSR in Cd_{1-x}-Mn_xSe is its temperature dependence, shown in Fig. 2. The Zeeman splitting can be described by an effective g factor which includes a term proportional to the magnetization of the paramagnetic sample through the s-d exchange interaction.[1,8] Consequently, the effective g factor is very large, e.g., 110 ± 2 at 4.2 K and 1.1 T, and it decreases rapidly as the temperature rises, as can be seen in Fig. 2. As this figure also shows, the EDSR splits into a doublet at high temperatures $T \gtrsim 10$ K. This splitting is seen at all frequencies at which the EDSR is observed and it corresponds to a new line appearing on the low-field side of EDSR for $\hbar\omega \gtrsim 9$ meV and on the high-field side for $\hbar\omega \lesssim 9$ meV. We believe that this new line represents optical processes which involve the exchange interaction between the donor electron and the Mn ions within its Bohr orbit. However, this high-temperature line is not completely understood at present.

The intensity of EDSR is seen in Fig. 1 to increase dramatically with frequency. In Fig. 3 we plot the frequency dependence of the absorption strength $\alpha\Gamma$, obtained from the data, where α is the peak absorption coefficient due to the EDSR and Γ is its full width at half maximum. To understand the dependence of $\alpha_{\rm EDSR}$ on frequency, we relate the absorption coefficient to the dipole matrix element in the standard manner through the imaginary part of the dielectric function $\epsilon''(\omega)$:

$$\alpha_{\rm EDSR} = \omega\epsilon''(\omega)/cn = (8\pi\omega N e^2/cn\hbar\Gamma)|x|^2 \qquad (6)$$

is the peak value, where N is the number density of electrons, n the refractive index, and $|x| = \langle\psi_{\kappa\uparrow}|x|\psi_{\kappa\downarrow}\rangle$ with κ the orbital quantum number.

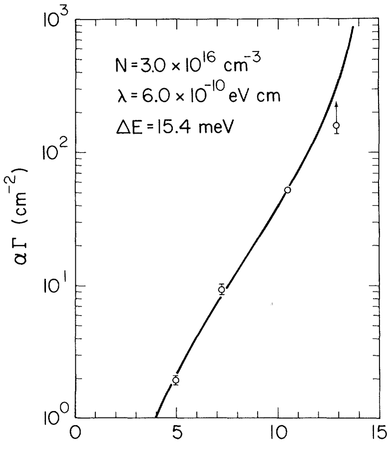

FIG. 3. Frequency dependence on the integrated absorption $\alpha\Gamma$ for the EDSR. Because of the distorted line shape at 96.5 μm only a lower limit to $\alpha\Gamma$ could be determined. The solid line is the theoretical curve [Eqs. (4) and (6)] with parameters determined by least-squares analysis.

We now compare the frequency dependence of EDSR of electrons in the donor ground state and in the conduction band. For the donor electrons, the EDSR intensity is given by Eq. (4). For electrons in the conduction band[9] the result is $|x| = \lambda/\hbar\omega_s(1-r)$, where $r = \omega_c/\omega_s$ and $\omega_c = eB/m^*c$ is the cyclotron frequency. The details of this calculation will be presented elsewhere.

Since for our experiments $\hbar\omega_c \ll \hbar\omega_s \lesssim \Delta E$, the frequency dependence predicted for the two cases is quite different. For conduction-band electrons $\alpha\Gamma$ depends on ω^{-1} whereas for donor electrons there is an ω^3 dependence and a resonant behavior ensuing from the denominator of $|x|$ which becomes appreciable when $\hbar\omega_s \sim \Delta E$. The data are in agreement with the donor model and they are sensitive to ΔE. A best fit gives $N\lambda^2 = 0.0106$ eV cm^{-2} and $\Delta E = 15.4$ meV which compares favorably with $E_{2p} - E_{1s} = \frac{3}{4}R^* \cong 15$ meV (R^* is the effective Rydberg constant) estimated from the band mass and dielectric constant in pure CdSe.[10] In the determination of λ the value of N, the number of occupied donors, is the largest uncertainty at this point. Estimation of N as the room-temperature Hall density (3×10^{16} cm^3) should be accurate to within a factor of 2. Therefore we find $\lambda = 6\times10^{-10}$ eV cm with an uncertainty of perhaps 30%. These results give strong evidence for the conclusion that the EDSR is occurring at donor sites. They also indicate that donor levels in $\mathrm{Cd}_{1-x}\mathrm{Mn}_x\mathrm{Se}$ do not differ significantly from those in CdSe. The solid line in Fig. 3 shows the absorption coefficient calculated with these parameters. The parameter λ is close to the value of 1.6×10^{-10} eV cm for CdS,[4] and is expected to be larger for CdSe because of the larger spin-orbit splitting in the latter.[4]

Note also in this context that the overall spectrum for 96.5 μm (12.9 meV) differs qualitatively from the data for longer wavelengths in Fig. 1. At 84 μm ($\hbar\omega = 14.7$ meV) the transmission is even smaller at low fields and remains near zero until 7 T, where it rises abruptly and increases continuously to our maximum field (10 T). We believe that the low-field transmission is so weak at 96.5 and 84 μm because we are on the tail of the $1s$-$2p$ absorption line, estimated earlier as 15.4 meV at $B = 0$. As the magnetic field is raised, however, the $2p$ energy levels become perturbed by the orbital Zeeman effect, so that the $1s \to 2p^+$ splitting increases while the $1s \to 2p^-$

splitting decreases, and the sample then should become more transparent (to one circular polarization) at high magnetic fields, as observed.

The donors in CdMnSe clearly provide a novel system for atomiclike spectroscopy. The spin splitting can be made as large as the Rydberg spacings for small magnetic fields ($\hbar\omega_c < R^*$) and the uniaxial acentric crystal symmetry, through H', couples these spin and orbital levels which can then resonantly interact. Studies on thinner samples or ones with lower donor concentrations, transparent to the shorter wavelengths, should display an exotic spectroscopy. But perhaps more importantly, these spectroscopic measurements provide a highly sensitive probe into the electronic structure of these interesting new magnetic and semiconducting materials.[1]

We wish to thank D. Heiman and J. R. Anderson for use of their transport results prior to publication, and to W. Giriat and H. Harrison for growing the excellent $Cd_{1-x}Mn_xSe$ crystal. This work was supported in part by the National Science Foundation through Grants No. DMR 80-25017 and No. DMR 79-23310 and by the U. S. Office of Naval Research through Contract No. N0014-81-0654. We also acknowledge the use of the Purdue Materials Research Laboratory Materials Preparation Facility and Laser Facility, supported by National Science Foundation Grant No. DMR 80-20249.

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