D^- Levels in $Cd_{1-x}Mn_xSe$

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The observation of cyclotron resonance in $Cd_{0.9}Mn_{0.1}Se$ implies the presence of free carriers at densities of $1.0\times10^{14}/cm^3$. Transport and far-infrared data are shown to be consistent with a model in which there are D^- levels in the sample under thermal-equilibrium conditions. It is argued that the D^- levels result from fluctuations in the conduction-band edge due to random Mn concentration fluctuations. An activated dc conductivity also supports the model.

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The semimagnetic semiconductor[1] $Cd_{1-x}Mn_xSe$ (CMS) has been found to display a negative magnetoresistance.[2] The sample resistance (transverse magnetoresistance) first rises slightly at low fields and then drops precipitously at fields above a few kilogauss (depending on the temperature). It has been suggested[3] that this behavior is associated with the so-called "bound magnetic polaron" observed in this material.[4] In this interpretation the exchange interaction between the donor electrons and the Mn ions which leads to spin polarization at $B=0$ and an increased donor binding energy would also produce a decrease in the hopping conductivity in the donor impurity band. In this paper we present far-infrared magneto-optical measurements on CMS which, together with the transport data, imply that there are free carriers in the high-field (low-resistance) range and only bound carriers in the low-field (high-resistance) region. We propose an interpretation of these results in terms of a small concentration of doubly occupied donors (D^- centers) in the crystal. Photogenerated D^- centers have recently been a subject of intense study in other semiconductor materials.[5] The novelty of the results presented here is that the D^- levels appear to exist under thermal-equilibrium conditions in CMS, and that they are ionized by application of a magnetic field as a result of the large exchange-induced Zeeman splitting in the material.

The sample is an n-type $Cd_{0.9}Mn_{0.1}Se$ single crystal grown at Purdue University, with a donor concentration, determined from the room-temperature Hall data, of 3×10^{16} cm^{-3}. A proton-induced x-ray-emission (PIXE) analysis of the sample indicates that the donors may arise from Ga impurities. The far-infrared experimental procedures were reported earlier.[6] In Fig. 1 we show the 4.2-K far-infrared magnetotransmission spectrum at 337 and 251 μm and the dc conductivity of the sample. In both experiments care was taken to prevent room radiation from reaching the sample. The sharp feature at 5.6 kG (7.7 kG) at 337 μm (251 μm) is an electric dipole spin resonance of electrons bound on donor sites, illustrating the large effective g factor ($g\sim110$) of these electrons.[6] The broad dips at 39 kG (53 kG)

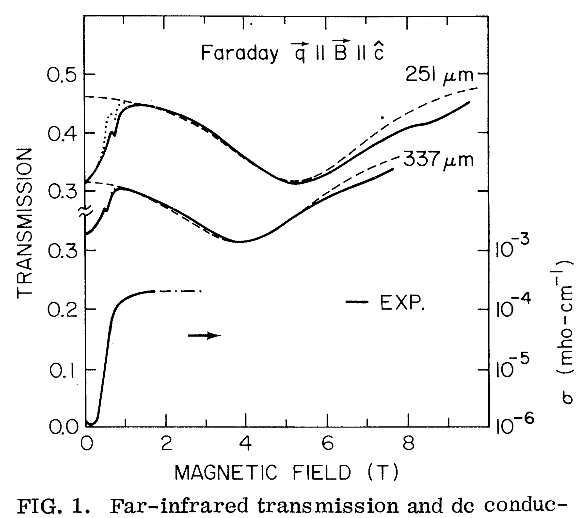

FIG. 1. Far-infrared transmission and dc conductivity of $Cd_{0.9}Mn_{0.1}Se$ at 4.2 K. For the transmission the solid lines represent the experimental data while the dotted and dashed lines are the calculated curves based on the D^- model discussed in the text. The parameters of the best fit are as follows: at 337 μm, $m^*=0.125$, $\hbar/\tau=1.7$ meV, $g=110$, $N_0=1.3\times10^{14}$ cm^{-3}, $E_{D^-}=2$ meV, $\alpha''=4.4\times10^{-17}$ cm^3, $E_b=5$ meV, and $N_b=4\times10^{14}$ cm^{-3}; and at 251 μm, $E_{D^-}=2.5$ meV and $\alpha''=3.2\times10^{-17}$ cm^3.

at 337 μm (251 μm) are free-carrier cyclotron resonances. This conclusion is supported by the values of the resonance fields and by measurements in circularly polarized light at 251 μm in which the absorption is found to occur only in the electron-cyclotron-resonance-active mode.[7] This identification is convincingly made by the following line-shape analysis from which we also obtain the free-carrier density n_c and the carrier relaxation time τ.

The optical response of the sample can be adequately described at these frequencies and for fields above about 10 kG in terms of the static dielectric function ϵ_0 and the classical free-carrier dielectric function

$$\epsilon^{\pm} = \epsilon_0 - \frac{\omega_p{}^2}{\omega[(\omega \mp \omega_c) + i/\tau]}, \qquad (1)$$

where the plus (minus) refers to right (left) circular polarization and $\omega_p{}^2 = 4\pi n_c e^2/m^*$. From the literature $\epsilon_0 = 9.4$ and $m^* = 0.13m_0$ in pure CdSe.[8]

We have used Eq. (1) to calculate the far-infrared transmission of the sample using n_c and τ as fitting parameters. It is assumed that the sample is sufficiently wedged that the standing-wave interference effects are absent. The position of the cyclotron resonance is in accord with $\omega = \omega_c = eH/m_c c$, with $m_c = 0.125m_0$. The best-fit curves are shown in Fig. 1 (dashed lines) for $n_c = 1.0 \times 10^{14}$ cm^{-3} and $\hbar/\tau = 1.7$ meV. The calculated spectrum is seen to agree well with the experimental trace above 10 kG. Below 10 kG the dielectric function given by Eq. (1) predicts a flat transmission spectrum (dashed curves in Figs. 1 and 3) while the experiments show a dip over the same field range where the magnetoresistance is rapidly changing. The high-field cyclotron resonance shows that there are free carriers in the conduction band. The high sample resistance at low fields suggests some kind of impurity-band conduction process.

We propose that these results can be understood in terms of a small concentration of doubly occupied donor sites in the crystal. These sites, called D^- centers, have been observed in Si and Ge but only under nonequilibrium conditions (photoexcitation).[5] In CMS it appears that there is a small excess of electrons over the donor concentration, N_d, so that these D^- centers can exist in thermal equilibrium at low temperatures. The doubly occupied donor is analogous to the negative hydrogen ion in which the second electron is bound with an ionization energy of 0.005$\mathcal{R}$.

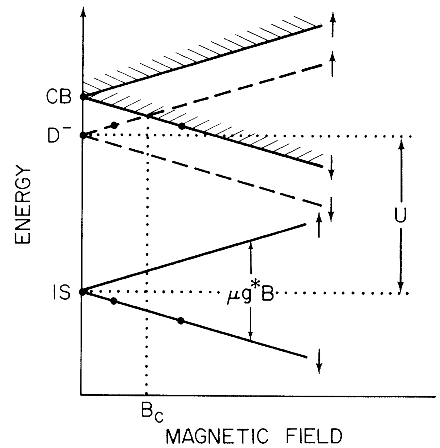

FIG. 2. Energy-level diagram for the D^- centers in an applied magnetic field (schematic). The diagram shows the one-electron energy levels as solid lines and hatched regions and the energy of the second electron is shown as dashed lines. A configuration for the D^- state is indicated by two dots at a field below B_c and the ionized case is shown for a field greater than B_c.

Because of the nearly isotropic and parabolic conduction band of CdSe the second electron in the D^- center should be bound with an ionization energy of $\sim E_{D^-} = 0.055\mathcal{R}^*$ where $\mathcal{R}^* = m^* e^4/2\epsilon_0{}^2\hbar^2 \approx 20$ meV.

Because of the large effective g factor in $Cd_{1-x}Mn_xSe$ it turns out that the D^- levels will ionize at a relatively low magnetic field. This we can see with the aid of Fig. 2. The total energy of the D^- center relative to the conduction band is

$$E_t = E_{1s\downarrow} + E_{1s\uparrow} + U = -2\mathcal{R}^* + U = -\mathcal{R}^* - E_{D^-},$$

where U is the Coulomb repulsion between the two electrons and E_{D^-} is the ionization energy of the D^- center when $B = 0$. The lowest energy of the dissociated D^- ion consisting of a neutral donor plus an electron in the conduction band is

$$E_I = E_{1s\downarrow} + E_{k\downarrow} = -\mathcal{R}^* - \mu_0 g^* B,$$

where $E_{k\downarrow}$ is a conduction-band state and where $\mu_0 g^* B$ is the Zeeman splitting. The condition for the ionization of the D^- level is therefore $E_I < E_t$ or $\mu_0 g^* B > E_{D^-}$. For $g^* \sim 110$ and $E_{D^-} \sim 2$ meV this gives a critical magnetic field of about $B_c = 3$ kG.

Now the D^- levels will modify the conductivity and far-infrared transmission of the sample as follows. Above B_c the free carriers in the conduction band will produce a high dc conductivity and a cyclotron resonance signal. At low fields the far-infrared response will be optical ionization of D^- centers and the electrical conductivity will be occurring within the D^- band (at low temperatures). These features can be demonstrated with a model calculation in which we must first determine the densities of free carriers, n_c, and of the occupied D^- levels, n_{D^-}. The density of D^- centers can be written as[9]

$$n_{D^-} = N_d \frac{\exp[+\beta(\mathcal{R}^* + E_{D^-} + 2\mu)]}{1+\exp[-\beta(E_{1s\uparrow} - \mu)] + \exp[-\beta(E_{1s\downarrow} - \mu)] + \exp[\beta(\mathcal{R}^* + E_{D^-} + 2\mu)]}, \tag{2}$$

where N_d is the donor density, μ is the chemical potential, and $\beta = 1/kT$, and where we have ignored the excited donor levels. The conduction-electron density can be written as

$$n_c = \int d\epsilon\, g_\downarrow(\epsilon) f(\epsilon) + \int d\epsilon\, g_\uparrow(\epsilon) f(\epsilon), \tag{3}$$

where $g_\downarrow(\epsilon)$ and $g_\uparrow(\epsilon)$ are the densities of states of the spin-up and spin-down conduction bands (Landau quantization has been ignored) and $f(\epsilon)$ is the Fermi-Dirac distribution function.

The magnetic-field and temperature dependence of the chemical potential and therefore of n_c and n_{D^-} are determined by Eqs. (2) and (3) plus the requirement that the total electron density remain constant, $n_{D^-} + n_c = n_0 = \delta N_d$, where $\delta \simeq 0.004$ from the Hall data and the cyclotron resonance. Now to calculate the corresponding transmission spectrum we must include an additional contribution to the dielectric function that describes the optical ionization of the D^- sites. The imaginary part of ϵ_{D^-} can be expressed as

$$\mathrm{Im}\,\epsilon_{D^-} = 4\pi n_{D^-} \alpha''(\omega),$$

where $\alpha''(\omega) = \frac{1}{3}\pi e^2 |x|^2 g(\hbar\omega - E_{D^-})$ is the imaginary part of the D^- center polarizability and where $e|x|$ is the dipole matrix element for the ionization process in which the final state is a neutral donor and the second electron is in a conduction-band state of either spin and kinetic energy $\hbar\omega - E_{D^-}$. $g(E)$ is the $B=0$ total density of states.

The results of the transmission calculation based on the D^--state model show a low-field dip for values of $\alpha''(\omega)$ which are in reasonable agreement with the calculated values, and the response can be made to switch back to the free-carrier response (dashed curves in Figs. 1 and 3) for reasonable values of E_{D^-}. There is a discrepancy, however, in that the calculated spectra switch from D^- absorption to free-carrier response too abruptly in comparison with the measurements. We take this as evidence of a broadening mechanism not included in the model. Indeed, changing the temperature in the calculation to 10 K (but keeping the same g^*) gives much better agreement. Consideration of a spread in g^* due to Mn inhomogeneity does not resolve this discrepancy, for the required spread in g^* is much too large to be consistent with the observed linewidth of the spin resonance observed in these same spectra.[6] Model calculations including a broadening of the D^- band have also been performed but the results were not improved. Because $n_{D^-} \ll N_d$ the electrons sit near the bottom of the D^- band which leads to similar spectra as the delta-function D^- density case, except for a shift equal to half of the D^- bandwidth. A broadened D^- band may therefore account for the fact that the observed E_{D^-} is larger than predicted.

Another broadening mechanism which may be important is band tailing. To model this we have included a nonconducting state density below the conduction band starting at $-E_b$ and terminating at the band bottom. The other parameter characterizing these states is their total density N_b (states/cm^3). The model is seen to give a good fit (dotted lines below B_c and dashed lines above) to the experimental data at 4.2 K (Fig. 1) and at higher temperatures (Fig. 3). Although these results provide compelling evidence for the D^- model more study is needed before it can be said that the broadening is understood.

A critical question raised by our D^- interpretation is the source of the excess electrons needed to produce doubly occupied donors. This is very difficult to understand in terms of defect states since any site that would liberate an electron would leave behind a localized positive charge and thus tend to behave as a donor. We suggest that the excess electrons come from inhomogeneities in the Mn concentration in the sample. These fluctuations produce spatial fluctuations in the band gap and the conduction-band minimum. Therefore there will be regions of the crystal where the Mn concentration will be higher than average and the donor levels will be pulled above the chemical potential liberating their electrons, which will then travel to regions where a lower Mn concentration has pulled the donor low enough that a second electron can be bound. The required rms band-bottom fluctuation $\delta E_c = \alpha\mathcal{R}^*$ where $\alpha \ll 1$ (~ 0.2), because μ lies between E_d ($-\mathcal{R}^*$) and E_c and because only a small fraction ($\delta N \sim 0.4\%$) of the donors have to be above μ. To achieve this the required fluctuation in Mn con-

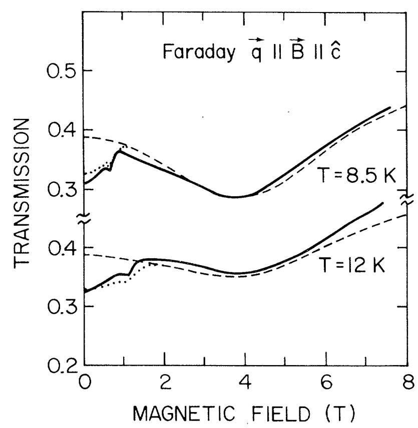

FIG. 3. Temperature dependence of the far-infrared transmission of $Cd_{0.9}Mn_{0.1}Se$ at 337 μm. The dotted and dashed lines indicate the calculated transmission based on the 4.2-K fit without adjustment of the parameters excepting $\hbar/\tau = 2.1$ meV, $g = 91$ (at 8.5 K) and $\hbar/\tau = 2.3$ meV, $g = 57$ (at 12 K).

centration is $\delta x \sim \delta E_c (dE_g/dx)^{-1}$, if we assume $dE_c/dx \sim dE_g/dx$. For $dE_g/dx = 1.6$ eV we find $\delta x \sim 0.006$. If we consider only the statistical fluctuations in Mn concentration for an ideal solid solution with randomly distributed Mn we get a lower bound on δx. A given donor contains $N \sim 400$ Mn ions within its Bohr radius in $Cd_{0.9}Mn_{0.1}Se$. Therefore the rms fluctuation would be $\delta x = (\delta N/N)x \sim 0.005$ which agees well with the above estimate.

This idea may also explain another puzzle. At fields above B_c the cyclotron resonance linewidth gives a carrier relaxation rate $\hbar/\tau \sim 1.7$ meV. From this result the dc conductivity, from $\sigma = n_c e^2 \tau / m^*$, is predicted to be 0.09 mho cm^{-1} which is about 400 times larger than observed.[10] Moreover, the high-field dc conductivity is activated with an $\sim$1-K activation energy. Since the fluctuation model predicts that the free carriers will only populate the low-E_c regions, which comprise only ~0.4% of the sample, these carriers may be Anderson localized and conduct only by thermally activated hopping. To test these ideas further more detailed transport studies are being carried out. The initial rise in the magnetoresistance is not easily explained by our model. We believe that this feature may arise from effects of the "bound magnetic polaron"[4] on the D^--band conduction.

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