Magnetization of bound magnetic polarons in Ga-doped $\text{Cd}_{1-x}\text{Mn}_x\text{Te}$

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Light-induced persistent changes in magnetization of n -type $\text{Cd}_{1-x}\text{Mn}_x\text{Te}$ ($0.01 \leq x \leq 0.20$) single crystals have been measured at $T=2$ and 5 K and in magnetic fields of up to 0.5 T. The effect observed correlates with an increase (upon illumination) in shallow donor concentration measured on the same samples. It also saturates with increasing magnetic field. The bound magnetic polaron theory accounts for the variation of the excess persistent magnetization with temperature and magnetic-field strength if the antiferromagnetic exchange coupling between magnetic ions is included. [S0163-1829(97)05943-2]

Strong exchange interactions between localized spins of magnetic ions and spins of charge carriers in diluted magnetic semiconductors (DMS's) give rise to interesting effects. One of these is the formation of a bound magnetic polaron (BMP) in which charge carriers bound to impurities polarize the spins of magnetic ions within their orbit, thus lowering the total energy of the system. Several different theoretical approaches have been developed to treat the BMP problem.^{1,2} Although formalisms used are rather different, these theories give identical results in the continuum limit. It has been shown that polarons evolve continuously from a high-temperature fluctuation dominated regime to a low-temperature collective state with large net moment. Binding energies of polarons and their variation with temperature and magnetic field have been measured experimentally in various DMS's.⁴ However, magnetization measurements of persistent BMP have been reported only once.⁵ The magnetic ions give rise to a strong paramagnetic background in these materials that makes such measurements difficult. One way to overcome this difficulty is to use the persistent photoconductivity effect which has been observed in In- and Ga-doped $\text{Cd}_x\text{Mn}_{1-x}\text{Te}$ crystals.⁶ This effect arises from the Ga dopant metastability (which can form both deep and shallow trapping centers) analogous to the behavior of DX centers in $\text{Al}_x\text{Ga}_{1-x}\text{As}$.⁷ Illumination of the sample at low temperatures raises (by several orders of magnitude) the shallow donor concentration which persists after the light is shut off for a long time (if the sample temperature is not raised). A contribution of BMP (formed on light-induced neutral shallow donors) to the magnetization may be thus measured as the host magnetization does not change upon illumination otherwise. (We note that, according to the negative- U model for DX -like centers in II-VI compounds,⁸ Ga impurities do not form polarons either in the deep relaxed DX^- state or in the ionized shallow donor state.) Such measurements have been made in Ga-doped $\text{Cd}_{1-x}\text{Mn}_x\text{Te}_{1-y}\text{Se}_y$ crystals ($x=0.10$) at 2.1 and 4.2 K in magnetic fields of up to 0.02 T and have been described by the BMP theory.⁵ In small magnetic fields such as studied in Ref. 5, the polaron magnetization increases linearly with field. Therefore, some effects predicted by the BMP theory could not be observed. The magnetic ion content of host material is also important in BMP's forma-

tion. However, there is no systematic study of the BMP magnetization as a function of magnetic ion concentration.

Here, we report BMP magnetization studies in $\text{Cd}_{1-x}\text{Mn}_x\text{Te}$ ($0.01 \leq x \leq 0.20$) single crystals doped with Ga. We measured light-induced persistent remanent changes in magnetization at $T=2$ and 5 K and in magnetic fields of up to 0.5 T. A gradual saturation of the BMP magnetization with increasing magnetic field is observed. To our knowledge, this is the first direct observation of such effect. The BMP theory predicts such behavior. However, we have found that the antiferromagnetic exchange coupling between magnetic ions should be included in the calculations³ to account for magnetic-field variation of polaron magnetization that is observed experimentally. There are no fitting parameters in our calculations for $x=0.01$ and 0.05 crystals. All parameters needed have been obtained from Hall effect and susceptibility measurements that we have performed on the same samples. For the $x=0.20$ sample, the only fitting parameter is light-induced change in concentration of shallow donors. No remanent change in magnetization was observed upon illumination of undoped $\text{Cd}_{1-x}\text{Mn}_x\text{Te}$ crystals.

Single crystals of $\text{Cd}_{1-x}\text{Mn}_x\text{Te}$, both undoped and doped with gallium, were grown by a modified Bridgman method. Intentional doping with Ga (which substitutes the cation) was applied to ensure n -type conductivity. However, the as-grown doped alloys were of high resistivity, presumably because there is a large density of Cd vacancies. To reduce the compensation, $\text{Cd}_{1-x}\text{Mn}_x\text{Te}:\text{Ga}$ was annealed in Cd vapor at a temperature of 1000 °C for 100 h. The manganese concentrations were checked by photoluminescence measurements; they agreed well with the nominal x values. We measured four different compositions, namely, $x=0.01$, 0.05, 0.10, and $x=0.20$. Samples used in our study were cleaved from the bulk material. Hall effect measurements before and after illumination were carried out in a temperature range from 1.6 to 300 K. We used light emitting diodes ($\lambda=860$ nm or 780 nm) as a source of illumination at low temperatures. Magnetization measurements were done using a commercial Quantum Design SQUID magnetometer with an optical fiber insert that was designed by us. To reestablish the initial conditions for each experimental run, we heated the sample to about 150 K and then slowly cooled it down.

Figure 1 shows how the electron concentration varies with

FIG. 1. Temperature dependence of the Hall concentration in $\text{Cd}_{0.99}\text{Mn}_{0.01}\text{Te:Ga}$ and $\text{Cd}_{0.95}\text{Mn}_{0.05}\text{Te:Ga}$ in dark and after long illumination at low temperatures.

temperature in $\text{Cd}_{1-x}\text{Mn}_x\text{Te:Ga}$ ($x=0.01$ and 0.05) samples before and after illumination. As the sample is cooled in darkness, the carrier concentration decreases, because the electrons freeze out on the relaxed deep donor levels. In this region, the slope of the reciprocal of the Hall coefficient versus $1/T$ gives an activation energy of the order of 7 and 90 meV for $x=0.01$ and $x=0.05$, respectively. Below ~ 100 K, the energy required to produce lattice distortion around the defect is greater than kT and further electron freeze out may occur only at the unrelaxed state of the defect with smaller activation energy. Light excites electrons from deep traps to the conduction band, where they remain persistently, if their energy is lower than the capture barrier. The maximum photoinduced change in concentration of shallow donors, ΔN_D , is about $2.1 \times 10^{16} \text{ cm}^{-3}$ and $4.1 \times 10^{15} \text{ cm}^{-3}$ for $x=0.01$ and 0.05 , respectively.

Figure 2 shows the change in the magnetization upon illumination (that is the difference between signals measured by and without illumination) in doped $\text{Cd}_{1-x}\text{Mn}_x\text{Te}$ samples as a function of applied magnetic field for two different temperatures: $T=2$ and 5 K. Several samples of each composition were studied. We found that the total change in magnetization (upon illumination that is long enough to reach saturation) scales with the mass of the samples and with light induced persistent donor concentration. Therefore, it is a measure of the magnetization of BMP's formed on shallow donors. Inspection of Fig. 2 shows that the BMP magnetization gradually saturates as magnetic field increases. This effect is more pronounced at lower temperatures and for samples with larger Mn content. The solid curves in Fig. 2 have been calculated using the donor-BMP theory² in which we have included the effect of the antiferromagnetic exchange coupling between the magnetic ions. As shown in Ref. 3, this coupling leads to a modified Brillouin function description of the magnetic properties of DMS's. Next-

FIG. 2. Experimental change in the magnetization (solid squares) and calculated BMP magnetization (solid lines) as a function of magnetic field at two temperatures, 2 and 5 K, and for three different compositions shown of $\text{Cd}_{1-x}\text{Mn}_x\text{Te:Ga}$. The experimental points stand for the difference between the signals measured with and without illumination.

nearest-neighbor $\text{Mn}^{2+}\text{-Mn}^{2+}$ exchange interactions cause the Mn^{2+} susceptibility in DMS's to saturate, and it is therefore no longer strictly Curie-like. To account for this, the lattice temperature T in the Curie law susceptibility is replaced by the effective value $T_{\text{eff}} = T + T_o$, where T_o is related to the exchange integrals involving non-nearest-neighbor magnetic ions.¹⁰ This replacement also modifies the thermal fluctuations of the magnetization considered for the formation of BMP. On the other hand, not all magnetic ions contribute to the net magnetization of DMS. A significant fraction of the Mn^{2+} ions form clusters with total spin less than $5/2$. Consequently, the spin S of the magnetic ion is also replaced by an (composition dependent) effective value S_o ($S_o < S$). The BMP contribution to the magnetization has been calculated from the BMP partition function.² It can be equally obtained by taking the partial derivative of the donor-BMP free energy with respect to magnetic field.¹ In the former case, values of T_o and S_o are required. For the latter case, the magnetic properties of the material are given

by the susceptibility, whose temperature and magnetic-field variation should be known. Values of the donor Bohr radius and of donor concentration are needed in both cases.

The parameters T_o and S_o have been obtained from the experimentally measured magnetic susceptibility of the samples at various temperatures and magnetic fields. The values of $x_{\text{eff}} = xS_o/S$ are 0.009 for $x=0.01$, 0.03 for $x=0.05$, and 0.06 for $x=0.20$. The parameter T_o is 0.9 K, 1.9 K, and 3 K for $x=0.01$, 0.05, and 0.20, respectively. These values are very close to the values of x_{eff} and T_o determined from spin-flip Raman scattering in $\text{Cd}_{1-x}\text{Mn}_x\text{Te:Ga}$.⁹ We used a value of 220 meV (Ref. 9) for the s - d exchange constant in all compositions. The donor Bohr radius value is 50 Å, 45 Å, and 35 Å for $x=0.01$, 0.05, and 0.20, respectively.⁹ The values of ΔN_D are taken from the Hall-effect measurements that we have performed on the $x=0.01$ and $x=0.05$ crystals. There are no fitting parameters in our calculations for these two compositions. For the $x=0.20$ sample, the only fitting parameter is ΔN_D . We find that the BMP theory² accounts very well for our experimental data. In particular, it describes correctly the saturation of the BMP magnetization with increasing magnetic field. This effect had not been observed in earlier experiments. We note

that the BMP theories^{1,2} rely on the Gaussian approximation, in which the polarization of the magnetic ions within an impurity orbit is regarded to be small, with respect to its saturation value. This approximation is accurate for donor BMP, which is the case considered here, although it fails for acceptor-BMP complexes, in which spin saturation occurs.

In summary, we have measured the BMP contribution to the total magnetization of $\text{Cd}_{1-x}\text{Mn}_x\text{Te:Ga}$ as a function of magnetic field and composition. We have found that this contribution may be quite significant at low temperatures and small magnetic fields although it saturates in magnetic field of few kOe. The saturation of the BMP magnetization occurs at smaller magnetic fields for samples with higher magnetic ion content. Excellent agreement between experiment and the BMP theory^{1,2} confirms the existing picture of the BMP behavior. The correlation between the BMP magnetization and the light-induced persistent donor concentration is consistent with the negative- U defect model for DX -like centers in II-VI semiconductors.⁸

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