Acceptor-bound magnetic polarons in $Cd_{1-x}Mn_xTe$

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Photoluminescence measurements have been used to determine bound magnetic polaron energies in intentionally doped, high-purity p-type $Cd_{1-x}Mn_xTe$ samples. The binding energy of acceptor-bound magnetic polarons has been found to increase with Mn content in the alloy up to about $x = 0.2$. Beyond this value the polaron energy saturates with increasing x, as a result of the antiferromagnetic nearest-neighbor Mn^{2+}-Mn^{2+} interactions. This behavior and the values of polaron binding energy are in agreement with the predictions of phenomenological polaron theory, which uses the measured high-field magnetization of the host crystal as an input to determine the Mn^{2+} response.

I. INTRODUCTION

Magnetic polarons (MP's) are ferromagnetic spin clusters created by the exchange interaction of a carrier spin with localized spins embedded in a semiconductor lattice.[1] MP's occur in both magnetic and semimagnetic semiconductors (SMSC's) such as $Cd_{1-x}Mn_xTe$.[2] SMSC's are favorable media for magnetic-polaron studies because they have simple s-p bands and excellent optical properties. Two types of magnetic polarons have been identified in SMSC's—the bound magnetic polaron (BMP), whose carrier is localized by an impurity,[3] and the free polaron (FP) consisting of a carrier trapped by its own, self-consistently maintained exchange potential.[4]

For diluted magnetic semiconductors $Cd_{1-x}Mn_xTe$ with $x < 0.1$, a polaron theory[5] assuming that unpaired Mn^{2+} spins respond paramagnetically to the carrier exchange field gives good agreement with optical experiments.[3,5,6] For larger x values, however, this theory predicts polaron binding energies much higher than those observed experimentally. In such materials the situation is complicated by the presence of many nearest-neighbor Mn^{2+} ions, whose spins are coupled antiferromagnetically. A phenomenological polaron theory has recently been developed for large-x alloys.[7] Instead of calculating the Mn^{2+} magnetization under these circumstances, it uses the measured high-field magnetization[8] of the host crystal as an input to determine Mn^{2+} response.

The aim of this paper is to experimentally test the predictions of the phenomenological polaron theory. We present systematic measurements of acceptor-bound magnetic polaron photoluminescence (PL) of $Cd_{1-x}Mn_xTe$ over a wide range of the manganese mole fraction x and temperature T. The acceptor-bound magnetic polaron luminescence is perfectly suited for the test of the theory due to the relative simplicity of acceptor-related transitions.

In the present study of high-purity materials the PL lines associated with neutral acceptors (electron-acceptor and donor-acceptor pairs) are narrow due to small LO-phonon replicas. This allows us to determine the energy levels to an accuracy of ± 3 meV, without resorting to time-resolved measurements,[6] which require the acceptor binding energy to be deconvoluted from a generally complicated dependence of line position on inter-ion distance and excitation intensity.

II. EXPERIMENT

A. Sample preparation

Phosphorus-doped $Cd_{1-x}Mn_xTe$ single crystals with x ranging from 0.02 to 0.35 were grown by the vertical Bridgman technique. Doping was achieved by incorporation of phosphorous into the melt. Initial concentration of the dopant impurities was about 10^{17} cm^{-3}. Prior to the synthesis of the $Cd_{1-x}Mn_xTe$:P alloys, the single elements Cd, Mn, and Te were purified by vacuum sublimation. The elements were carefully weighted to obtain the desired molar composition and impurity concentration. The prepared mixture was sealed in 19-mm-i.d. graphitized quartz ampoule and placed in the hot zone of the Bridgman furnace. The reaction temperature was slowly raised from 500 to 1120 °C. The ampoule was held at 1120 °C for about 24 h to homogenize the melt, and then lowered through the furnace at the rate of 1.2 mm/h. The solidification gradient in the furnace was about 15 °C/cm. The as-grown boules were then sliced perpendicular to the growth direction.

Differential etching[9] was used to expose grain boundaries, precipitates, and dislocations. This showed that most of the slices contained one to three grains, although some of the grains were heavily twinned. The typical etch-pit density was in the range of 10^3–10^5 cm^{-2} near the tip, and about 10^5 cm^{-2} at the tail. Room-temperature measurements, performed on successive slices, have shown p-type conductivity in all cases. The room-temperature hole mobility in the as-grown samples

was in the range of 35–60 cm^2/V s. Considerably larger variations, however, were observed in sample resistivity and carrier concentration, e.g., the concentration of un-compensated acceptors in some crystals changes by a factor of 10^2 along the boule. These variations are commonly attributed to the high-segregation coefficient and self-compensation of $Cd_{1-x}Mn_xTe$ alloys.[10,11] For further investigation only the samples cut from the head of the boule were used. The concentration of uncompensated acceptors in these samples was in the range of $2 \times 10^{17} - 4 \times 10^{16}$ cm^{-3} for $0.02 \leq x \leq 0.35$. In order to minimize the self-compensation and to reduce the concentration of native defects, samples were annealed at 600 °C under Cd pressure of 0.02 atm for 5 d. As has been discussed in our previous paper,[10] annealing decreases the concentration of cadmium vacancies and redistributes the phosphorus impurities in the crystal. The typical concentration of uncompensated acceptors, i.e., $N_A - N_D$, in annealed samples was in the range of $8 \times 10^{15} - 3 \times 10^{14}$ cm^{-3} for $0.02 \leq x \leq 0.35$. A slight increase of the hole mobility up to 70 cm^2/V s has also been observed. In addition, significant improvement has been achieved in the optical properties due to the annealing. The absorption coefficient α in the infrared region decreased by a factor of 10^2 and the PL peaks increased in intensity and became much narrower. High-quality samples are essential for this investigation. We have found that for unambiguous determination of acceptor binding energy, low-concentration p-type samples with low compensation are required, i.e., the samples in which free-electron to neutral-acceptor (e, A^0) transitions dominate over donor-acceptor transitions. The low overall concentration is desirable since it also improves the quality of the excitonic part of the spectrum. Increased resolution in that part of the spectrum allows the line identification and precise determination of alloy composition. We have found that the composition of $Cd_{1-x}Mn_xTe$ crystals determined in this way was in all cases slightly lower than the one calculated from the weights of ingredients.

B. Photoluminescence measurements

Photoluminescence was excited by the 514-nm line of an argon-ion laser. The excitation intensity was kept below 10 W/cm^2 to avoid sample heating. Samples were mounted on the cold finger of a variable-temperature, continuous-flow liquid-helium cryostat. The temperature was measured with a calibrated silicon diode located on the copper sample holder, immediately next to the sample. Temperature stabilization was achieved with a temperature controller. The luminescence spectra were measured with a 0.75-m grating spectrometer and a germanium detector cooled to liquid-nitrogen temperature. The exciting beam was modulated with a mechanical chopper and the luminescence signal was measured using a phase-sensitive lock-in detection system. The spectral resolution of the system was of the order of 0.2 meV.

III. RESULTS AND DISCUSSION

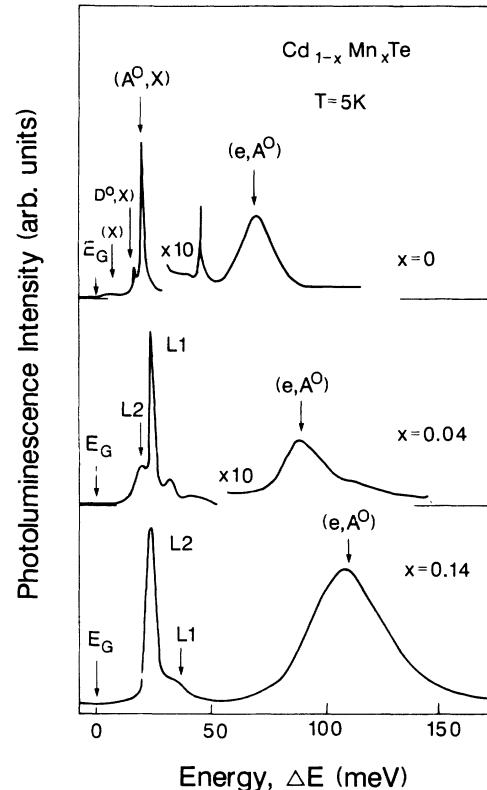Typical PL spectra of phosphorus doped $Cd_{1-x}Mn_xTe$ crystals used in this study are shown in Fig. 1. The PL

FIG. 1. Photoluminescence spectra of $Cd_{1-x}Mn_xTe$ crystals.

spectrum of binary CdTe is also shown for reference. It consists of well-resolved excitonic lines at energy around 1.59 eV and the acceptor-related line with a maximum at about 1.54 eV. Taking the energy gap of CdTe to equal 1.606 eV, an ionization energy of approximately 66±2 meV is obtained for the acceptor in question, which is equal, within an experimental error, to the value 68.2±0.5 meV reported for phosphorus.[12] The dominant line in the excitonic part of the spectrum at energy 1.5889 eV can be attributed to neutral-acceptor–bound-exciton transitions (A^0,X); two weaker higher-energy features at 1.5926 and 1.5969 eV correspond to neutral-donor–bound-exciton transitions (D^0,X) and free excitons (X). These follow from the agreement of the above listed values with previously reported[13,14] energies: 1.5883, 1.5925, and 1.5976 eV of these transitions. PL spectra of $Cd_{1-x}Mn_xTe$ alloy with low Mn content $(x < 0.1)$ contain features which are similar, though less sharp, to those observed in the binary compound. Again the most prominent line is that of the (A^0,X) transition. Its position is shifted towards lower energies indicating an increase in binding energy of the exciton to the neutral acceptor. Measurements of this increase of energy in magnetic alloys have been performed by Golnik, Ginter, and Gaj[4] who attributed it to BMP formation around the bound exciton complex. The (A^0,X) line has been denoted in their work and in subsequent papers by $L2$. In the case of bound-exciton transitions one faces a complicated three-body problem in interpreting the data. Thus, to make a direct comparison of experiments with theoretical

predictions, we focus on the (e, A^0) transitions. As can be seen from the appropriate spectra in Fig. 1, the (e, A^0) line shifts towards lower energies by a sizeable amount as manganese context increases. For $x > 0.1$ the excitonic part of the spectrum consists of one appreciably broadened line which has been attributed[4,14] to a magnetically localized free exciton (self-trapped magnetic polaron). Adopting the notation used in the quoted papers, we call this the $L1$ line. The manganese content x, in $Cd_{1-x}Mn_xTe$ samples was determined from the energies of (expressed in eV) of the exciton recombination at $T = 5$ K using empirically determined relations,[14]

$$E_{L1} = 1.5888 + 1.440x \quad \text{for } 0 < x \le 0.1 , \tag{1}$$

$$E_{L2} = \begin{cases} 1.6047 + 1.397x & \text{for } 0.05 < x \le 0.2 , \\ 1.575 + 1.536x & \text{for } 0.2 \le x \le 0.4 . \end{cases} \tag{2}$$

The only difficulty with this method is in identifying the exciton PL lines ($L1$ and $L2$). However, an incorrect line identification, as estimated in Ref. 15, amounts to an additional error in x of only 0.01, which is still an acceptable value.

The binding energy of phosphorus acceptor in $Cd_{1-x}Mn_xTe$ versus manganese context is shown in Fig. 2. An increase of the binding energy from 68 meV in CdTe up to about 122 meV at $x = 0.25$, followed by a slight decrease for $x > 0.25$, is observed. We interpret the observed increase in acceptor binding energy as resulting from the formation of magnetic polaron within the hole localization volume. We do not expect the bare-acceptor energy (neglecting BMP effects) to vary with x since the dielectric function and hole effective mass are slowly varying, as evidenced by the nearly equal values in CdTe and ZnTe. Thus the additional energy is almost totally magnetic.

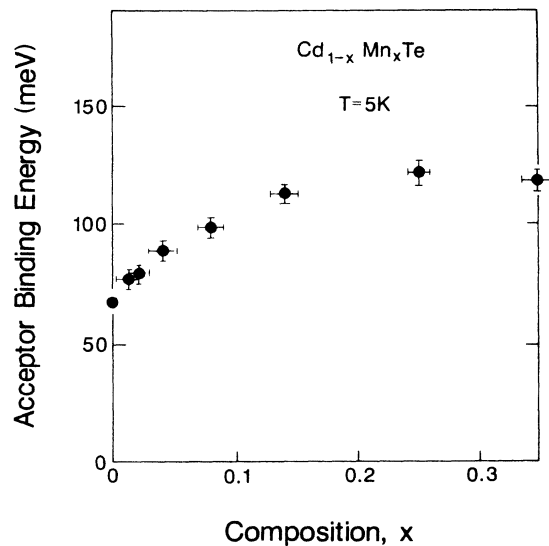We now present a careful experimental determination of the magnetic part of acceptor binding energy, i.e.,

acceptor-bound magnetic polaron energy. This goal was achieved by studying temperature variations of the acceptor-related PL line. Peak positions of this line plotted as a function of temperature for different values of the manganese context x are shown in Fig. 3. The dashed line represent temperature variations of acceptor-related PL line positions calculated under the assumption that deviation occur at low temperatures. The magnitude of that deviation and the temperature range in which it occurs depends on the manganese content in the alloy. Both effects increase with Mn context (x). In contrast to what is typically observed in nonmagnetic materials, the peak of (e, A^0) transitions first shifts to higher energies as temperature increases, then goes through a maximum and eventually follows the line calculated under the assumption that there is no magnetic contribution to the acceptor binding energy. Thus the experimental data clearly suggest that in the $Cd_{1-x}Mn_xTe$ alloy there is a sizeable temperature-dependent magnetic contribution to the acceptor binding energy whose value depends on the composition. This effect is due to the formation of a bound magnetic polaron (BMP) whose carrier is localized by the acceptor. The acceptor-bound MP energies versus temperature in $Cd_{1-x}Mn_xTe$ alloys of different composition are shown in Fig. 4. These data have two important features: (a) BMP energies do not decay to zero at high temperatures, and (b) there is a gradual increases of BMP energies with an increase of manganese content in the al-
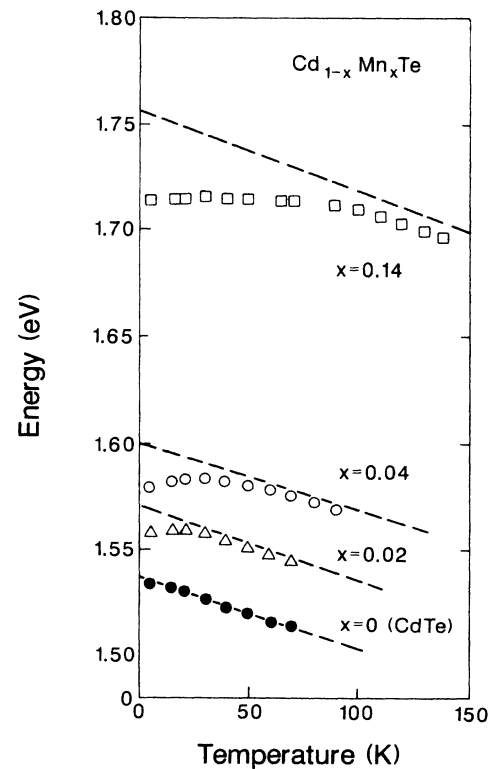

FIG. 3. Positions of the maxima of acceptor related (e, A^0) transitions as a function of temperature for different values of Mn content in the $Cd_{1-x}Mn_xTe$ alloy.

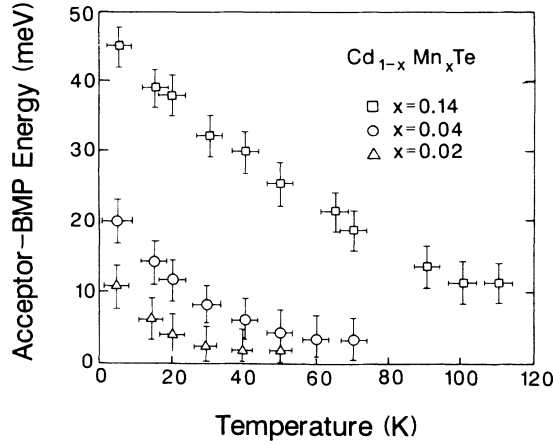FIG. 2. Binding energy of phosphorus (P) acceptor vs Mn context in the $Cd_{1-x}Mn_xTe$ alloy.

FIG. 4. Binding energies of acceptor-bound MP vs temperature in $Cd_{1-x}Mn_xTe$ alloys.

loy (at least in the composition range covered by the samples shown in Fig. 4). The degree of spin alignment around the acceptor impurity may be caused not only by the molecular field produced by the hole, but also by the thermodynamic fluctuations of magnetization. The influence of the latter factor can be relatively large because of the finite size of the system under consideration. Thus BMP energy can be expressed as a sum of cooperative energy E_c and fluctuation energy E_f,[5]

$$E_{BMP} = E_c + E_f \ . \tag{3}$$

E_c has a finite value at $T = 0$ and decays down to zero as T increases. E_f is equal to zero at $T = 0$ and tends to saturate at high temperatures. The value reached by E_f at high temperatures equals $\sqrt{2}W_0$, where W_0 can be expressed as[5]

$$W_0 \sim \frac{\alpha N_0 \sqrt{\bar{x}}}{[\pi(a_0)^3 N_0]^{1/2}} = \frac{W_{max}}{\sqrt{N}} \ . \tag{4}$$

The (αN_0) is the effective exchange energy, $\bar{x}$ is the effective x, and N is the number of Mn^{2+} ions within the spin cloud around the impurity. W_{max} is the energy gain by the system of perfectly aligned spins, i.e., it is $E_c(T = 0)$. Two important features can be derived from Eq. (4). First, because N is of the order of 20–30. W_0 is roughly five times smaller than W_{max}. Second, $W_0 \sim \sqrt{\bar{x}}$, where $\bar{x}$ is the effective manganese content, i.e., the concentration of Mn^{2+} ions active in polaron formation. Note that $\bar{x} < x$ due to Mn^{2+}-Mn^{2+} antiferromagnetic interaction. The composition dependence of the acceptor-bound MP binding energy in low-temperature limit where the Mn^{2+} spins are fully aligned with that of the hole is shown in Fig. 5. Our experimental results show that BMP energy increases with composition, reaches a maximum at about $x = 0.2$; then it saturates or even slightly decreases. We have been able to investigate acceptor-bound MP luminescence in the composition range up to about $x = 0.35$.

At higher compositions the PL spectra are dominated by a 2.0 eV band originating from the transitions between
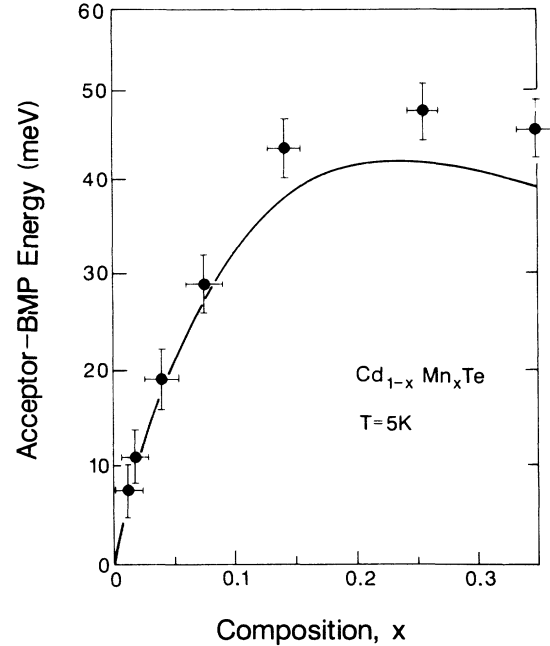

FIG. 5. Composition dependence of acceptor-bound MP binding energy in low-temperature limit in $Cd_{1-x}Mn_xTe$ alloys. Solid line represents the values calculated according to phenomenological polaron theory developed in Ref. 7.

the crystal-field-split $3d^5$ levels of Mn^{2+} ion.[16,17] The 2.0-eV band intensity grows up rapidly as the band gap of the material approaches 2.2 eV for $x > 0.35$. This is due to the fact that excitation from the near-band-gap states is effectively transferred to Mn^{2+} ions, which at the same time prohibits observation of these states in luminescence.

The experimental results are compared with the theoretical calculation of acceptor-bound MP energies in Fig. 5. For low manganese content, $x < 0.1$, a polaron theory[5] that assumes that unpaired Mn^{2+} spins respond paramagnetically to the carrier exchange field gives satisfactory agreement with optical experiments.[3,5,6] The large BMP energies predicted by this theory in crystals with high manganese content ($\simeq 0.3$ eV at $x = 0.3$) are not confirmed by experiment. The reason for this discrepancy is that in such materials polaron formation is severely inhibited by the antiferromagnetic, nearest-neighbor Mn^{2+}-Mn^{2+} interactions. The result is a much more complicated magnetic behavior than that of the dilute alloys. To avoid the difficult problem of calculating the Mn^{2+} magnetization under these circumstances, a phenomenological theory of polarons has been developed that uses the measured high-field magnetization of the host crystal as an input to determine the Mn^{2+} response.[7] This approach leads to a nonlinear Schrödinger equation for the polaron wave function that is equivalent, for small x (case of noninteracting Mn^{2+} spins), to the one derived by Spałek.[18] To calculate the BMP binding energy in the large-x regime, one has to replace the free-spin magnetization by the measured values. The result is that beyond $x = 0.2$, the polaron energy decreases with increasing x, whereas in the absence of such Mn^{2+}-Mn^{2+} interaction a

linear increase is predicted. For large x, most of the Mn^{2+} spins are "frozen out" of the polaron problem because the exchange field is not strong enough to break up their antiferromagnetic alignment. Figure 5 shows that the agreement between this theory and experimental results is excellent.

IV. CONCLUSIONS

The photoluminescence experiments described in the present paper give quantitative evidence of bound magnetic polaron formation in semimagnetic $Cd_{1-x}Mn_xTe$. They demonstrate that as the temperature is lowered the system continuously evolves from a fluctuation-dominated regime to a mean-field polaronlike regime. The binding energy of acceptor-bound MP increases with an increase of manganese content in the alloy up to about 37 meV at $x=0.2$. Beyond $x=0.2$ the polaron energy decreases with increasing x, as a result of the antiferromagnetic, nearest-neighbor Mn^{2+}-Mn^{2+} interactions. This general behavior and numerical values of polaron binding energies for different composition are in excellent agreement with the predictions of the phenomenological polaron theory that uses the measured high-field magnetization of the host crystal as an input to determine the Mn^{2+} response.

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