PHYSICAL REVIEW B VOLUME 47, NUMBER 15 15 APRIL 1993-I

Optical study of Mn^{2+} intraionic transitions in zinc-blende MnTe

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(Received 17 August 1992)

Mn^{2+} d-d^* multiplet transitions in zinc-blende MnTe were studied with photoluminescence, absorption, and magnetic circular dichroism spectroscopy. A simple ligand-field theory with Racah parameters, $B=0.045\,91$ eV, $C=0.4363$ eV, and $Dq=0.077\,63$ eV, can well reproduce the observed absorption bands from ${}^6A_1({}^6S)$ to ${}^4T_1({}^4G)$, ${}^4T_2({}^4G)$, ${}^4A_1({}^4G)$, ${}^4E({}^4G)$, ${}^4T_2({}^4D)$, ${}^4E({}^4D)$, and ${}^2T_2({}^2I)$ multiplets. The magnetic circular dichroism spectrum clearly showed the existence of the Zeeman effect for Mn^{2+} multiplet transitions. The effective g value of Mn^{2+} multiplets was roughly estimated to be ~ 2.2, which implies that the strong optical-absorption bands of Mn^{2+} d-d^* multiplets are nonmagnon sideband-type transitions.

I. INTRODUCTION

Diluted magnetic semiconductors[1] (DMS) have been attracting much interest both for the study of their unique optical and magnetic effects and for optoelectronic-device possibilities. $Cd_{1-x}Mn_xTe(0\leq x\leq 0.77)$ with zinc-blende structure, which is a prototype DMS system, has been extensively studied. However, considerable controversy exists in the literature regarding the nature of the optical transitions in $Cd_{1-x}Mn_xTe$ in the 2.0–2.3-eV energy range.[2,3]

Absorption measurements[4,5] up to $x=0.7$ showed two bands centered at ~ 2.4 and ~ 2.6 eV at liquid-He temperature. Lee, Ramdas, and Aggarwal[6] observed another band at ~ 2.18 eV in $Cd_{1-x}Mn_xTe$ for $x>0.4$ by piezomodulated reflectivity measurements. The energy of this peak did not show a noticeable compositional dependence. A Zeeman splitting was not observed either. They assigned the observed structure together with the two absorption bands to the crystal-field split Mn^{2+} d-d^* multiplet transitions: ${}^6A_1({}^6S)\rightarrow{}^4T_1({}^4G)(\sim 2.18\text{ eV})$;${}^6A_1({}^6S)\rightarrow{}^4T_2({}^4G)(\sim 2.4\text{ eV})$;${}^6A_1({}^6S)\rightarrow{}^4A_1^4E({}^4G)(\sim 2.6\text{ eV})$. Benecke, Busse, and Gumlich[7] made a tentative analysis of these peaks by using the Racah parameters B and C and the crystal-field parameter Dq. But only three observed bands were not enough for unambiguous assignments.

These transitions between $(3d)^5$ multiplets, namely from the ground state ${}^6S$ to the excited states ${}^4G$, are both electric dipole forbidden and spin forbidden in the free ion. But unexpectedly large absorption intensities on the order of $\sim 4000\text{ cm}^{-1}$ have been observed experimentally. Such strong d-d^* transitions[2] have also been observed in other DMS systems, such as $Cd_{1-x}Mn_xSe$.[8]

Lacueva and Overhauser[9] proposed a model in which the electric quadrupole transition, which is usually very weak, is enhanced by eight orders of magnitude by a collective, many-electron response of a host crystal to the electric field of a photon. But Villeret and Rodriquez[10] pointed out that the above superallowed quadrupole transition model is appropriate only for transitions having energies of 20 eV or more, and is not applicable to the Mn^{2+} d-d^* ${}^6S\rightarrow{}^4G$ transitions. Instead, they concluded that the transitions are of an electric-dipole nature and are parity allowed by the lack of inversion symmetry in T_d symmetry and spin allowed by the presence of the spin-orbit interaction. However, whether the lack of inversion symmetry in the ligand field can quantitatively explain the observed large optical absorption or not is still an open question.

MacKay *et al.*[11] proposed another model which can explain the allowed Mn^{2+} ${}^6A_1({}^6S)\rightarrow{}^4T_1({}^4G)$ transition. The photoluminescence (PL) energy of the Mn^{2+} ${}^6A_1({}^6S)\rightarrow{}^4T_1({}^4G)$ transition band in $Zn_{1-x}Mn_xS$ and $Cd_{1-x}Mn_xTe$ decreases with temperature increase up to ~ 60 K, and again increases with further temperature rise.[12] Such anomalous temperature dependence strongly suggests the influence of an inter-Mn^{2+} magnetic interaction on the optical transitions. Mackay *et al.* explained the anomalous temperature dependence in terms of an optical transition accompanied by a pair of spin flips of neighboring Mn^{2+} ions. In this model, one Mn^{2+} ion makes an electronic d-d^* transition, while an antiferromagnetically coupled neighboring Mn^{2+} ion makes a spin flip. This mechanism is analogous to the magnon sideband model[13] which was developed to explain the strong satellite absorption peaks observed in antiferromagnetic MnF_2.

One of the reasons for the controversy is the difficulty of unambiguous identification of the various Mn^{2+} intraionic transitions, since any features seen are already broad (or overlap) for x values at which they become fully observable ($x\sim 0.7$). The solubility limit of Mn^{2+} ions in $Cd_{1-x}Mn_xTe$ is $x=0.77$ in bulk crystals, and the small energy gap of $Cd_{1-x}Mn_xTe$ limited the observation of Mn d-d^* multiplet structures.

By using molecular-beam epitaxy, Durbin *et al.*[14] recently succeeded in growing thin films of zinc-blende MnTe with a wide band gap, which had been previously considered as hypothetical. Because when alloyed with a CdTe it forms $Cd_{1-x}Mn_xTe$, understanding of its magnetic and optical properties are indispensable for the clarification of the electronic structure of DMS systems. Band calculations,[15,16] magnetic susceptibility,[17] neutron scattering,[18] and magneto-optical effects[19] of MnTe, as well as photoluminescence and Raman scattering of CdTe/MnTe quantum wells,[14] have been reported in the literature.

In this paper, we report the results of our study on the Mn^{2+} intraionic transition in zinc-blende type MnTe in the antiferromagnetic ordered state. Because of the absence of the effects due to alloy disorder and wide band gap (~ 3.3 eV) of zinc-blende MnTe, absorption peaks due to the Mn^2 d-d^* multiplets can be clearly observed. PL and magnetic circular dichroism (MCD) data are also shown, and their relation with possible models are discussed.

II. EXPERIMENTS

Zinc-blende MnTe samples were grown by the ionized cluster beam method[20] on [0001]-oriented sapphire substrates. Pure zinc-blende phase [111]-oriented MnTe films were obtained at a substrate temperature of 300 °C by using a buffer layer of [111]-oriented CdTe of 1000-Å thickness. Two samples with MnTe layers of 5000 Å and 2-μm thickness were used in this study. The antiferromagnetic phase transition temperature was ~ 60 K.[17,19] A $Cd_{0.15}Mn_{0.85}Te$ sample was also grown to check the dependence of the energy of the photoluminescence peak in $Cd_{1-x}Mn_xTe$ as a function of composition.

The optical-absorption spectrum was measured in transmission using xenon lamp light. MCD was measured by applying the magnetic field along the light propagation direction (Faraday configuration) up to 12 k Gauss. MCD is the magnetic-field-induced difference between the optical-absorption coefficients for the two circular polarizations. The state of the polarization of input light was modulated between the $\sigma+$ and $\sigma-$ polarizations with 50 kHz by a photoelastic modulator. The transmitted light was detected by a photomultiplier tube and a lock-in amplifier. PL was measured by exciting the samples with 488-nm line of an argon laser. Samples were mounted on a cold finger of a closed-cycle He-gas refrigerator, and were cooled down to 15 K.

III. RESULTS AND DISCUSSIONS

The PL spectrum of MnTe at 15 K is shown in Fig. 1, together with that of $Cd_{0.15}M_{0.85}Te$. The peak position for MnTe is 2.103 eV, which is noticeably higher than the reported Mn^{2+} ${}^4T_1({}^4G) \rightarrow {}^6A_1({}^6S)$ PL peak positions of 2.020 eV for $Cd_{0.35}Mn_{0.65}Te$.[12] We assigned the PL peak to the Mn^{2+} ${}^4T_1({}^4G) \rightarrow {}^6A_1({}^6S)$-related transition because (1) its width of 0.10 eV is the same as the reported width[12] of the Mn d-d^* yellow photoluminescence in $Cd_{1-x}Mn_xTe$, (2) the compositional dependence of the PL peak positions of MnTe and $Cd_{0.15}Mn_{0.85}Te$ are compatible with the reported PL peak position of $Cd_{0.35}Mn_{0.65}Te$, and (3) the PL peak position of MnTe showed the anomalous temperature dependence[12] that is typical for Mn^{2+} intraionic PL in DMS with a minimum energy of 2.072 eV at ~ 50 K.

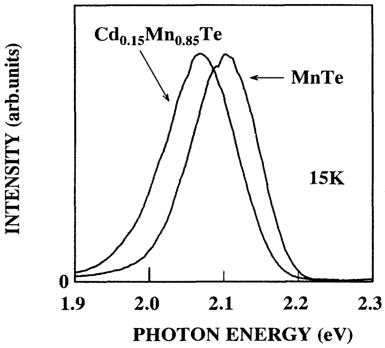

FIG. 1. Photoluminescence spectra of MnTe and $Cd_{0.15}Mn_{0.85}Te$ at $T = 15$ K. $E_{ex} = 2.54$ eV.

Due to the large band gap of zinc-blende MnTe, the optical-absorption spectrum clearly shows several peak structures (Fig. 2). Large optical absorption for photon energy higher than 3.2 eV is due to the $\Gamma_8 \rightarrow \Gamma_6$ band-to-band optical transition.[19] At an energy range lower than 2.3 eV, a strong interference pattern due to the multiple reflections within the films made it impossible to distinguish weak absorption peaks.

We tried to assign the observed features to the Mn^{2+} d-d^* multiplets by using basic ligand-field theory[21] in terms of the Racah parameters B and C and the crystal-field parameter Dq. Assigning the peaks at 2.397, 2.641 and 2.830 eV to ${}^6A_1({}^6S) \rightarrow {}^4T_2({}^4G)$, ${}^6A_1({}^6S) \rightarrow {}^4A_1^4E({}^4G)$, and ${}^6A_1({}^6S) \rightarrow {}^2T_2({}^2I)$, we determine values of the parameters to be $B = 0.04591$ eV, $C = 0.4363$ eV, and $Dq = 0.07763$ eV by a least-squares fit. From these parameter values, the energies of the $(3d)^5$ multiplets with respect to the Mn^{2+} ground state ${}^6A_1({}^6S)$ were calculated (Table I) and shown in Fig. 1 by vertical bars. Difficulties have been reported in explaining the absorption-band positions of $Cd_{1-x}Mn_xTe$ by a simple ligand-field theory. However, agreements between the observed peak energies and the calculated ones are surprisingly good. Although the ${}^6A_1({}^6S) \rightarrow {}^4T_1({}^4G)$ absorption band is not observed clearly, the calculated position of this absorption band at 2.175 eV is in accordance of the observed structure at ~ 2.18 eV in piezoreflection.[6]

In addition to the peaks assigned to the Mn^{2+} d-d^* multiplets, there seems to exist weak structure around

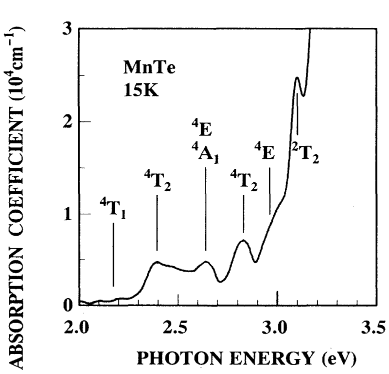

FIG. 2. The absorption spectrum of MnTe at 15 K. Mn^{2+} d-d^* multiplet energies calculated by a simple ligand-field theory with parameters $B = 0.04591$ eV, $C = 0.4363$ eV, and $Dq = 0.07763$ eV are also shown by vertical bars.

TABLE I. Observed and calculated energies of the Mn^{2+} d-d^* multiplets in T_d symmetry of zinc-blende MnTe. Racah parameters used for the calculations are $B = 0.045\,91$ eV, $C = 0.4363$ eV, and $Dq = 0.077\,63$ eV.

Observed energy (eV)	Assignment	Calculated energy (eV)
	${}^4T_1({}^4G)$	2.1751
2.397	${}^4T_2({}^4G)$	2.3966
2.641	${}^4A_1({}^4G), {}^4E({}^4G)$	2.6406
2.830	${}^4T_2({}^4D)$	2.8296
~2.97	${}^4E({}^4D)$	2.9620
3.101	${}^2T_2({}^2I)$	3.1019

2.47 eV. Its origin is not clear. A possible origin is an interference effect. But it is interesting that the energy difference of ~0.07 eV between this weak feature and the ${}^6A_1({}^6S) \rightarrow {}^4T_2({}^4G)$ absorption band is almost the same as the energy shift, probably a Stokes shift, of 0.07 eV of the PL peak from ${}^6A_1({}^6S) \rightarrow {}^4T_1({}^4G)$. This suggests that this weak feature is a kind of sideband ${}^6A_1({}^6S) \rightarrow {}^4T_2({}^4G)$ absorption band.

The MCD spectrum is shown in Fig. 3. MCD is the magnetic-field-induced difference between the optical-absorption coefficients for the two circular polarizations. The MCD signal was linear both in film thickness and in applied magnetic-field intensity. MCD peak positions did not show any magnetic-field dependence. Mn^{2+} intraionic transitions in DMS have been considered not to be affected by the external magnetic field.[6] But the MCD spectrum shown in Fig. 2 clearly shows the existence of a magneto-optic effect. The large MCD signal above 2.9 eV comes mainly from the $\Gamma_8 \rightarrow \Gamma_6$ interband transition at ~3.38 eV, which we had discussed in Ref. 19. We tried to estimate the Zeeman splitting energy and the effective g value. We made a plausible assumption that external magnetic field causes the Zeeman shift of optical-absorption spectra without changing the shape. Under this assumption, MCD is related to the absorption coefficient $k(E)$ by a relation,[19]

$$\theta(E) = -\frac{180}{4\pi}\Delta E\frac{dk(E)}{dE} . \tag{1}$$

ΔE is an energy difference between σ^+ and σ^- optical transitions induced by a Zeeman effect. For Mn^{2+} intraionic exciton transitions, ΔE is given as

$$\Delta E = 2\mu_B H(g_1 m_1 - g_0 m_0) , \tag{2}$$

where g_1 and $m_1 = \frac{3}{2}$ are the g factor and spin-projection quantum number of Mn^{2+} in the excited state, and g_0 and $m_0 = \frac{5}{2}$ those of the ground state; μ_B is the Bohr magneton. If we further assume that g factors in the ground and excited states are identical, i.e., $g_1 = g_2 = g$, ΔE is equal to $2g\mu_B H$.

dk/dE was numerically calculated from Fig. 2 and is given in Fig. 4. Equation (1) implies the same spectral forms for MCD and dk/dE spectra. But the two observed spectra are not completely the same. The reason is not clearly understood. The disagreement at an energy range higher than ~3 eV is due to the effect of the $\Gamma_8 \rightarrow \Gamma_6$ interband transition. Further study is needed to account for the spectral shape of MCD. However, the overall similarity between MCD and the dk/dE spectrum enables us to make a rough estimate of ΔE by using Eq. (1). ΔE, estimated from amplitude of the structures around 2.8 eV, was 0.030 meV/k Gauss, and that around 2.4 eV was 0.021 meV/k Gauss. By using these values, the effective g factor was estimated to be about 2.2 ± 0.5, which is nearly equal to the g factor of the free atom. The absence of the magnetic-field dependence of Mn d-d^* transitions has been reported.[6,11] But the expected Zeeman splitting for $g = 2$, i.e., ΔE of ~0.023 meV/k Gauss, is smaller than their experimental errors. Such a small Zeeman effect can be detected only by the polarization modulation technique used in this study.

Mackay *et al.*[11] proposed a magnon sideband-type model to explain the anomalous temperature dependence of Mn^{2+} photoluminescence. Since the photoluminescence process and the optical-absorption process are complementary processes, the strong absorption of Mn^{2+} must also be of magnon sideband type in this model. The magnon sideband transitions in antiferromagnetic MnF_2 have been intensively studied.[13] The magnon sideband transition process conserves the total spin-projection number, because a spin change of Mn^{2+} exciton excitation in a magnetic sublattice is cancelled by a spin change

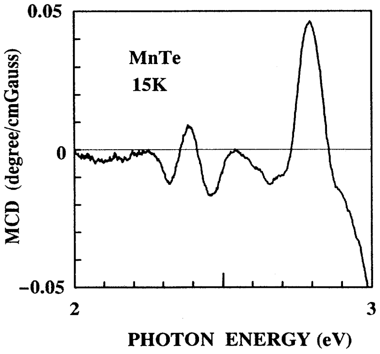

FIG. 3. The photon-energy dependence of magnetic circular dichroism MCD in MnTe at $T = 15$ K.

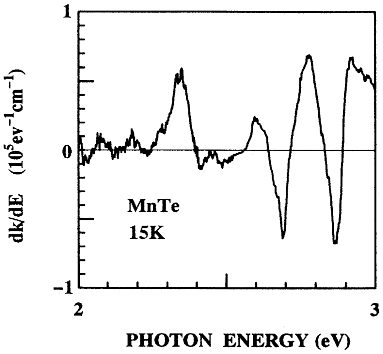

FIG. 4. The spectrum of the energy derivative of the optical-absorption coefficient dk/dE of MnTe at 15 K.

in a magnon excitation in the other antiferromagnetically coupled lattice. Then the magnon sideband transition does not show a Zeeman splitting.[13] Indeed, MacKay *et al.* argued that the magnetic-field independence of the PL transition energy supported their magnon sideband-type model for Mn^{2+} transitions in DMS. However, as mentioned above, the Mn^{2+} d-d^* transitions do show the Zeeman effect and their g factors are nearly equal to the g factor of the free Mn^{2+} ion. Our results indicate that the magnon sideband-type model is not appropriate for the Mn^{2+} d-d^* transitions in DMS. The magnon sideband model for DMS was proposed to explain the anomalous temperature dependence of their PL peak positions. At present, it is not clear how other proposed models explain it. It should be noted that the magnetic susceptibility of DMS deviates from a simple Curie-Weiss law,[22] which implies that even a temperature higher than the magnetic-phase-transition temperature there exists strong local magnetic correlation. As MacKay *et al.*[11] pointed out, the local mean field can affect the energy level of the Mn^{2+} d-d^* transition. Such a magnetic effect on Mn^{2+} d-d^* transitions may be possible even for zero-magnon optical transitions.

The surprisingly good agreement between the observed absorption peak positions and the calculated ones by a ligand-field theory seems to support the localized nature of the Mn^{2+} electronic state in $Cd_{1-x}Mn_xTe$. However, it is well known that the 3d electrons in DMS are strongly hybridized with the anion p states. This strong hybridization is essential for the occurrence of interesting magnetic and optical effects such as giant magneto-optical effects. In order to treat such coexistence of the localized aspect and the one-electron delocalized aspect of the Mn^{2+} 3d electron, one needs a configuration interaction model.[23] Detailed comparison between the experimentally observed absorption and MCD spectra with such theoretical study is expected.

IV. CONCLUSIONS

PL, absorption, and MCD spectra of zinc-blende MnTe films were measured. Structures in optical-absorption spectra are well explained by a simple ligand-field theory. MCD spectra clearly show that Mn^2 d-d^* multiplet transitions show magneto-optic effects. The effective g factors were estimated to be ~ 2.2, which implies that the magnon sideband-type model is not appropriate for Mn^{2+} optical transitions in DMS.

ACKNOWLEDGMENTS

The author is grateful to K. Takahashi for his assistance in film preparations. Stimulating discussions with M. Umehara, Y. Yamaguchi, and H. Akinaga are also acknowledged. He also thanks K. Tanaka and S. Yoshida for their encouragement.

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