

## Pressure dependence of the optical absorption edge of $\text{Cd}_{1-x}\text{Mn}_x\text{Se}$

S. Jiang, S. C. Shen, \* Q. G. Li, H. R. Zhu, and G. L. Ju

Laboratory for Infrared Physics, Shanghai Institute of Technical Physics, Academia Sinica,  
420 Zhong Shan Bei Yi Road, Shanghai, China

W. Giriat

Centro de Física, Instituto Venezolano de Investigaciones Científicas, Apartado Postal 21827,  
Caracas 1020A, Venezuela

(Received 5 August 1988; revised manuscript received 22 June 1989)

The effect of pressure on the absorption edge of  $\text{Cd}_{1-x}\text{Mn}_x\text{Se}$  with different compositions has been measured. A pinninglike behavior has been observed for the mixed crystal with  $x=0.45$ , that is, the pressure coefficient decreases from about  $6 \times 10^{-3}$  eV/kbar at low pressures to almost zero at pressures  $P > 10$  kbar. The pinning is attributed to the effect of the intraionic transitions of  $\text{Mn}^{2+}$ . Furthermore, the energy of the absorption edge becomes independent of the polarization of incident light for the same sample at pressures at which the absorption edge is pinned, which confirms the above interpretation. The relation between phase-transition pressure and composition in  $\text{Cd}_{1-x}\text{Mn}_x\text{Se}$  is also presented.

$\text{Cd}_{1-x}\text{Mn}_x\text{Se}$  is a semimagnetic semiconductor<sup>1-3</sup> (SMSC) which crystallizes in the wurtzite structure for  $0 < x < 0.5$ .<sup>4</sup> Multiple phases coexist in the mixed crystals in the composition range of  $0.5 < x < 0.95$  while pure MnSe itself may crystallize in three different forms. Due to the difference in structure, the physical properties of mixed crystals may be quite different too, but only the wurtzite structure is of interest in this work.

Several interesting effects have been observed in SMSC materials in addition to the magnetic behavior, such as the intraionic  $d-d$  transition between levels of the  $\text{Mn}^{2+}$  and their influence on interband transitions in some SMSC's with a wide band gap.<sup>5-8</sup> Shan *et al.*<sup>5</sup> found for the first time the anomalous pressure coefficient of the absorption edge in  $\text{Cd}_{1-x}\text{Mn}_x\text{Te}$  with large values of  $x$ , which is caused by the  ${}^6A_1 \rightarrow {}^4T_1$  intraionic  $d-d$  transition of  $\text{Mn}^{2+}$ . The  ${}^6A_1$  state of  $\text{Mn}^{2+}$  in  $\text{Cd}_{1-x}\text{Mn}_x\text{Te}$  can hybridize strongly with the valence band, apparently increasing the absorption strength of the  ${}^6A_1 \rightarrow {}^4T_1$  transition. When the energy of the  ${}^6A_1 \rightarrow {}^4T_1$  transition is close to that of the interband excitation, the behavior of the absorption edge can be remarkably affected by this transition. The optical absorption of  $\text{Mn}^{2+}$  in  $\text{Zn}_{1-x}\text{Mn}_x\text{Se}$  (Ref. 9) is different from that in  $\text{Cd}_{1-x}\text{Mn}_x\text{Te}$ , because the energy gap is wider and the hybridization of  $3d$  levels of  $\text{Mn}^{2+}$  with the valence band is weaker in the Se compounds. We have observed three absorption peaks associated with the intraionic  $d-d$  transitions of  $\text{Mn}^{2+}$  for this mixed crystal at 77 K and different pressures.<sup>10</sup> Not much attention has been paid to the  $d$  levels of  $\text{Mn}^{2+}$  in  $\text{Cd}_{1-x}\text{Mn}_x\text{Se}$ . In addition, no data are available in the literature with regard to the effect of pressure on the interband transition of  $\text{Cd}_{1-x}\text{Mn}_x\text{Se}$ . In this paper we report the pressure dependence of the absorption edge of  $\text{Cd}_{1-x}\text{Mn}_x\text{Se}$  for different compositions. We find a pinninglike behavior of

the transition energy for the sample with  $x=0.45$ . We also report the pressure dependence of the polarized  $\Gamma_9 \rightarrow \Gamma_7$  and  $\Gamma_7 \rightarrow \Gamma_7$  transitions which become degenerate in energy for the sample with  $x=0.45$  at pressures at which the absorption edge is pinned.

A gasketed diamond-anvil cell and a 4:1 methanol-ethanol pressure medium are used to produce a hydrostatic-pressure environment. Pressures are measured by the ruby luminescence method. In optical absorption measurements we use a tungsten lamp as the light source, a 51W monochromator as the spectrometer, and an R456 photomultiplier or Si and Ge photodiodes as detectors. A microcomputer is used to control the measurement and collect the data. With this arrangement, absorption spectra and modulated absorption spectra can be measured in the wavelength range varying from 0.4 to 1.6  $\mu\text{m}$  and the pressure range of 0–100 kbar at both room and low temperatures. The  $\text{Cd}_{1-x}\text{Mn}_x\text{Se}$  single crystals were grown by the use of the modified Bridgman method. The samples were cut from a single-crystal ingot and mechanically polished to a thickness of about 30  $\mu\text{m}$ , then ground or etched finely to 10–20  $\mu\text{m}$ .

Absorption spectra of  $\text{Cd}_{0.7}\text{Mn}_{0.3}\text{Se}$  in the interband transition region under different pressures are shown in Fig. 1. We take the energy position of the upper turning point of the absorption curves, where the absorption coefficient is around  $5 \times 10^3 \text{ cm}^{-1}$ , as the absorption edge or the observed band gap. For measuring the pressure coefficient of the absorption edge, we simply determine the energy shift of the absorption edge at optical densities of about 2.9. The absorption edge shifts to higher energy with increasing pressure at a rate of  $(6.1 \pm 0.1) \times 10^{-3}$  eV/kbar.

The shifts of the absorption edges for different samples with different compositions are similar to that of  $\text{Cd}_{0.7}\text{Mn}_{0.3}\text{Se}$ , except for the sample with  $x=0.45$ . The

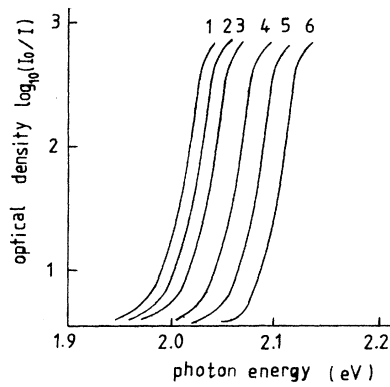


FIG. 1. Absorption spectra of  $\text{Cd}_{0.7}\text{Mn}_{0.3}\text{Se}$  at different pressures. The pressures for the curves 1–6 are 0, 2.0, 3.5, 9.0, 13.5, and 20.0 kbar, respectively.

dependence of the absorption edges or the energy gap on pressure for six measured samples with different composition is summarized in Table I and Fig. 2. Open circles in Fig. 2 indicate the experimental values of the absorption edge observed at different pressures and the curves are the least-squares fits of the formula  $E_g = E_g^0 + aP + bP^2$  to the experimental data. The first- and second-order pressure coefficients are listed in Table I. We also list in Table I the linear pressure coefficient for CdSe estimated by means of the dielectric theory.<sup>11</sup> As shown in Fig. 2 a “turning-point-like” behavior occurs in the shift of the absorption edge for  $\text{Cd}_{0.55}\text{Mn}_{0.45}\text{Se}$  at about 10 kbar. The absorption edge of  $\text{Cd}_{0.55}\text{Mn}_{0.45}\text{Se}$  hardly shifts with further increase of pressure after the turning point, as if it were pinned.

In an investigation of the dependence of the energy gap on temperature for the same material reported by Ma,<sup>12</sup> a similar turning point was observed at about 200 K. Below this temperature the shift of the energy gap with further decrease of temperature slowed down abruptly. The energy positions of the turning point in both temperature- and pressure-dependent measurements are almost the same.

A phase transition occurs under pressure for all the samples measured. The new phase is opaque to visible light and its absorption edge is beyond the spectral region of our instrument. The pressure for the phase transition is dependent on  $x$ , as is shown in Fig. 3 and also listed in the last row of Table I.

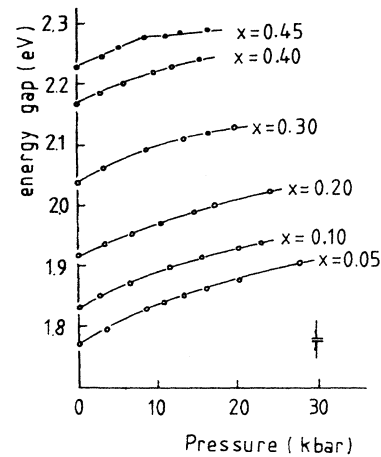


FIG. 2. The energy gap of  $\text{Cd}_{1-x}\text{Mn}_x\text{Se}$  with different  $x$  as a function of pressure. The error is indicated by the arrows.

In order to understand the anomaly of the dependence of the absorption edge on pressure for the mixed crystal  $\text{Cd}_{0.55}\text{Mn}_{0.45}\text{Se}$ , we measure the absorption spectra again for the samples  $\text{Cd}_{0.95}\text{Mn}_{0.05}\text{Se}$  and  $\text{Cd}_{0.55}\text{Mn}_{0.45}\text{Se}$  by using polarized incident light which allows one to observe the  $\Gamma_9 \rightarrow \Gamma_7$  and  $\Gamma_7 \rightarrow \Gamma_7$  interband transitions separately.<sup>13</sup> The results are shown in Fig. 4.

The degeneracy of the  $\Gamma_9$  and  $\Gamma_7$  valence bands in the zinc-blende structure is lifted at the  $\Gamma$  point of the wurtzite structure. The transition between the  $\Gamma_9$  valence band and  $\Gamma_7$  conduction band is observed for light with polarization vector perpendicular to the  $C$  axis ( $\mathbf{E} \perp \mathbf{C}$ ), while the transition between the  $\Gamma_7$  valence band and  $\Gamma_7$  conduction band is observed for  $\mathbf{E} \perp \mathbf{C}$  as well as  $\mathbf{E} \parallel \mathbf{C}$ . Thus we can measure the pressure dependence of the  $\Gamma_7 \rightarrow \Gamma_7$  and  $\Gamma_9 \rightarrow \Gamma_7$  transitions of  $\text{Cd}_{1-x}\text{Mn}_x\text{Se}$  separately by polarized absorption experiments. As shown in Fig. 4, the transition energies for  $\Gamma_7 \rightarrow \Gamma_7$  ( $\mathbf{E} \parallel \mathbf{C}$ ) and  $\Gamma_9 \rightarrow \Gamma_7$  ( $\mathbf{E} \perp \mathbf{C}$ ) for the sample with  $x = 0.05$  differ from each other, but their pressure coefficients are almost the same. The dependences of the polarized absorption edges on pressure for  $\text{Cd}_{0.55}\text{Mn}_{0.45}\text{Se}$  are different from that of  $\text{Cd}_{0.95}\text{Mn}_{0.05}\text{Se}$ . The splitting between the  $\Gamma_7 \rightarrow \Gamma_7$  and  $\Gamma_9 \rightarrow \Gamma_7$  transitions decreases with increasing pressure. At pressures  $P > 10$  kbar, the optical absorption no longer shows a polarization dependence; the pressure

TABLE I. The absorption edge energies and their dependences on pressures for  $\text{Cd}_{1-x}\text{Mn}_x\text{Se}$  with different  $x$ .

Sample	$E_g^0$ (eV)	$a$ ( $10^{-3}$ eV/kbar)	$b$ ( $10^{-5}$ eV/kbar <sup>2</sup> )	$P_t$ (kbar)
CdSe		6.9 (theory)		
$\text{Cd}_{0.5}\text{Mn}_{0.95}\text{Se}$	$1.775 \pm 0.002$	$5.7 \pm 0.1$	-4.4	$28.5 \pm 1.0$
$\text{Cd}_{0.10}\text{Mn}_{0.90}\text{Se}$	$1.882 \pm 0.002$	$5.8 \pm 0.1$	-6.4	$27.3 \pm 1.5$
$\text{Cd}_{0.20}\text{Mn}_{0.80}\text{Se}$	$1.908 \pm 0.002$	$5.9 \pm 0.1$	-4.9	$25.7 \pm 1.5$
$\text{Cd}_{0.30}\text{Mn}_{0.70}\text{Se}$	$2.023 \pm 0.002$	$6.1 \pm 0.1$	-8.5	$23.4 \pm 1.5$
$\text{Cd}_{0.40}\text{Mn}_{0.60}\text{Se}$	$2.164 \pm 0.002$	$6.1 \pm 0.2$	-1.1	$19.3 \pm 1.5$
$\text{Cd}_{0.45}\text{Mn}_{0.55}\text{Se}$				$17.8 \pm 1.8$

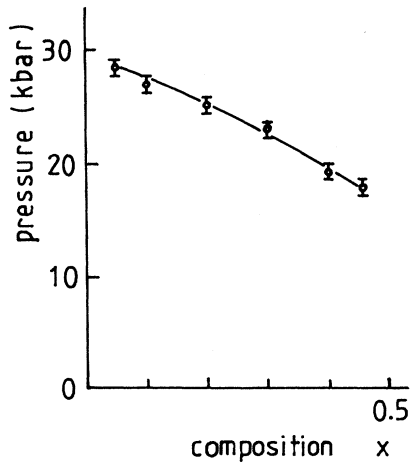


FIG. 3. The relation between the pressure of phase transition for  $\text{Cd}_{1-x}\text{Mn}_x\text{Se}$  and the composition  $x$ . The error bars are indicated.

coefficient decreases notably and the pinninglike behavior is observed again.

We can explain qualitatively the anomaly described above by considering the effect of intraionic  $d-d$  transition of  $\text{Mn}^{2+}$ . In terms of the crystal-field theory,<sup>14</sup> the  ${}^6A_1 \rightarrow {}^4T_1$  intraionic transitions of  $\text{Mn}^{2+}$  in  $\text{Cd}_{1-x}\text{Mn}_x\text{Se}$ , like those in  $\text{Cd}_{1-x}\text{Mn}_x\text{Te}$ ,<sup>5</sup> have a negative pressure coefficient. For  $\text{Cd}_{1-x}\text{Mn}_x\text{Se}$  with higher  $x$  value, such as  $x=0.45$ , the  ${}^6A_1 \rightarrow {}^4T_1$  transition of  $\text{Mn}^{2+}$  can be degenerate with the interband transition and the  ${}^6A_1$  state (the ground state of the  $d$  electron of  $\text{Mn}^{2+}$ ) can be hybridized with the top of the valence band. This is similar to the case of  $\text{Cd}_{1-x}\text{Mn}_x\text{Te}$  with large  $x$  values.<sup>5</sup> The interband transitions and the absorption edge of the mixed crystals can be affected significantly by the  ${}^6A_1 \rightarrow {}^4T_1$  hybridized transition, and the shift of the observed absorption edge with pressure

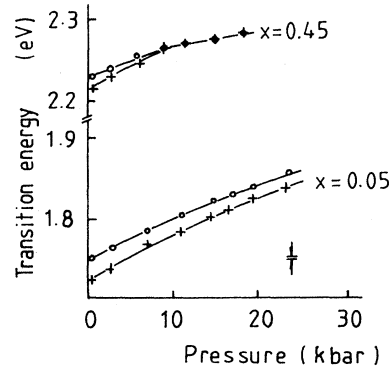


FIG. 4. The pressure dependence for transition energies of  $\Gamma_7 \rightarrow \Gamma_7$  ( $\circ$ ) and  $\Gamma_9 \rightarrow \Gamma_7$  ( $+$ ). The error is indicated by the arrows.

can be pinned. The polarization experiment further confirms this conclusion. The hybridization of ground-state  $3d^5$  levels of  $\text{Mn}^{2+}$  with the top of the valence band and probably also the excited state with the bottom of the conduction band results in a loss of the polarization dependence of the absorption edge under high pressure. The energy of the  ${}^6A_1 \rightarrow {}^4T_1$  transition of  $\text{Mn}^{2+}$  determined in the experiment is about 2.3 eV, which basically agrees with the values obtained by other measurements.<sup>12,15</sup> The  ${}^6A_1 \rightarrow {}^4T_1$  transition controls the observed absorption edge and changes the sign of the pressure coefficient of the absorption edge from positive to negative in  $\text{Cd}_{1-x}\text{Mn}_x\text{Te}$  with  $x > 0.5$ . This effect is not observed in  $\text{Cd}_{1-x}\text{Mn}_x\text{Se}$ . When the content of  $\text{Mn}^{2+}$ , that is,  $x$ , is increased further, the structure of  $\text{Cd}_{1-x}\text{Mn}_x\text{Se}$  will become complicated. Thus the pinning effect or the pinninglike effect of the absorption edge under high pressure is probably the most significant evidence of the influence of the  $3d^5$  intraionic transition to be observed in this SMSC Se-based mixed crystal.

\*Also at Center of Condensed Matter and Radiation Physics, CCAST (World Laboratory), P.O. Box 8730, Beijing, China.

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