

## Raman-scattering study of the high-pressure phase transition in $\text{Zn}_{1-x}\text{Mn}_x\text{Se}$

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Optical phonons of the mixed crystal  $\text{Zn}_{1-x}\text{Mn}_x\text{Se}$  ( $0 \leq x \leq 0.33$ ) in the zinc-blende phase are investigated by Raman scattering. The optical phonons of  $\text{Zn}_{1-x}\text{Mn}_x\text{Se}$  exhibit behavior intermediate between the two-mode and one-mode situations. The LO phonon of ZnSe continuously evolves into that of the "hypothetical" zinc-blende MnSe whereas the TO phonon and one component of the impurity mode merge into the gap mode of MnSe. The other component of the impurity mode transforms into the TO phonon of MnSe. Under hydrostatic pressure, in contrast to pure ZnSe, the mixed crystals undergo a high-pressure phase transition between 28 and 52 kbar depending on the composition. A new Raman peak appears in the high-pressure phase, which shows marked softening. When the pressure is reduced, the reverse transition occurs at a significantly lower pressure. At pressures below the reverse transition, the mixed crystal appears to be a mixture of the zinc-blende and another phase whose structure is closely related to that of the high-pressure phase. The energy of the  $\text{Mn}^{2+}$  internal transition shows a negative pressure coefficient.

### I. INTRODUCTION

Properties of semiconductor alloys have gained special importance in view of the role they play in the behavior of devices utilizing them. In this context it is useful to establish the nature of the vibrational spectra characterizing the alloys.<sup>1,2</sup> This information is also valuable in view of many fundamental aspects of the physics of alloys. Zone-center optical phonons in semiconducting alloys show a variety of behavior patterns; they exhibit "one-mode," "two-mode," or an "intermediate-mode" behavior depending on the vibrational characteristics of the end members.<sup>3</sup> The pressure dependence of the vibrational modes provides additional insight into the nature of the lattice vibrations. Such information is important in characterizing strained-layer superlattices and heterostructures where the constituents have different lattice constants.

Diluted magnetic semiconductors (DMS's), mixed crystals of tetrahedrally coordinated II-VI semiconductors where a fraction of cations is replaced by a magnetic element like  $\text{Mn}^{2+}$ , are of special interest due to their unique combination of semiconducting and magnetic properties.<sup>4</sup> The recent successful fabrication of DMS superlattices using the molecular-beam-epitaxy technique<sup>5</sup> has stimulated interest in the DMS heterostructures which incorporate the properties of the bulk in specially interesting ways and make way for novel devices.

The zone-center optical phonons in some of the DMS alloys have been investigated at ambient pressure,<sup>6</sup> e.g., Raman scattering studies show that  $\text{Cd}_{1-x}\text{Mn}_x\text{Te}$  exhibits a two-mode behavior whereas  $\text{Zn}_{1-x}\text{Mn}_x\text{Te}$  displays an interesting intermediate-mode behavior. We have carried out Raman scattering studies on  $\text{Zn}_{1-x}\text{Mn}_x\text{Se}$  at ambient pressure as well as at high hydrostatic pressures accessible with a diamond anvil cell (DAC).

A number of tetrahedrally coordinated III-V, and II-VI compound semiconductors as well as group-IV semiconductors undergo a high-pressure phase transition to the  $\beta$ -Sn metallic phase (body-centered tetragonal) around or above 100 kbar.<sup>7-10</sup> Optical absorption and luminescence measurements show that the band gap increases with pressure in the low-pressure phase.<sup>11-13</sup> Some of the semiconductors like the Cd chalcogenides, e.g.,  $\text{Cd}_{1-x}\text{Mn}_x\text{Te}$ , experience an intermediate-phase transition to a NaCl structure at a much lower pressure before they transform into the  $\beta$ -Sn structure.<sup>14,15</sup> It is interesting to note that pure ZnSe undergoes a transition from the zinc-blende to the  $\beta$ -Sn structure at 137 kbar (Ref. 9) without this intermediate transition; on the other hand, recent x-ray measurements on  $\text{Zn}_{1-x}\text{Mn}_x\text{Se}$  show that the mixed crystals experience an intermediate transition at a much lower pressure.<sup>16</sup> This evidence provided us with additional motivation to investigate pressure-induced phase transitions and establish some of the pressure-dependent parameters in  $\text{Zn}_{1-x}\text{Mn}_x\text{Se}$ .

In this paper we report the result of a detailed Raman scattering investigation of the zone-center optical phonons and the intermediate high-pressure phase transition in  $\text{Zn}_{1-x}\text{Mn}_x\text{Se}$  which we conducted by studying the behavior of the zone-center optical phonons as a function of hydrostatic pressure in a diamond anvil cell.

### II. EXPERIMENT

The  $\text{Zn}_{1-x}\text{Mn}_x\text{Se}$  occurs in a cubic zinc-blende structure in the composition range  $0 \leq x \leq 0.30$ , and in a wurtzite structure for  $0.33 \leq x \leq 0.57$ .<sup>17</sup> The crystals used in the present investigation were grown by the Bridgman method. Polarized Raman scattering measurements were made on oriented single crystals of zinc-blende structure, in the back-scattering configuration as well as in the right-angle scattering geometry. Raman

spectra were excited with laser power  $P_L \leq 20$  mW, with the 4880 and 5145 Å lines of an Ar<sup>+</sup> laser and the 6471 Å line of a Kr<sup>+</sup> laser. Raman scattering measurements at high pressure were carried out in a gasketed DAC of NBS design<sup>18</sup> in the back-scattering configuration. The precompressed Inconel X750 with a 300 μm circular hole was used as a gasket. A 4:1 methanol-ethanol mixture was used as a pressure-transmitting medium. The pressure in the diamond anvil cell was measured using the standard ruby-fluorescence technique.<sup>19</sup> A computer-controlled double-triple monochromator and a standard photon-counting unit were used to analyze the scattered radiation.

### III. RESULTS AND DISCUSSIONS

#### A. Polarized Raman measurements on oriented single crystals at ambient pressure

ZnSe in the zinc-blende structure has only one Raman-active polar phonon of  $F_2$  symmetry. Figures 1(a) and 1(b) show the Raman spectra of pure ZnSe and that of the mixed crystal  $Zn_{1-x}Mn_xSe$  ( $x=0.33$ ), respectively. Spectra were obtained in the  $y'(xz')\bar{y}'$  scattering configuration, where  $x \parallel [100]$ ,  $y' \parallel [011]$ , and  $z' \parallel [0\bar{1}1]$ . In this configuration both LO and TO phonons are allowed. Note that in the mixed crystal a new

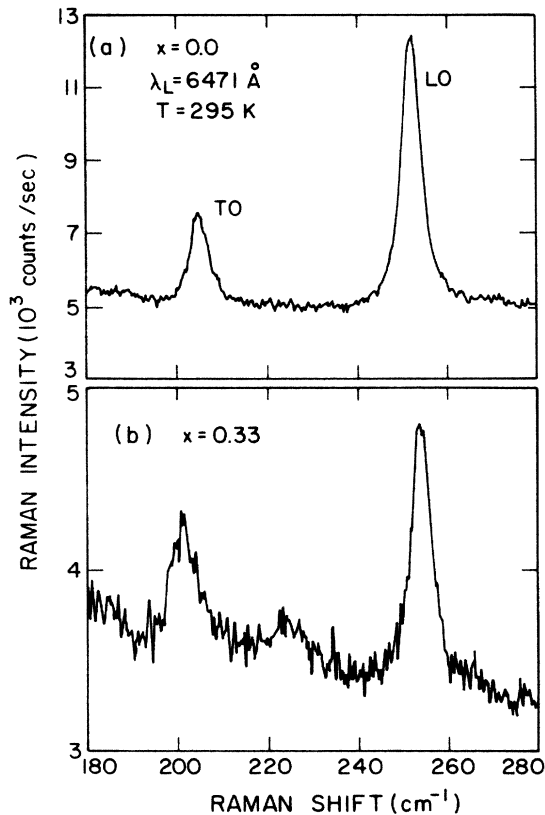


FIG. 1. Raman spectra of (a) pure ZnSe with the laser wavelength  $\lambda_L=4880$  Å, and (b)  $Zn_{1-x}Mn_xSe$  ( $x=0.33$ ) with  $\lambda_L=6471$  Å. Spectra were obtained in the back scattering configuration  $y'(xz')\bar{y}'$ , where  $x \parallel [100]$ ,  $y' \parallel [011]$ , and  $z' \parallel [0\bar{1}1]$ .

peak appears between LO and TO frequencies which we assign to the impurity mode of Mn in ZnSe, in the low  $Mn^{2+}$  concentration limit. Polarized Raman measurements in the right-angle scattering geometry reveal the LO and TO components of this impurity mode whose frequencies are not very far apart.

The composition dependence of the zone-center optical phonons in the mixed crystals is shown in Fig. 2. In the context of the multimode behavior of this system, it is important to consider different theoretical models of the long-wavelength optical phonons in a mixed crystal  $A_{1-x}B_xC$ . In the initial studies on the zone-center optical phonons in such alloys a model called random element isodisplacement was developed. (See, e.g., the review by Chang and Mitra.<sup>2</sup>) This predicts the two extreme types of behavior, viz., one-mode behavior where the mixed crystal has a single mode whose frequency varies continuously between the values corresponding to the end members or a two mode behavior where two optical phonon frequencies are observed which are close to the frequencies of the end members and can be identified as AC-like and BC-like modes. The criteria which favor one or the other behavior pattern have been discussed in the literature. Genzel *et al.*<sup>3</sup> proposed another theoretical model which predicts two additional types of intermediate-mode behavior besides the traditional one-mode and two-mode types. [See, for example, Figs. 1(b) and 1(c) of Ref. 3.] As we see in Fig. 2, the zone-center optical phonons of  $Zn_{1-x}Mn_xSe$  crystals exhibit an intermediate-mode behavior of the type (b) where the Mn impurity mode in ZnSe lies between the LO and TO frequencies whereas the Zn impurity mode in the hy-

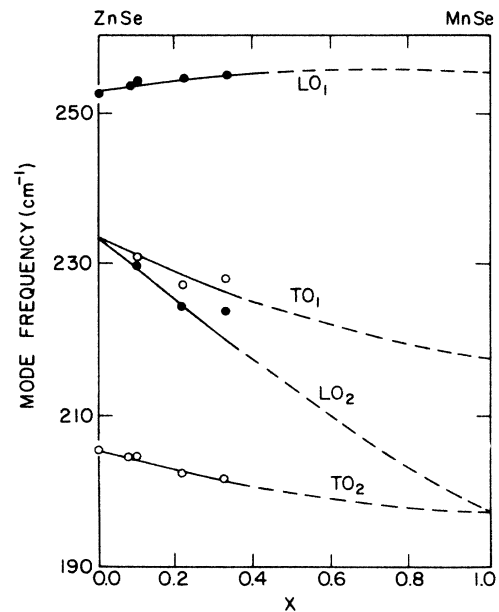


FIG. 2. Composition dependence of the optical phonon frequencies in  $Zn_{1-x}Mn_xSe$ . Solid and dashed curves are guides for the eye. The assignments of the modes for the intermediate-mode behavior follow the scheme in Genzel *et al.*<sup>3</sup>

pothetical zinc-blende MnSe lies below the corresponding LO-TO range<sup>20</sup> and hence is a "gap" mode. A similar intermediate-mode behavior is observed in  $Zn_{1-x}Mn_xTe$  also.<sup>6</sup>

### B. High-pressure Raman measurements in diamond anvil cell

Figure 3 shows the Raman spectra of pure ZnSe at (a) ambient and (b) 36 kbar pressure. Note that the Raman lines due to LO and TO phonons shift to higher frequencies as pressure is increased. The dependence of the LO and TO frequencies on pressure is shown in Fig. 4. From the slope of the pressure dependence, we obtained the mode Grüneisen parameters,  $\gamma_i = (1/\beta\omega_i)(\partial\omega_i/\partial P)$ , which are given in Table I; here  $P$  is the pressure,  $\beta$  the isothermal compressibility, and  $\omega_i$  the mode frequency. It is evident from Fig. 4 that the phonon frequencies while decreasing and increasing the pressure match, and as expected, no phase transition is observed up to 55 kbar. The LO-TO splitting decreases with increasing pressure suggesting an increase of covalency with pressure.<sup>18</sup>

Figure 5 shows the Raman spectra of the  $Zn_{1-x}Mn_xSe$  ( $x=0.08$ ) at three different pressures. As in pure ZnSe, the LO and TO frequencies in  $Zn_{1-x}Mn_xSe$  also increase with pressure up to 28 kbar, as can be seen in Fig. 5(b). With a further increase of pressure, a new Raman peak, labeled as A in Fig. 5(c), appears suggesting that a structural phase transition has occurred at  $32 \pm 4$  kbar. In the high-pressure phase, the frequency of the new mode A decreases as the pressure is increased. The peak labeled B has a frequency close to that of TO phonon in the zinc-blende phase but with a different pressure dependence. When the pressure is reduced from the highest pressure applied, a "reverse" transition occurs at  $22 \pm 3$  kbars, at significantly lower pressure than that of the forward transition. After the reverse transition has occurred, an additional peak labeled C appears between LO and TO phonons of the zinc-blende phase as shown in Fig. 6(b).

The behavior of the LO and TO frequencies and that of the peaks A, B, and C as a function of pressure is shown in Fig. 7 with increasing as well as decreasing the applied pressure. Note that the pressure dependence of the LO phonon exhibits a small discontinuity across the forward and the reverse transitions. The new peak A in

TABLE I. Mode Grüneisen parameter,  $\gamma$ , of zone-center optical phonons in  $Zn_{1-x}Mn_xSe$ . Isothermal bulk modulus is obtained from Ref. 26. Previously reported values for pure ZnSe are also included for comparison. The numbers in the parenthesis give the accuracy of the parameter in the last or the last two significant numbers.

$x$	$\gamma$ (TO)	$\gamma$ (LO)	$\gamma$ (Impurity mode)
0.0 <sup>a</sup>	1.4 <sup>a</sup>	0.9 <sup>a</sup>	
0.0	1.55(4)	0.79(4)	
0.08	1.64(5)	1.04(4)	
0.15	1.66(5)	1.06(4)	1.30(15)
0.33	1.48(5)	0.96(4)	

<sup>a</sup>Reference 7.

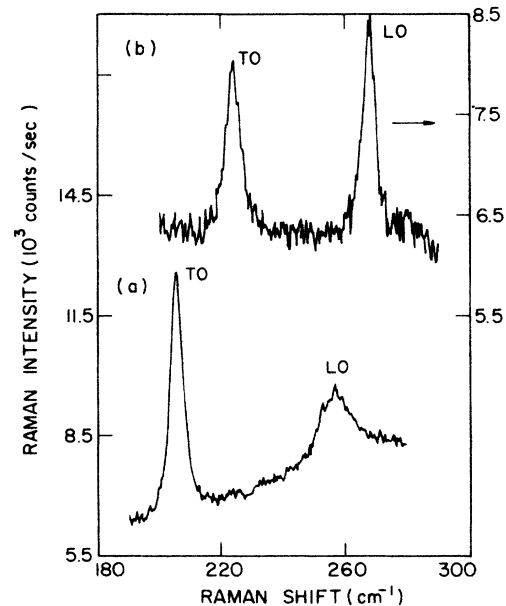


FIG. 3. Raman spectra of pure ZnSe (a) at ambient pressure with  $\lambda_L = 4880 \text{ \AA}$  and (b) at 36 kbar with  $\lambda_L = 5145 \text{ \AA}$ .

the high-pressure phase shows marked softening as a function of pressure. When the pressure is reduced, the frequency of peak B initially reduces and then starts increasing in a manner similar to that of peak A. Across the reverse transition both of these peaks merge into a single peak C whose frequency continues to increase as

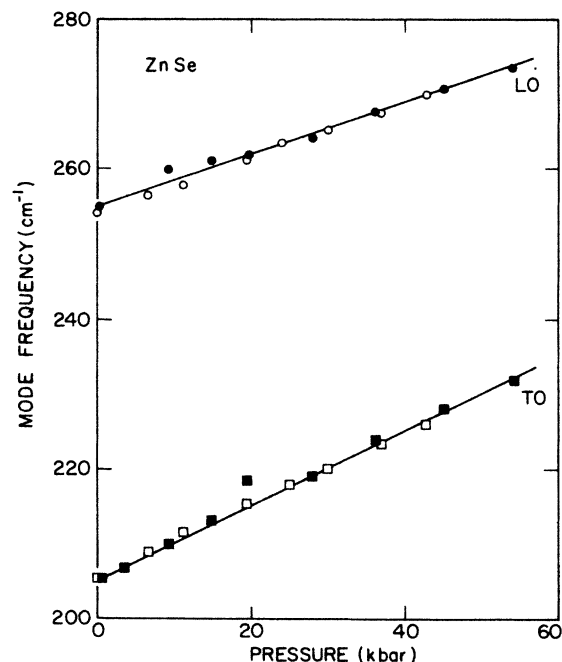


FIG. 4. LO and TO phonon frequencies in pure ZnSe as a function of hydrostatic pressure. Solid symbols, frequencies obtained with increasing pressure; open symbols, with decreasing pressure. The straight lines through the points are the linear least-squares fits to the data.

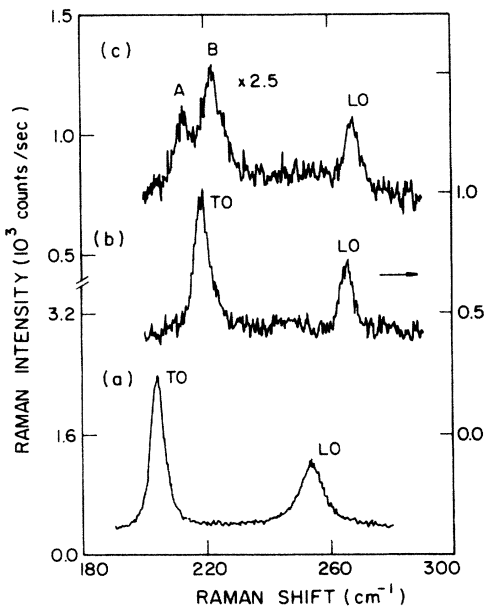


FIG. 5. Raman spectra of  $Zn_{1-x}Mn_xSe$  for  $x=0.08$  at three different pressures as the pressure is increased. (a) at ambient pressure with  $\lambda_L=4880 \text{ \AA}$ , (b) at 28 kbar with  $\lambda_L=4880 \text{ \AA}$ , and (c) at 36 kbar with  $\lambda_L=5145 \text{ \AA}$ .

the pressure is reduced further. After the reverse transition has occurred, the LO and TO phonons reappear and retrace their pressure dependence in the zinc-blende phase. The presence of the new peak C, even when the pressure is fully released, and the reappearance of the LO and TO frequencies characteristic of the zinc-blende phase suggests that below the reverse transition pressure the  $Zn_{1-x}Mn_xSe$  exists probably as a mixture of the zinc-blende phase and another phase which is closely related to the high-pressure phase. The pressure depen-

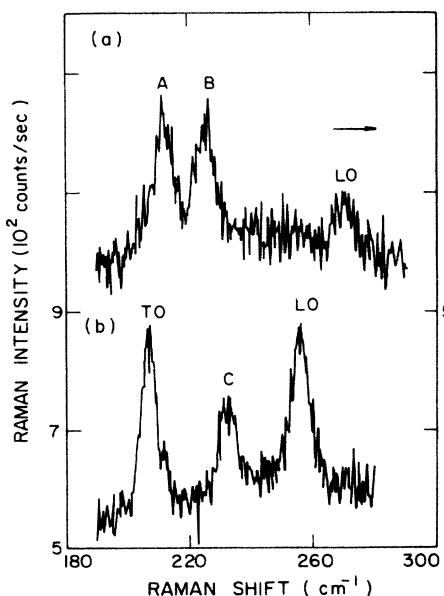


FIG. 6. Raman spectra of the  $Zn_{1-x}Mn_xSe$  for  $x=0.08$  at different pressures as the pressure is decreased. (a) at 43 kbar, (b) at 7 kbar, both (a) and (b) with  $\lambda_L=5145 \text{ \AA}$ .

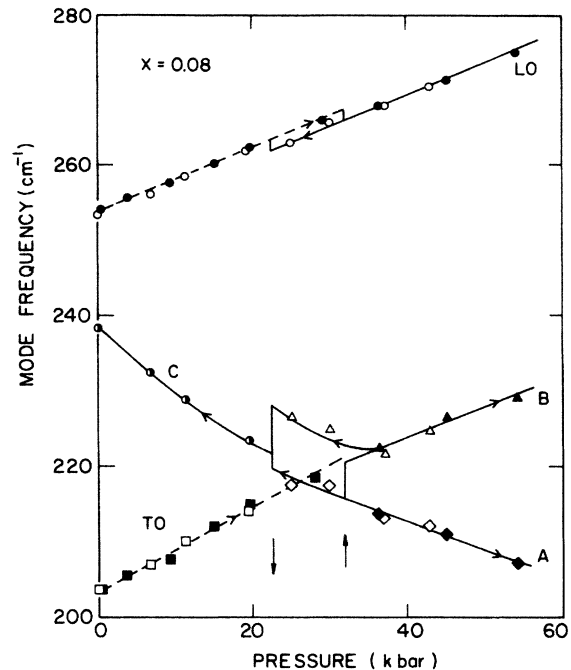


FIG. 7. Pressure dependence of various mode frequencies in  $Zn_{1-x}Mn_xSe$ ,  $x=0.08$ . Circles, LO phonon; squares, TO phonon; triangles, mode B; diamonds, mode A; half-filled circles, mode C. Note the solid symbols denote measurements with increasing pressure, whereas the open symbols correspond to those with decreasing pressure. Vertical up and down arrows indicate the forward and the reverse transition pressures, respectively. The dashed lines through the circles and squares are the linear least-squares fits to the corresponding data, the solid lines are guides for the eye.

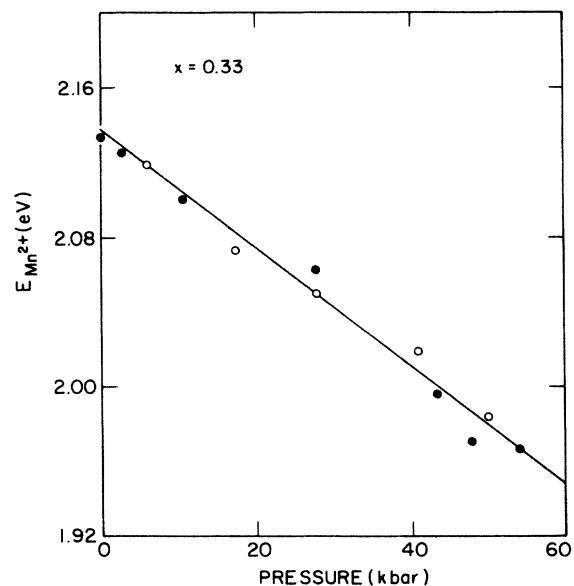


FIG. 8. The energy of the 2.1 eV  $Mn^{2+}$  luminescence peak in  $Zn_{1-x}Mn_xSe$  ( $x=0.33$ ) as a function of hydrostatic pressure. Solid symbols, with increasing pressure; open symbols, with decreasing pressure. The straight line is the linear least-squares fit to the data.

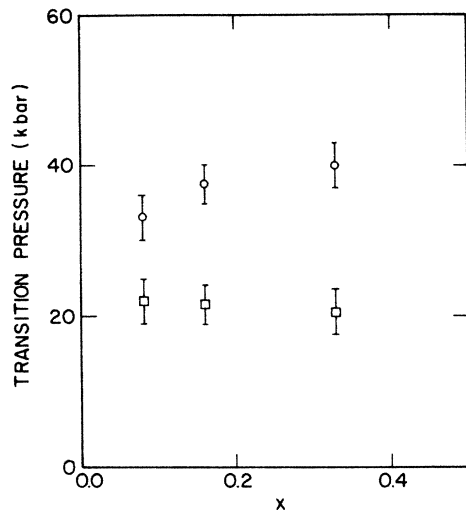


FIG. 9. Composition dependence of the forward and the reverse transition pressures in the mixed crystals. Circles, forward transition pressure; squares, reverse transition pressure.

dence of peaks A and B in the high-pressure phase and that of peak C in the low-pressure phase suggests that the high-pressure phase is perhaps a lower symmetry modification of the low-pressure phase, resulting in the splitting of the Raman line C into A and B. The structure of the high-pressure phase has not yet been determined. All the zinc-blende  $Zn_{1-x}Mn_xSe$  we have examined show this behavior. The mode Grüneisen parameters for LO and TO phonons in  $Zn_{1-x}Mn_xSe$  obtained from the pressure dependences of their frequencies are listed in Table I. In a comparable study on  $Cd_{1-x}Mn_xTe$ , an intermediate transition into NaCl structure has been observed.<sup>21</sup> However, in the present case the high-pressure phase cannot have the NaCl structure since the latter does not have any Raman active phonons in the first order. Furthermore, it is known that in a transition to NaCl structure the band gap changes from direct to indirect and has a lower value,<sup>11,14</sup> whereas the recent optical absorption measurements on  $Zn_{1-x}Mn_xSe$  under hydrostatic pressure

do not show any noticeable change in the band gap across this transition.<sup>22</sup> Detailed x-ray investigation of the structures of these phases are needed in order to interpret the Raman peaks A, B, and C.

In the zinc-blende phase the band gap is known to increase with hydrostatic pressure whereas the energies of electronic transitions associated with the crystal field split levels of  $Mn^{2+}$  ions in the DMS's show the opposite pressure dependence.<sup>14,22-24</sup> A luminescence peak at 2.1 eV in  $Zn_{1-x}Mn_xTe$  and in  $Cd_{1-x}Mn_xTe$  ( $x > 0.5$ ) is believed to be associated with the  ${}^4T_1 \rightarrow {}^6A_1$  transition of the  $3d^5$  levels of  $Mn^{2+}$  ion.<sup>15,23,25</sup> The energy of this luminescence peak ( $E_{Mn^{2+}}$ ) as a function of pressure for  $Zn_{1-x}Mn_xSe$  with  $x = 0.33$  is shown in Fig. 8. As in  $Cd_{1-x}Mn_xTe$ ,  $E_{Mn^{2+}}$  in  $Zn_{1-x}Mn_xSe$  also shows a negative pressure coefficient. This behavior is understood on the basis of the change in crystal field splitting and that in the  $p-d$  hybridization occurring due to the changes in the lattice parameter.<sup>24</sup> Recently, the energy of the transition  ${}^6A_1 \rightarrow {}^4A_1, {}^4E$  of the  $Mn^{2+}$  levels occurring at 2.62 eV in  $Zn_{1-x}Mn_xSe$  has been investigated with optical absorption.<sup>22</sup> This transition of  $Mn^{2+}$  also shows a negative pressure coefficient similar to the  ${}^4T_1 \rightarrow {}^6A_1$  transition observed in the present investigation. From the reported optical absorption results<sup>22</sup> and from the present  $Mn^{2+}$  luminescence measurements, it is interesting to note that neither the band gap nor the  $Mn^{2+}$  electronic transition energies show any significant discontinuities or changes in the slopes across the intermediate-phase transition. The insensitivity of the band gap and the  $Mn^{2+}$  electronic transition energies to the intermediate transition is not well understood.

Finally, Fig. 9 shows the composition dependence of the forward and the reverse transition pressures in the mixed crystals. Note that the transition pressure does not show a strong dependence on the  $Mn^{2+}$  concentration.

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