PHYSICAL REVIEW B VOLUME 52, NUMBER 15 15 OCTOBER 1995-I

High-pressure phase transitions in $Zn_{1-x}Mn_xSe$: A Raman-scattering and photoluminescence study

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(Received 17 June 1994; revised manuscript received 18 May 1995)

High-pressure phase transitions in semiconductor mixed crystals $Zn_{1-x}Mn_xSe$ ($x \leq 0.29$) are investigated using Raman scattering and photoluminescence (PL) up to a pressure of 150 kbar. The samples are characterized for composition and crystal structure. A new Raman mode is observed between TO and LO frequencies for samples with $x \leq 0.097$ and is assigned to a disorder activated zone boundary phonon. Apart from the PL band at 2.1 eV due to the $^4T_1 \rightarrow {}^6A_1$ transition between the crystal field split levels of Mn^{2+}, a PL band is observed at 1.94 eV in the samples with $x = 0.063$ which is assigned to a native defect forming a complex with Mn^{2+}. The intensity of the PL band reduces drastically with pressure and completely disappears at about 15 kbar. A possible model for this behavior is presented. The pressure dependence of the phonon frequencies and the behavior of PL suggest three transitions P_1, P_2, and P_3 for the mixed crystals with $x = 0.29$, whereas those with $x = 0.063$ and 0.097 show only P_2 and P_3 transitions. In the sample with $x = 0.29$, TO mode splits into two components across P_1 and the low-frequency component exhibits softening. The crystals turn opaque across P_2 and the PL signal disappears suggesting that the band gap changes from direct to indirect. Intensities of Raman lines decrease and completely disappear across P_3. The difference in the behavior of the phase transitions for the low and the high values of x is understood on the basis of their different crystal structures.

I. INTRODUCTION

High-pressure phase transitions and pressure-induced metallization in semiconductors[1,2] have been subjects of great interest for more than a decade. Under the application of pressure, tetrahedrally coordinated semiconductors often undergo a transition to a metallic phase that has a body centered tetragonal (bct) structure.[3,4] Some semiconductors exhibit intermediate phase transitions before transforming into a metallic phase, e.g., Cd chalcogenides transform to NaCl structure at much lower pressures[5] and this transition is also associated with a change in electronic band structure from direct to an indirect band gap.[6] Diluted magnetic semiconductors, (DMS), the mixed crystals of II-IV tetrahedral semiconductors, and the magnetic chalcogenides are of special interest, due to their unique combination of the semiconducting and magnetic properties[7,8] and their device applications.

Mixed crystals $Zn_{1-x}Mn_xSe$ have been reported to have many unusual properties, e.g., anomalous dependence of band gap[9] on composition and the additional blueshift of the band edge photoluminescence (PL) at low temperature.[10] Some of the anomalous behavior are attributed[11] to the *s*-*d* and the *p*-*d* exchange interaction between the band electrons and the $3d^5$ electrons of the Mn.$^{2+}$ This system has also been reported to exhibit polytypism and coexistence of zinc-blende and wurtzite structures over a wide range of composition.[12]

Optical absorption studies on these mixed crystals at high pressures reveal that the transition pressure decreases with the increasing Mn content.[13,14] On the other hand, high-pressure Raman spectroscopic studies suggest[15,16] that these mixed crystals exhibit an intermediate transition at much lower pressures before the metallization transition, while pure ZnSe does not show such transitions. In order to understand its complex behavior under various conditions, the mixed crystal system $Zn_{1-x}Mn_xSe$ needs to be investigated in detail. In the present work, we report detailed high-pressure PL and Raman spectroscopic investigations in this system in a diamond anvil cell (DAC) up to a pressure of 150 kbar. Intermediate transitions are reported in this system, which are also identified.

II. EXPERIMENT

The mixed crystals of $Zn_{1-x}Mn_xSe$ have been reported to crystallize[12] in the zinc-blende structure for $x \leq 0.19$, as a mixture of zinc-blende and wurtzite structures for $0.19 \leq x \leq 0.34$ and in the wurtzite structure for $x \geq 0.34$. The transition from cubic to hexagonal structure as a function of x is not sharp and as a result, complicated structures like microtwins and polytypes are present in the mixed crystals.[11] Crystals used in the present investigations were grown using the Bridgeman method. These are analyzed for their structure and composition using powder x-ray diffraction and x-ray fluorescence. Characteristic x-ray fluorescence of the constituting elements is measured in a scanning electron microscope (SEM), using energy dispersive x-ray analysis (EDAX). The intensity of 8.59 keV peak of Zn from undoped ZnSe is used for obtaining the fraction $1 - x$ of Zn in the mixed crystals. The fraction x of Mn thus found is consistent

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with the intensity of the 5.86 keV peak of Mn from the mixed crystals. The actual composition turns out to be rather different from the starting nominal composition before crystal growth, as shown in Table I. The structure for crystals with $x = 0.063$ and 0.097 is found to be zinc-blende whereas that for $x = 0.29$ fits best to the wurtzite structure. Most of the diffraction peaks of the samples with $x = 0.29$ appear as doublet, which are better resolved at large θ. From these results, this sample appears to be a mixture of two wurtzite phases with lattice parameters different from each other by 0.27%. This may arise due to compositional inhomogeneity; however, in the EDAX analysis using a SEM, large composition fluctuations are not detected either with the point focus (1000 Å) or with the area scan (0.5 mm). It may be mentioned that the diffraction peaks in $x = 0.29$ sample could also be fitted to the orthorhombic structure ($a = 6.643$, $b = 3.520$, and $c = 2.032$ Å) with a somewhat poorer figure of merit. Table I also shows the results of the structural analysis.

Raman spectra of unoriented single crystal bits of $Zn_{1-x}Mn_xSe$ at high pressure are recorded in backscattering geometry in a gasketed diamond anvil cell. Other details of DAC loading are described elsewhere.[17] A 4:1 methanol-ethanol mixture is used as a pressure transmitting medium. Pressure in the DAC is estimated using the ruby fluorescence technique. Raman and PL spectra are excited using several blue lines of an argon ion laser. The Raman and the PL spectra are analyzed using a Spex double monochromator and detected using a cooled photomultiplier tube and a photon counting unit. Scanning of the spectra and data acquisition are done using a home-built micro-processor based acquisition-control system. Data are transferred from the micro-processor system to a PC after each scan is over, for further processing. All the high-pressure Raman and photoluminescence measurements are carried out at ambient temperature. In order to record low temperature PL spectra at ambient pressure, samples are cooled in a cold-finger type liquid nitrogen optical cryostat.

III. RESULTS AND DISCUSSIONS

A. Raman scattering

Pure ZnSe in the zinc-blende phase has only one Raman active polar optical phonon of F_2 symmetry that exhibits LO-TO splitting. The zone-center optical phonons in the mixed crystals exhibit a mixed mode behavior; however, the impurity modes are weak as compared to that of the host.[15] For the mixed crystals with $x = 0.097$, the TO mode at ambient pressure is found to appear around 204 cm^{-1} and the LO mode around 254 cm^{-1}. The dependence of the mode frequencies on the composition is found to be consistent with that reported earlier.[15] Figure 1 shows the Raman spectra of the mixed crystals with $x = 0.097$ recorded at various pressures. Frequencies of all modes increase with pressure. Note the presence of a Raman peak labeled "A" seen between the TO and the LO modes even at ambient pressure. Behavior of this mode as a function of pressure is also shown in Fig. 2 along with those of TO and LO phonons for the mixed crystal with $x = 0.097$. Note that beyond 90 kbar, all the modes exhibit a weaker dependence on pressure. The Raman spectra of the samples with $x = 0.063$ at high-pressure exhibit a behavior similar to those with $x = 0.097$. Frequency of the mode "A" at the ambient pressure (227 cm^{-1}) is close to that of the impurity mode frequency in this system,[15] as well as to that of zone boundary optical phonons at point X and L in the Brillouin zone.[18] These phonons also give rise to a peak in phonon density of states. The Grüneisen parameter of the mode "A" is 1.9, which is much larger than the value 1.3 corresponding to that of the impurity mode reported earlier.[15] Hence, this peak can be assigned to the density of states rather than to the impurity mode. The Grüneisen parameter of the TO and the LO modes are found to be the same as those reported earlier.[15]

Intensities of all Raman modes decrease as the pressure is increased. This is because the band gap increases with pressure, making the interband transition energy move away from the exciting photon energy. However, if a shorter wavelength is used, much higher Raman intensities are observed suggesting resonance enhancement. The decrease of the LO phonon intensity is much more rapid as compared to that of the TO phonon. This is probably due to several scattering mechanisms contributing to the LO phonon intensity[19] and the resonance Raman profiles can be different for different mechanisms. Decrease of the intensities of the Raman modes is rather rapid above 100 kbar and no Raman signal is seen above 112 kbar in the mixed crystals with $x = 0.063$ and above 115 kbar in those with $x = 0.097$. The disappearance of Raman intensities is often taken as an indirect evidence of transformation of the sample to a metallic phase, due to the extremely poor scattering effeciency in the metallic phase. It is worth mentioning that although the direct band gap in these materials is known to increase with pressure,

TABLE I. Composition and the crystal structures of the mixed crystals $Zn_{1-x}Mn_xSe$. Numbers in the parentheses represent the standard errors in the last significant digits.

Sample	Nominal Mn composition (x)	Actual Mn composition (x)	Structure	Lattice parameter (Å)
I	0.08	0.063(5)	zinc-blende	5.687(0)
II	0.15	0.097(8)	zinc-blende	5.681(1)
III	0.33	0.29(2)	wurtzite	a: 4.064(0) c: 6.643(1)

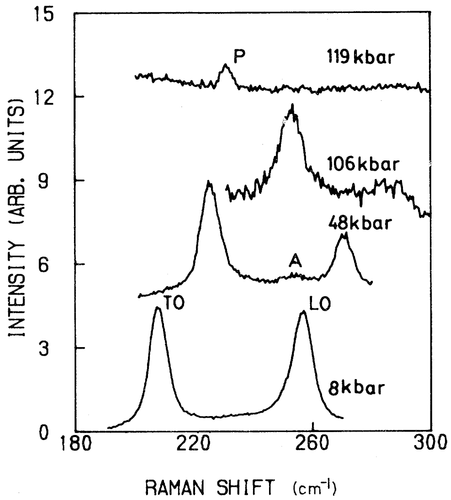

FIG. 1. Raman spectra of $Zn_{1-x}Mn_xSe$ mixed crystal ($x = 0.097$) at different pressures, using 4765 Å line of argon ion laser. A peak labeled "A" is seen between TO and LO modes at high pressures. The feature marked P in the spectrum at 119 kbar is a plasma line. Note the disappearance of all the Raman lines at this pressure.

the mixed crystals are found to turn opaque around 100 kbar, a pressure somewhat lower than that corresponding to the disappearance of Raman lines. Samples turning opaque could be due to a direct to indirect gap transition, as evidenced from the disappearance of the photoluminescence intensity across this transition, with the indirect band gap energy less than the lowest energy of the photon in the visible region. This is discussed in more detail in the next section.

The behavior of phonons in the mixed crystals with $x = 0.29$ is strikingly different from those of lower compositions. Figure 3 shows the Raman spectra at several pressures. The TO mode splits into two components, labeled TO1 and TO2 in Fig. 3, above 35 kbar. The frequency of the component TO1 decreases as a function of pressure, while the frequency of the other component TO2 exhibits rather weak pressure dependence. Figure 4 shows the dependence of different mode frequencies on pressure in this mixed crystal. From the behavior of the phonon frequencies it is evident that the mixed crystal with $x = 0.29$ exhibits a phase transition (say P_1) at around 35 kbar. Splitting of the TO mode in the high-pressure phase may probably be due to the lowering of the crystal symmetry. Intermediate transitions before metallization have also been reported in other tetrahedral semiconductors with wurtzite structure. As indicated in Fig. 4, the change of slope of the pressure dependence of TO1 mode suggests another transition (say P_2), occuring at 79 kbar. The sample also turns opaque at this pressure. This may again be due to an associated change from a direct to an indirect band gap. In these mixed crystals, the Raman signal is found to disappear above 130 kbar. The weaker dependence of the Raman modes at high pressure in the mixed crystals with $x = 0.063$ and 0.097 could also be viewed to be arising due to the transition to an indirect gap semiconductor around 100 kbar. Phase transition pressures for various compositions obtained in the present investigation can now be compared with those obtained from optical absorption experiments (Table II), which show a decrease in the transition pressure as x increases. Identification of the phase transition pressures from different techniques and its implications on the present results are discussed further in the next

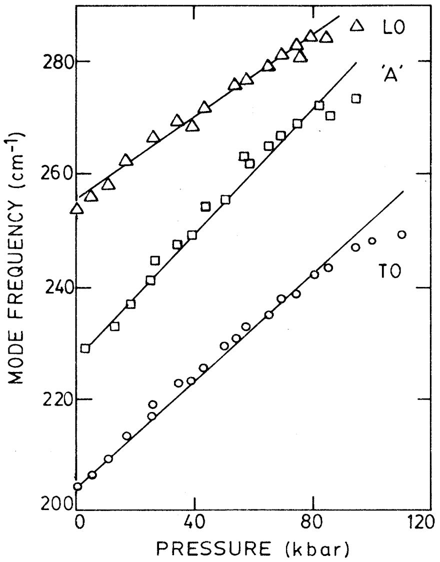

FIG. 2. Phonon frequencies in $Zn_{1-x}Mn_xSe$ mixed crystal ($x = 0.097$), as a function of pressure. Note that mode "A" has much stronger pressure dependence than those of LO and TO modes.

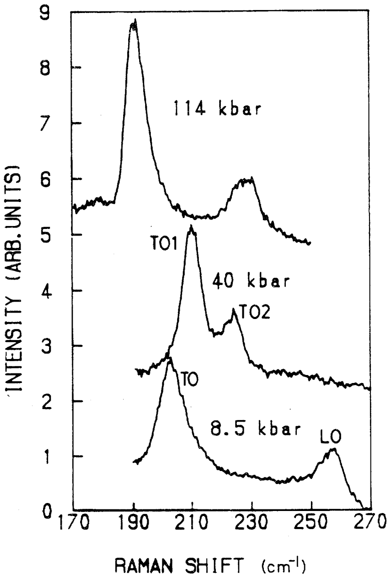

FIG. 3. Raman spectra of $Zn_{1-x}Mn_xSe$ mixed crystal ($x = 0.29$) at different pressures. Spectra at 8.5 and 40 kbar are recorded using 4765 Å and that at 114 kbar using 4579 Å line of argon ion laser. The TO mode splits into TO1 and TO2 above 35 kbar and the splitting increases as the pressure is increased further.

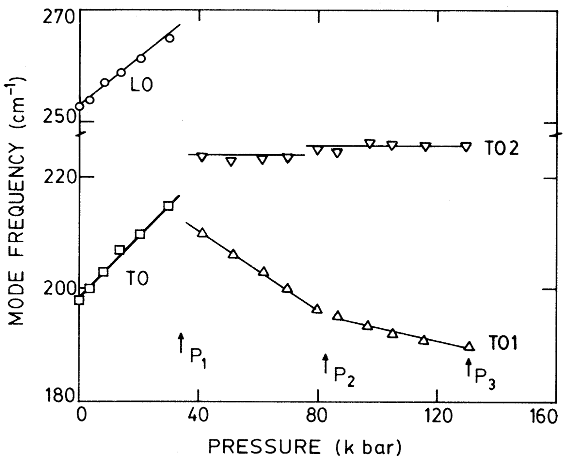

FIG. 4. Pressure dependence of phonon frequencies in the mixed crystals with $x = 0.29$. Note the softening of the low-frequency component TO1 at high pressure and change of slope around 83 kbar. Vertical arrows mark the transition pressures.

section. Upon reducing the pressure, transparency of the sample is regained with a large hysterisis of a few tens of kbar.

The behavior of the mixed crystals with $x = 0.29$ is similar to that reported in the previous study,[16] which was only up to 50 kbar; however, it may be mentioned that the mixed crystal with nominal compositions of 0.08 and 0.15 are earlier reported[15] to also undergo phase transition similar to that found in mixed crystals with $x = 0.29$. The reason for an apparently different behavior at low x, is not clear. This may probably be due to compositional inhomogeneities and polytypism, which is well known to occur in this system. The mixed crystals used in the present investigation have been well characterized for their composition and structure; whereas, those used in the earlier study were not.

B. Photoluminescence

The $3d^5$ levels of Mn^{2+} in the tetrahedral crystal field of ZnSe host split and give rise to optical absorption and PL. The ground state of Mn^{2+} is $^6A_1$ and the excited states $^4T_1$, $^4T_2$, and $^4A_1+^4E$ are reported to lie around 2.2, 2.4, and 2.6 eV, respectively, above the ground state. Similar intra-Mn^{2+} levels are found in other DMS mixed crystals also. Optical absorption measurements in the mixed crystals $Zn_{1-x}Mn_xSe$ at high pressures show a redshift of $^6A_1 \rightarrow ^4A_1+^4E$ transition energy as a function of pressure.[14] This is believed to occur due to the changes in the crystal-field splitting and in the p-d hybridization arising from the changes in the lattice parameter.[20] The behavior of PL arising due to $^4T_1 \rightarrow ^6A_1$ and other radiative transitions in the mixed crystals at high pressures are also investigated in the present work. The PL band shifts to lower energies as pressure is increased. Figure 5 shows the pressure dependence of the PL band energy for various mixed crystals. Note that the PL energy, due to intra-Mn^{2+} transition in mixed crystals with $x = 0.29$, is approximately 30 meV higher than that in the mixed crystals with lower x; however, the pressure coefficient of PL energy is the same for all the mixed crystals and has a value -3.6 meV/kbar. This is in excellent agreement with that of -3.4 meV/kbar corresponding to the same transition in $Zn_{1-x}Mn_xS$.[21] However, this may be compared with the values -2.1 and -1.5 meV/kbar reported for $^6A_1 \rightarrow ^4A_1+^4E$ transitions (2.6 eV) from optical absorption measurements of Ves *et al.*[14] and Shan *et al.*[22] respectively. A stronger pressure dependence for the $^4T_1$ level than that of $^4A_1+^4E$ suggests that these crystal-field split levels separate further upon the application of pressure.

TABLE II. Phase transition pressures in the mixed crystal system $Zn_{1-x}Mn_xSe$. Pressure P_2 corresponds to the disappearence of photoluminescence and P_3 to the disappearence of Raman signal. P_t are the reported transition pressures from the optical absorption measurements.

Composition x	P_1 (kbar)	P_2 (kbar)	P_3 (kbar)	P_t (kbar)
0.0				137[a]
0.063		103±3	122±3	
0.097		103±3	115±4	
0.10				117[b]
0.15				111[b]
0.25				92[b]
0.29	35±2	79±3	130±6	

[a] Ves *et al.* (Ref. 13).

[b] Ves *et al.* (Ref. 14).

The PL disappears at around 103 kbar for the mixed crystals with $x = 0.063$ and 0.097 and at 79 kbar for the crystals with $x = 0.29$. As mentioned earlier, the samples also turn opaque at these pressures at which PL disappears, suggesting some electronic transition, prob-

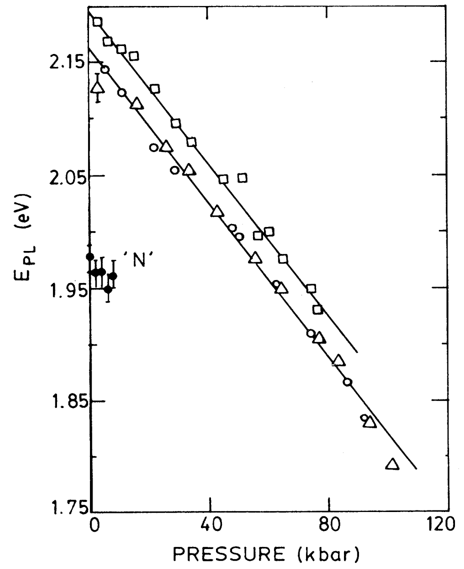

FIG. 5. Pressure dependence of the Mn^{2+} PL energy for all the mixed crystals. $x = 0.063$: (△); 0.097: (○); and 0.29: (□). The additional band "N" at 1.97 eV in the mixed crystal with $x = 0.063$ is insensitive to pressure.

ably direct to indirect gap, occurring at these pressures. In the mixed crystals with $x = 0.29$, this transition is also accompanied by changes in the phonon spectrum, as discussed in the previous section and the transition pressure is labeled as P_2. However, mixed crystals with lower x do not exhibit the transition P_1. As mentioned earlier, disappearance of Raman lines is often taken as an indirect evidence of transition to a metallic phase. Based on this criterion, one may be tempted to assign the transition pressure P_3, at which the Raman intensities disappear, to the metallization transition; however, one needs to confirm this speculation by resistivity measurements. In this context, it may be mentioned that the optical absorption measurements in pure ZnSe and ZnS show that the high-pressure phase is indirect gap semiconductor[23,24] up to much higher pressures. On the other hand, in the case of pure ZnS, a large drop in resistivity has been observed across the phase transition at 150 kbar.[25] This drop in resistivity has been assigned by Ves *et al.* to the high-density of defects in the high-pressure phase rather than to metallization.[24] From the closeness of values of the transition pressures P_2 and P_3 in the case of mixed crystals with $x = 0.063$ and 0.097, one may also suspect that these could be associated with the onset and the completion of the same phase transition and the small difference in transition pressures as seen by Raman and by PL measurements may be due to pressure induced defects. However, the values of P_2 and P_3 for samples with $x = 0.29$ are distinctly different and there is no ambiguity that the two correspond to different transitions. Table II summarizes the phase transitions observed in the present investigation together with those reported in other mixed crystals using other techniques. Note the qualitative agreement of the phase transition pressures reported from optical absorption experiments with the direct to indirect band gap transition pressure P_2 identified in the present investigation. This is expected as optical absorption would detect the direct to indirect band gap transition as the phase transition pressure, because of the characteristic changes in the spectral shape and the accompanying changes in the color of the sample. The decrease in the value of P_2 as a function of x also being similar to that reported by Ves *et al.*[14] confirms the present assignment. The high-pressure phase across the first phase transition in pure ZnSe has also been theoretically predicted to be nonmetallic.[26] This is consistent with the present results in the mixed crystals.

The difference in the behavior of PL energies and phase transition pressures between mixed crystals with low x and that with $x = 0.29$ can now be understood on the basis of the different structures of these mixed crystals. The mixed crystals in the zinc-blende phase do not exhibit the intermediate transition P_1, whereas only the wurtzite phase exhibits this transition. Intermediate phase transitions at pressures much lower than the metallization pressure are well known in Cd chalcogenides, of which CdS and CdSe also have wurtzite structure. It is surprising that the transition P_1 in the mixed crystals with $x = 0.29$ is not accompanied by any detectable changes in the behavior of its PL energy. Similar observations are reported earlier also.[15]

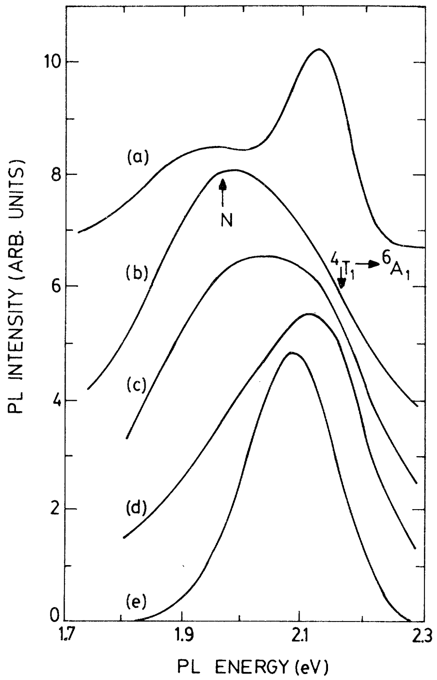

FIG. 6. PL spectra of the mixed crystal with $x = 0.063$ at $T = 90$ K (a) and at 300 K (b) and ambient pressure excited using 4880 Å line of argon ion laser. PL spectra at 2, 6, and 21 kbar are shown as curves (c), (d), and (e), respectively. At low pressures, intensity of the peak marked "N" is stronger than that of ${}^4T_1 \to {}^6A_1$ Mn^{2+} transition and reduces drastically at high pressures.

The PL spectrum of the mixed crystal with $x = 0.063$, apart from the ${}^4T_1 \to {}^6A_1$ intra-Mn^{2+} transition at 2.16

TABLE III. Energies of the PL band observed at ambient temperature and at 90 K in the mixed crystals of Zn$_{1-x}$Mn$_x$Se.

Composition (x)	Energies of PL bands (eV) 300 K	90 K	Assignment
0.00	2.29	2.31	
	2.00	1.98	Native defect
0.063	2.12	2.13	${}^4T_1 \to {}^6A_1$ (Mn^{2+})
	1.95	1.93	Native defect+Mn^{2+}
0.097	2.14	2.13	${}^4T_1 \to {}^6A_1$ (Mn^{2+})
0.29	2.16	2.02	${}^4T_1 \to {}^6A_1$ (Mn^{2+})

eV, shows another band at around 1.97 eV. The position of this new band is rather insensitive to pressure; however, its intensity shows rather interesting pressure quenching effects, i.e., intensity decreases rapidly as the pressure is increased, which is also found to be reversible. Figure 6 shows the PL spectra for $x = 0.063$ at different pressures. Note that the PL band, marked "N," strongly overlaps with and is even stronger than the ${}^4T_1 \rightarrow {}^6A_1$ transition of Mn.$^{2+}$ However, as pressure is increased, its intensity drastically reduces and completely vanishes above 15 kbar. The pressure dependence of the position of "N" is also shown in Fig. 5. Another remarkable feature of the band "N" is that its intensity is fully recovered upon release of pressure.

In order to resolve the PL band from the ${}^4T_1 \rightarrow {}^6A_1$ transition and to understand its origin, PL spectra of all the mixed crystals and that of the pure ZnSe are recorded at low temperature and ambient pressure. Mixed crystals with $x = 0.097$ and 0.29 show only one PL band at low temperatures corresponding to the ${}^4T_1 \rightarrow {}^6A_1$ transition of Mn,$^{2+}$ whereas those with $x = 0.063$ exhibit two clearly resolved PL bands. Figure 6 also shows the low temperature PL spectrum of the mixed crystals with $x =$ 0.063. Interestingly, pure ZnSe also shows two PL bands, one of which occurs at energy close to that of the band at "N" in the samples with $x = 0.063$. The presence of PL band around 1.97 eV even in pure ZnSe suggests that it could be either due to native defects or due to trace impurities. Table III gives the position of the PL bands in various mixed crystals and in pure ZnSe. A somewhat lower energy of the PL band "N" as compared to that of native defect in pure ZnSe may arise, due to the formation of a complex of the native defect and Mn^{2+} at a neighboring site. Recent band structure calculations show that the Zn vacancy (V_{Zn}) is the most dominant native defect in ZnSe.[27] Cu impurity in the singly ionized state at the Zn site is also reported to give a PL at 1.97 eV.[28]

We now attempt to understand the reversible pressure quenching of the PL band "N" at 1.97 eV in the mixed crystals with $x = 0.063$. Figure 7 shows schematically the positions of the impurity and the defect bands in the band gap region. At ambient pressure, the PL band "N" can arise due to nonradiative excitation transfer from ${}^4T_1$ of Mn^{2+} to the defect complex D. As the pressure is increased, the energy of the level ${}^4T_1$, reduces, whereas that of the level D remains practically unchanged. This makes the nonradiative excitation transfer to the level D more and more inefficient as the pressure is increased leading to quenching of the intensity of the band "N." The proposed mechanism of excitation transfer to understand the pressure quenching of the PL band "N" is also consistent with the assignment of the defect level D to a native defect complex involving Mn.$^{2+}$

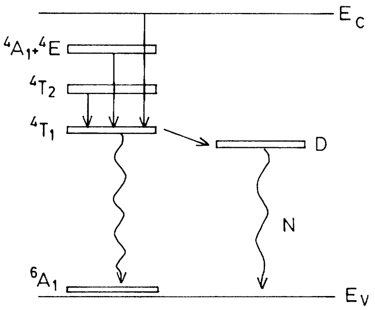

FIG. 7. Schematic representation of the position of the crystal-field split $3d^5$ levels of Mn^{2+} along with the defect band D. Vertical and the inclined arrows represent the nonradiative transition. E_c and E_v are the conduction and the valence bands.

IV. SUMMARY AND CONCLUSIONS

Raman spectroscopic and photoluminescence investigations at high pressures in the mixed crystal system $Zn_{1-x}Mn_xSe$ have revealed that these transform from direct to indirect gap semiconductors before the metallization transition. The direct to indirect gap transition pressure is found to decrease with increasing Mn concentration, which is consistent with the optical absorption results. Further, mixed crystals with wurtzite structure exhibit an additional intermediate structural transition at rather low hydrostatic pressure, whereas those with the zinc-blende structures do not. The intermediate phases of the mixed crystals with $x = 0.29$ exhibit a soft phonon. From the splitting of the TO mode in this system, one may speculate the intermediate phase to be of lower symmetry than cubic; however, detailed x-ray investigations are required to identify the structure of these phases. A PL band in the mixed crystals with $x =$ 0.063 is observed, which is assigned to a defect complex involving a native defect and Mn^{2+}. Intensity of this PL band is found to quench reversibly at moderate pressures of 20 kbar.

ACKNOWLEDGMENTS

The authors are grateful to Professor A. K. Ramdas for the gift of the mixed crystals and for stimulating discussions. The authors also thank Professor U. D. Venkateswaran for helpful discussions. In addition, the authors thank U. Debska of Purdue University for growing the crystals. The help of Mr. G. V. N. Rao in x-ray structural analysis and that of Ms. M. Radhika in SEM-EDAX analysis is also acknowledged. The authors also thank Dr. Kanwar Krishan for his keen interest in the work and Dr. P. Rodriguez for encouragement.

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