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Photoluminescence of ZnSe/ZnMnSe superlattices under hydrostatic pressure

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Photoluminescence near 4450 Å (violet) and 5900 Å (yellow) from ZnSe/Zn_{1-x}Mn_xSe strained-layer superlattices (SLS) is studied as a function of applied hydrostatic pressure up to ~90 kbar for $x=0.23, 0.33$, and 0.51 at 9 K. For each of the three SLSs, the peak energy of the near-band-gap violet photoluminescence (PL) from exciton recombination increases sublinearly with pressure, and closely follows that of ZnSe. The observed dependence is consistent with type-I band alignment, at least at pressures where the violet PL intensity remains strong. For the $x=0.23$ SLS, the energy of the biexciton PL increases faster than that of the exciton, which suggests decreased confinement. The yellow PL is due to the ${}^4T_1 \rightarrow {}^6A_1$ intraionic transition in Mn²⁺ and the nearly linear decrease of the peak energy of this signal with pressure is explained by crystal-field theory. In most cases examined, the intensities of the violet and/or yellow PL decrease abruptly above a certain pressure that increases with x from ~65 to ~90 kbar. For the different cases, this suggests either the occurrence of a phase transition in the Zn_xMn_{1-x}Se layers or a band crossing.

I. INTRODUCTION

The electronic structure and vibrational properties of II-VI semiconductor heterostructures have been studied in great detail, in part because they are potential active media in optical devices involving visible light emission.^{1,2} The interesting properties of II-VI strained-layer superlattices (SLS), in particular, arise from interfacial strain, quantum confinement or delocalization, and band alignment. One such class of structures includes ZnSe/ZnMnSe strained-layer superlattices,³ which have band gaps in the blue and violet. There are still many fundamental questions about these SLSs, including their band alignment. We present the first study of the effect of hydrostatic pressure on photoluminescence in ZnSe/ZnMnSe strained-layer superlattices to help better understand the electronic structure and strain in these SLSs.

ZnSe and Zn_{1-x}Mn_xSe are both direct gap materials. ZnSe is zinc blende. Bulk Zn_{1-x}Mn_xSe has predominantly zinc-blende structure for $x < 0.3$, while for $x > 0.3$ it has wurtzite structure. For $x < 0.66$, the Zn_{1-x}Mn_xSe layers in ZnSe/ZnMnSe heterostructures are still zinc blende.³⁻⁵ At ambient pressure, the band gap in ZnSe is 2.80 eV ($T=6.5$ K), while that of bulk Zn_{1-x}Mn_xSe (Ref. 6) increases linearly with Mn content, after an initial anomalous decrease at low concentrations; ZnMnSe epilayers have a qualitatively similar behavior.^{3,5}

The photoluminescence (PL) spectrum of bulk ZnSe at 9 K shows emission near 4430 Å, which is due to near-band-gap exciton recombination, which includes a weak free-exciton peak and, at slightly lower energy, stronger peaks due to various bound excitons.⁷ For low concentrations of Mn ($x < 0.1$) in the alloy, near-band-gap excitonic recombination is still dominant. However, broad fluorescence near 2.1 eV begins to dominate with increasing Mn

mole fraction,³⁻⁵ which has been attributed to intraionic transitions in Mn²⁺.⁸

In ZnSe/Zn_{1-x}Mn_xSe superlattices, the ZnSe layers are in tension while the ZnMnSe layers are in compression, with the magnitude of the strain increasing linearly with Mn concentration.⁹ Consequently, the light-hole (lh) band is the highest valence band in the ZnSe layers and the heavy-hole (hh) band is the highest valence band in the ZnMnSe layers. PL analysis of these ZnSe/Zn_{1-x}Mn_xSe superlattices at ambient pressure shows one dominant peak due to a light-hole exciton that is redshifted with respect to that in ZnSe.^{3,9} It is not known whether the exciton is free or bound to a donor, though several studies have suggested that it is free.³ For superlattices with thin wells, a low-energy shoulder is also visible⁹⁻¹¹ that is identified with biexciton decay.¹¹

PLE (PL excitation) spectra of the main band-edge PL in these SLSs have two peaks,^{9,10} which have been assigned to the light- and heavy-hole excitons. Magneto-optical measurements on ZnSe/Zn_{0.77}Mn_{0.23}Se SLSs have attributed the lower-energy PLE feature to light holes and the higher-energy feature to heavy holes. The strong stimulated emission¹² in these SLSs is evidence that the light holes may be confined to the ZnSe layers. Determining the location of the heavy holes is more uncertain because the Zeeman splitting for these states is in between that expected for (nonmagnetic) ZnSe and (magnetic) ZnMnSe. Using these observations, it has been concluded that ZnSe/ZnMnSe SLSs have type-I band alignment (at least for $x=0.23$), with electron and hole confinement in the ZnSe layers, and a valence-band offset of < 20 meV ($x=0.23$).¹⁰ Therefore, PL due to recombination is thought to come from the ZnSe layers,^{6,7,9,13} and the red shift in the PL spectrum of the SLS relative to bulk ZnSe is due to biaxial tension in the ZnSe, which causes the band gap to decrease as x increases. This strain shift is larger in magnitude than

TABLE I. Superlattice parameters. The SLS name denotes the Mn concentration in the alloy layers (x) and d is the layer thickness.

Sample	d_{ZnSe} Å	d_{ZnMnSe} Å	Number of periods	Buffer layer
$x=0.23$	63	104	67	480 Å $\text{Zn}_{0.77}\text{Mn}_{0.23}\text{Se}$ /5700 Å ZnSe
$x=0.33$	97	175	67	2200 Å ZnSe
$x=0.51$	100	180	67	5600 Å ZnSe

the concomitant increase in PL energy due to electron and hole confinement.

The presence of biaxial strain due to lattice mismatch in SLSs may be separated into hydrostatic and nonhydrostatic components. The hydrostatic part causes a shift in the band-gap energy, while the nonhydrostatic part causes a splitting in the Γ -point valence-band degeneracy between heavy and light holes.¹⁴ The application of hydrostatic pressure not only increases the net hydrostatic component of strain, but also changes the nonhydrostatic component due to the biaxial strain. This results from the difference in the compressibilities for the component materials, as has been detailed in Ref. 15.

The effect of hydrostatic pressure on the electronic structure in ZnSe has been examined in detail experimentally^{16–22} and theoretically.²³ As hydrostatic pressure is applied to bulk ZnSe, the lowest conduction band remains at the Γ point, with transmission,^{16,19} band-gap PL,^{20,21} donor-acceptor pair¹⁷ and self-activated¹⁸ luminescence, and photorefectance (PR)²² experiments showing a slightly sublinear increase in this direct gap with pressure. Zinc-blende ZnSe undergoes a phase transition to the β -Sn metallic structure at 137 kbar.^{19,24,25}

The effect of pressure on electronic structure has been studied to a lesser degree for ZnMnSe.^{26,27} Transmission measurements show an increase of the band-gap energy with pressure in ZnMnSe that is both slower and somewhat more nonlinear than in ZnSe.²⁶ Phase transitions in $\text{Zn}_{1-x}\text{Mn}_x\text{Se}$ occur at lower pressures than in ZnSe. For $x=0.25$, there is a phase transition at 92 kbar, probably also to the metallic structure. An intermediate transition to a structure that is a mixture of zinc blende and another unidentified structure (not thought to be NaCl), has also been reported for pressures ~ 35 kbar (forward transition) and ~ 20 kbar (reverse) for $\text{Zn}_{1-x}\text{Mn}_x\text{Se}$ ($x=0-0.33$).²⁷ Intraionic Mn^{2+} PL was studied as a function of pressure, and was unaffected by this intermediate transition.²⁷

II. EXPERIMENTAL PROCEDURE AND RESULTS

Photoluminescence measurements were made on three ZnSe/ $\text{Zn}_{1-x}\text{Mn}_x\text{Se}$ SLSs, each grown by molecular-beam epitaxy (MBE) on a MBE-grown ZnSe buffer on a GaAs (100) substrate. These three samples are referred to as the $x=0.23$, 0.33, and 0.51 SLSs. Structural details are presented in Table I, and details of the growth may be found in Ref. 4. These SLSs were grown commensurately on a ZnSe (or ZnMnSe/ZnSe) buffer layer; in each case, the

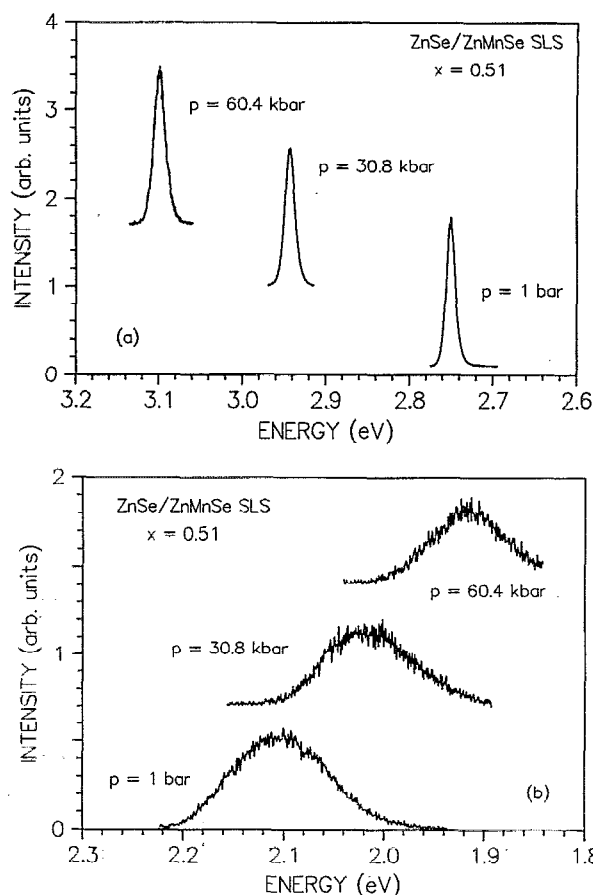


FIG. 1. Representative traces of (a) violet and (b) yellow PL for the $x=0.51$ SLS at various pressures.

combination of the SLS and the buffer layer is considered to be free standing.⁹ The current study supports this conclusion.

The GaAs substrates were mechanically thinned from 300 μm down to 50 μm for insertion in a diamond anvil cell (DAC). Spectra were compared before and after thinning to guarantee sample integrity. The DAC was made in house and is a modified version of the one described in Ref. 28, and was placed within a closed-cycle cryostat. Samples were inserted together with ruby chips, for pressure calibration,²⁴ within a gasketed liquid-argon bath to obtain near-hydrostatic conditions. Pressure was applied at ~ 300 K.

SLS photoluminescence was excited using the 4067 Å or the multiline UV lines (3375–3564 Å) from a krypton-ion laser with the sample in the DAC at 9 K. It was dispersed by a 0.85 m double spectrometer, and then detected by a cooled PMT or an intensity-enhanced diode array. Photon counting electronics were interfaced to an IBM AT for analog-to-digital (A/D) data conversion, storage, and analysis.

Representative PL spectra in the violet/near ultraviolet at ambient and elevated pressures are shown in Fig. 1(a). One strong peak dominates each spectrum, which is attributed to a light-hole exciton in ZnSe. For the $x=0.23$ superlattice, a weak biexciton feature is observed 7.5 meV below the main peak at 1 bar (Fig. 2). For all pressures,

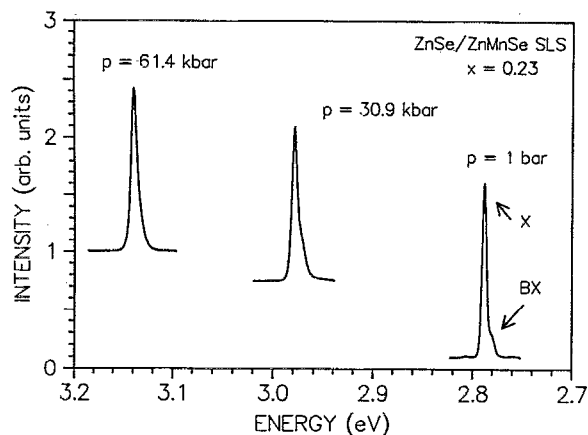


FIG. 2. Representative violet PL traces for the $x=0.23$ SLS showing the exciton (X) and biexciton (BX) peaks at various pressures.

the PL energy is always significantly smaller than the lowest-energy photons from the UV krypton-ion laser (3.48 eV).

The energies of these "violet" PL peaks are plotted in Fig. 3 as a function of pressure for each superlattice. Typical experimental errors in PL energy are $\sim \pm 1.0$ meV and in pressure are $\sim \pm 1$ kbar. These data come from several runs taken with only one of the three SLSs in the DAC and from one run in which the three samples were in the DAC together. For each SLS, the peak energy dependence on pressure p was fit to

$$E(p) = E_0 + \alpha p + \beta p^2. \quad (1)$$

Two sets of fit parameters are listed in Table II for the exciton peaks. In one set, all the data in Fig. 3 are used for each superlattice, while in the second set only the data taken with the three SLSs together in the DAC (the common run) are used. Some potential run-to-run variations in conditions are eliminated by analyzing this second set. In this second set, the magnitudes of α and β for the free-exciton peak both increase slightly with x , while such a trend is less clear in the first set. For the $x=0.23$ SLS, the

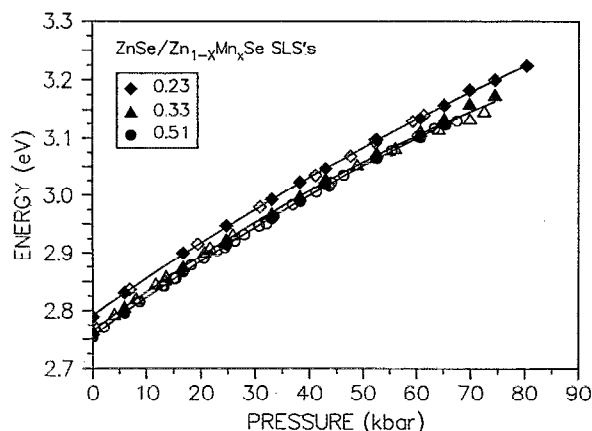


FIG. 3. PL energy vs pressure for the three SLSs for the violet PL. The solid symbols are for the common run, with the open symbols for the other runs. For the $x=0.23$ SLS only the exciton energy is plotted.

TABLE II. Parameter fit to the pressure dependence of the violet PL using Eq. (1). Unless otherwise stated, all fits are to the exciton.

SLS sample	E_0 (eV)	α (meV/kbar)	β (meV/kbar ²)	Data used in the fit
$x=0.23$	2.7908	6.66 ± 0.3	-0.016 ± 0.003	common run
	2.7918	6.55 ± 0.2	-0.014 ± 0.003	all data
	2.7909	6.55 ± 0.2	-0.014 ± 0.004	exciton/biexciton comparison run
(biexciton)	2.7824	6.71 ± 0.7	-0.016 ± 0.010	exciton/biexciton comparison run
$x=0.33$	2.7652	6.73 ± 0.3	-0.016 ± 0.003	common run
	2.7655	6.87 ± 0.2	-0.020 ± 0.002	all data
$x=0.51$	2.7549	6.91 ± 0.4	-0.019 ± 0.005	common run
	2.7564	6.80 ± 0.2	-0.018 ± 0.003	all data

energy of the biexciton peak increases 0.16 meV/kbar faster than does the main peak, and by 20 kbar it has essentially merged into the main peak (Fig. 2).

The widths of these PL peaks are ~ 6 , 12, and 13 meV for the $x=0.23$, 0.33, and 0.51 SLSs, respectively, at 1 bar. They slowly increase to ~ 12 , 13, and 18 meV at 80, 70, and 60 kbar, respectively for the three SLSs. This suggests only very weak deviations from hydrostaticity and is confirmed by the nearly constant ruby linewidth with increasing pressure.

In all three samples, there is also a weaker PL signal that is near 5900 Å (2.1 eV) at ambient pressure. The peak energy of this PL signal decreases with pressure, as seen in Figs. 1(b) and 4. Using Eq. (1), $\alpha_{\text{yellow}} \sim -3$ meV/kbar for each sample, as seen in Table III. The full width at half-maximum (FWHM) of this signal is ~ 400 Å (0.13 eV) for each sample, and is independent of p .

The intensities of the violet and yellow PL for the three SLSs are plotted in Figs. 5 and 6 versus p for the run where the three SLSs were in the DAC simultaneously. In addition to the normal fluctuations expected in measuring intensity, striking decreases in the PL strength are seen in most cases at high pressures. For the $x=0.51$ SLS, both

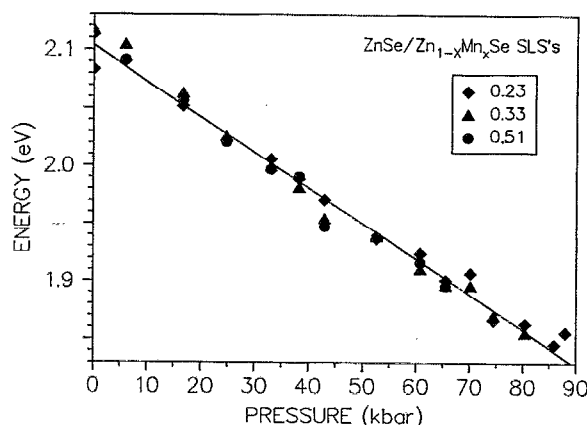


FIG. 4. PL energy vs pressure for the three SLSs in the common run, for the yellow PL.

TABLE III. Parameter fit to the pressure dependence of the yellow PL using Eq. (1) for the run with the three samples in the DAC, using either a quadratic or a linear fit.

SLS sample	E_0 (eV)	α (meV/kbar)	β (meV/kbar ²)
$x=0.23$	2.0964	-2.93 ± 0.4	0.001 ± 0.004
	2.0956	-2.87 ± 0.1	...
$x=0.33$	2.1222	-4.08 ± 0.4	0.010 ± 0.005
	2.1125	-3.27 ± 0.1	...
$x=0.51$	2.1146	-3.88 ± 0.6	0.009 ± 0.008
	2.1089	-3.30 ± 0.2	...

the violet and yellow PL decrease abruptly and vanish above ~ 67 kbar. For the $x=0.33$ SLS, the violet PL decreases rapidly near ~ 75 kbar, but the yellow PL remains strong. The yellow PL vanishes near 82 kbar. For the $x=0.23$ SLS, the violet PL decreases rapidly near 85 kbar, but the yellow PL remains strong up to the maximum pressure 88 kbar.

Each SLS became transparent above 35–45 kbar, as viewed through a microscope, due to the decreased absorption in the GaAs substrate. However, the $x=0.51$ SLS again became opaque above ~ 67 kbar, where the violet and yellow PL disappeared. The $x=0.23$ and 0.33 SLSs remained transparent even for pressures where the PL signals disappeared.

III. DISCUSSION

The violet PL data in Fig. 3 suggest a weak dependence of α and β on the Mn fraction in the alloy layer, which needs to be understood in terms of band alignment and strains. This section starts with a discussion of how biaxial strain changes in the SLS with pressure. Then the variation in the energy of the violet band-edge PL with pressure is addressed, which is followed by a discussion of the yellow PL. This section concludes with a discussion of the possible importance of phase transitions and band crossings in the SLSs at high pressure.

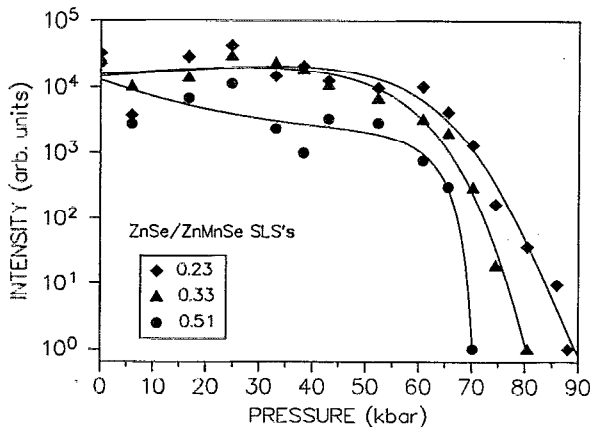


FIG. 5. PL intensity vs pressure for the three SLSs in the common run, for the violet PL.

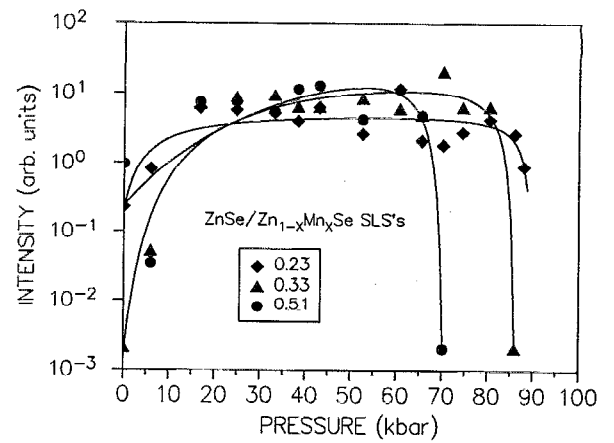


FIG. 6. PL intensity vs pressure for the three SLSs in the common run, for the yellow PL.

A. Changes in strain with pressure

For a material with bulk modulus B and $B' = dB/dp$, the lattice constant $a(p)$ varies with pressure by Murnaghan's equation of state,²⁹

$$a(p) = a(1 \text{ bar}) [1 + p(B'/B)]^{-1/3B'}. \quad (2)$$

Each component of strain in a heterostructure layer can be decomposed into a hydrostatic and a biaxial component, $\bar{\epsilon}_{ij} = \epsilon_{ij}^{(h)} + \epsilon_{ij}^{(b)}$, which are defined relative to unstrained bulk material at 1 bar. Using Eq. (2), the hydrostatic components of strain are

$$\epsilon^{(h)}(p) = \epsilon_{xx}^{(h)} = \epsilon_{yy}^{(h)} = \epsilon_{zz}^{(h)} = \frac{a(p) - a(1 \text{ bar})}{a(1 \text{ bar})}, \quad (3a)$$

which, in the low-pressure regime, reduces to

$$-p/3B \quad (3b)$$

[$B = (C_{11} + 2C_{12})/3$, where C_{11} and C_{12} are the elastic constants.]

The in-plane biaxial strain in a layer ϵ is given by

$$\epsilon^{(b)}(p) = \epsilon_{xx}^{(b)} = \epsilon_{yy}^{(b)} = [a_{eq}(p) - a(p)]/a(p), \quad (4)$$

and the uniaxial strain is

$$\epsilon_{zz}^{(b)} = (-2C_{12}/C_{11})\epsilon_{xx}^{(b)}. \quad (5)$$

a_{eq} is the weighted average, in-plane lattice constant for the heterostructure, which is

$$a_{eq}(p) = (a_1 t_1 + a_2 t_2)/(t_1 + t_2) \quad (6)$$

for this free-standing buffer layer/SLS system, where t_1 is the total thickness of all the ZnSe layers in the SLS and buffer and t_2 is that for ZnMnSe. (ZnSe and ZnMnSe are denoted by subscripts 1 and 2, respectively.) The variations of t_1 and t_2 with p are obtained by using Eq. (2). In the lower-pressure, linear regime this leads to the effective bulk modulus for the structure B_{eq} ,¹⁵

$$\frac{1}{B_{eq}} = \left(2 \frac{a_1}{a_{eq}} - 1\right) \frac{t_1}{t_1 + t_2} \frac{1}{B_1} + \left(2 \frac{a_2}{a_{eq}} - 1\right) \frac{t_2}{t_1 + t_2} \frac{1}{B_2}. \quad (7)$$

TABLE IV. Strain-induced perturbations on band-gap parameters. $\Delta\alpha = \alpha - \alpha_{\text{ZnSe}}$ for type-I band alignment is calculated from Eqs. (6), (7), (12), and (14) using either a ZnMnSe bulk modulus determined from $1/a^{3.6}$ scaling ($B_{2,a}$) or one extrapolated from the experiments on the wurtzite alloy in Ref. 34 ($B_{2,b}$). The bulk modulus for ZnSe at 9 K (642 kbar) is used. The ZnSe deformation potentials $a_{c1} - a_{v1} = -4.37$ eV and $b_1 = -1.14$ eV (Ref. 21) were used.

SLS sample	$B_{2,a}$ (kbar)	$\Delta\alpha_a$ (meV/kbar)	$B_{2,b}$ (kbar)	$\Delta\alpha_b$ (meV/kbar)
$x=0.23$	615	0.14	600	0.22
$x=0.33$	604	0.20	582	0.32
$x=0.51$	586	0.30	550	0.53

By inserting Eq. (2) into Eq. (4) an exact expression for $\epsilon(p)$ is obtained for either layer. If terms are kept only to second order in p , the biaxial strain becomes¹⁵

$$\epsilon^{(b)}(p) = \frac{a_{\text{eq}}}{a} \left\{ 1 + \frac{p}{3} \left(\frac{1}{B} - \frac{1}{B_{\text{eq}}} \right) + \frac{p^2}{18} \left[\frac{3B'_{\text{eq}} + 1}{B_{\text{eq}}^2} - \frac{3B' + 1}{B^2} + \frac{2}{B} \left(\frac{1}{B} - \frac{1}{B_{\text{eq}}} \right) \right] \right\} - 1, \quad (8)$$

which is for the ZnSe or ZnMnSe layers depending on the choice of a and B .

Using Eqs. (2)–(5), the fractional change in volume Ω can be written as

$$\frac{\Delta\Omega}{\Omega} = \bar{\epsilon}_{xx} + \bar{\epsilon}_{yy} + \bar{\epsilon}_{zz} = -\frac{p}{B} + \frac{1+B'}{2B^2} p^2 + 2 \left(1 - \frac{C_{12}}{C_{11}} \right) \epsilon^{(b)}(p), \quad (9)$$

where Eq. (2) has been expanded to second order for the hydrostatic strain term.

The ZnSe parameters $B=642$ kbar and $B'=4.77$ (Refs. 19 and 30) are used here. This value for B at 9 K was obtained by extrapolating the ZnSe bulk modulus at 300 K (610 kbar, which is an average of two published values, 595 kbar³¹ and 624 kbar^{19,30}) using the reported temperature dependence of bulk modulus down to 77 K.³²

Though the elastic constants of zinc-blende ZnMnSe have not been measured, they may be estimated from the known dependence of elastic constants with lattice constant and from measurements on bulk wurtzite ZnMnSe. For constant ionicity, the bulk moduli of binary semiconductors vary as $\sim 1/a^{3.6}$ or $1/a^{4.15,33}$. If this ternary were to follow the universal curve of B vs a for II-VI binary semiconductors, then the bulk modulus of $\text{Zn}_{1-x}\text{Mn}_x\text{Se}$ would be estimated to be 0.96, 0.94, and 0.91 times the ZnSe bulk modulus for the $x=0.23$, 0.33, and 0.51 ternaries respectively (Table IV).

However, Mayanovic, Sladek, and Debska³⁴ have found the elastic constants of bulk wurtzite $\text{Zn}_{1-x}\text{Mn}_x\text{Se}$ to be significantly lower than those expected from these scaling relations, when compared to ZnSe. [The comparison in Ref. 34 was made by using the approximate relations that relate the elastic constants for the zinc-blende (ZnSe) and wurtzite structures, which are estimated to be accurate to

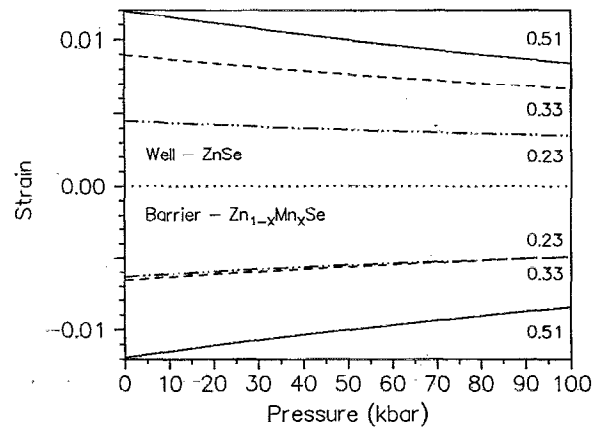


FIG. 7. Calculated strain vs pressure for ZnSe and ZnMnSe layers in the three SLSs using Murnaghan's equation, with $B=642$, 600, 582, and 550 kbar, and $B'=4.77$, 4.62, 4.37, and 3.91 assumed for $\text{Zn}_{1-x}\text{Mn}_x\text{Se}$, $x=0.00$, 0.23, 0.33, and 0.51, respectively.

$\sim 5\%$]. This deviation is thought to occur because adding Mn^{2+} to ZnSe decreases the strength of tetrahedral bonding. Using the elastic constants from Ref. 34, B is 546 and 512 kbar for bulk wurtzite $\text{Zn}_{1-x}\text{Mn}_x\text{Se}$ with $x=0.37$ and 0.53, respectively. For these two alloys $B_2/B_1=0.90$ and 0.84, respectively, while $1/a^{3.6}$ scaling gives 0.93 and 0.91, respectively. If B for zinc blende and wurtzite ZnMnSe are the same, then the B_2 estimates of the previous paragraph must be lowered to those presented in Table IV.

For many semiconductors, B' changes slowly with cation substitution, so one would normally assume that $B'_1 = B'_2$.¹⁵ However, Maheswaranathan and Sladek³⁵ have shown that the pressure derivatives of the wurtzite ZnMnSe alloy elastic constants are smaller than for ZnSe. Using their data, B' is 4.27 and 3.81 for the $x=0.37$ and 0.53 alloys, respectively, compared to their value of 5.17 for ZnSe (which is somewhat different from $B'=4.77$ used here). These values have been extrapolated to determine B' for the alloy concentrations used here, giving $B'=4.62$, 4.37, and 3.91 for $x=0.23$, 0.33, and 0.51, respectively.

Since for each x , $B_2 < B_1$ while $a_2 > a_1$, the magnitude of strain in each layer of the ZnSe/ $\text{Zn}_{1-x}\text{Mn}_x\text{Se}$ SLS decreases linearly with p as pressure is initially applied, thereby making the free-standing SLS more stable;¹⁵ however, because of the nonlinearities in Eq. (2), the changes in strain become slower with increasing pressure and the structure never achieves a strain-free crossover.¹⁵ $\epsilon^{(b)}(p)$ for the ZnSe and ZnMnSe layers are plotted in Fig. 7.

B. Band-edge transitions

The conduction-band energy of a direct-gap semiconductor varies as

$$\Delta E_c = a_c \left(\frac{\Delta\Omega}{\Omega} \right) + \delta_c \left(\frac{\Delta\Omega}{\Omega} \right)^2, \quad (10a)$$

where a_c is the conduction-band hydrostatic deformation potential and δ_c parameterizes the quadratic term for hydrostatic deformations. Using Eq. (9), this becomes

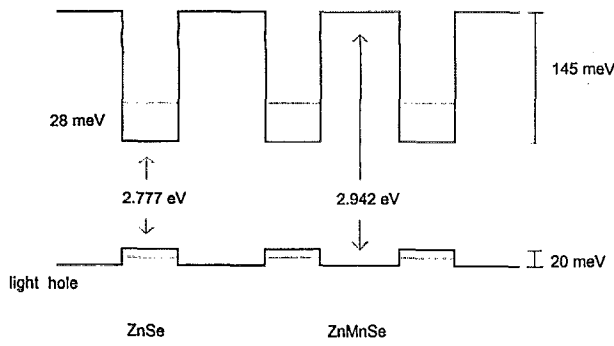


FIG. 8. Alignment of the conduction and light-hole valence bands for the ZnSe/Zn_{0.77}Mn_{0.23}Se SLS at ambient pressure, using data from Ref. 10 (not drawn to scale).

$$\Delta E_c = -\frac{a_c}{B}p + \frac{[(1+B')a_c + 2\delta_c]}{2B^2}p^2 + 2a_c\left(1 - \frac{C_{12}}{C_{11}}\right)\epsilon^{(b)}(p). \quad (10b)$$

Other second-order terms, of order ϵp and ϵ^2 , are small and have been neglected.

For these semiconductors, which have large spin-orbit coupling, the valence-band energy varies as

$$\Delta E_v = a_v\left(\frac{\Delta\Omega}{\Omega}\right) + \delta_v\left(\frac{\Delta\Omega}{\Omega}\right)^2 \mp b(\epsilon_{zz}^{(b)} - \epsilon_{xx}^{(b)}), \quad (11a)$$

where a_v and b are the hydrostatic and tetragonal deformation potentials for the valence band, respectively, δ_v describes the quadratic term for the hydrostatic potential of the valence band, and the upper (lower) sign refers to heavy (light) holes.¹⁴ In ZnSe the light hole is higher than the heavy hole ($\epsilon_1 > 0$), while the heavy hole is higher in ZnMnSe ($\epsilon_2 < 0$). Using Eq. (9) this gives

$$\Delta E_v = -\frac{a_v}{B}p + \frac{[(1+B')a_v + 2\delta_v]}{2B^2}p^2 + \left[2a_v\left(1 - \frac{C_{12}}{C_{11}}\right) \pm b\left(1 + \frac{2C_{12}}{C_{11}}\right)\right]\epsilon^{(b)}. \quad (11b)$$

Although there have been no calculations of the band offsets at the ZnSe/ZnMnSe interface, the common anion rule suggests that the valence-band offset is very small, as previous experiments suggest for this system.¹⁰ The model solid calculations of band offsets by Van de Walle³⁶ suggest that common anion and cation rules apply to interfaces of II-VI semiconductors. Exclusive of biaxial strain effects, the conduction-band offset was shown to be very small at ZnSe/ZnS interfaces (common cation), while the valence-band offset was shown to be very small at ZnTe/CdTe interfaces (common anion).

Figure 8 shows the ZnSe/ZnMnSe band alignment based on earlier work,¹⁰ which shows type-I alignment with the small valence-band offset expected in common anion heterostructures. From Eqs. 10(b) and 11(b), band

alignment at higher pressures is seen to depend on strain, the deformation potentials, and the band offset at ambient pressure.

If the superlattice were type I with electron and hole confinement in the ZnSe layers, then using Eqs. (10) and (11) the slope of the pressure dependence of the PL energy would be

$$\alpha_I = \alpha_{\text{ZnSe}} + [\gamma_1(a_{c1} - a_{v1}) - \eta_1 b_1] \frac{d\epsilon_1}{dp}, \quad (12)$$

where

$$\alpha_{\text{ZnSe}} = -(a_{c1} - a_{v1})/B_1, \quad (13)$$

and $\gamma = 2(1 - C_{12}/C_{11}) \cong 0.8$ and $\eta = (1 + 2C_{12}/C_{11}) \cong 2.2$. This does not include changes in exciton and confinement energies with pressure. With the superlattice/buffer layer system remaining freely standing as hydrostatic pressure is applied, using Eq. (8),

$$\frac{d\epsilon}{dp} = \frac{1}{3} \frac{a_{\text{eq}}}{a} \left(\frac{1}{B} - \frac{1}{B_{\text{eq}}} \right). \quad (14)$$

If the superlattice were type II, with electrons in ZnSe combining with holes confined to the ZnMnSe layers, then

$$\alpha_{\text{II}} = \alpha_{\text{ZnSe}} + \left(\frac{a_{v2}}{B_2} - \frac{a_{v1}}{B_1} \right) + \gamma_1 a_{c1} \frac{d\epsilon_1}{dp} - (\gamma_2 a_{v2} + \eta_2 b_2) \frac{d\epsilon_2}{dp}. \quad (15)$$

Depending on the magnitude and sign of the second term, this slope could be very different from that predicted by Eq. (12).

For the $x=0.23, 0.33$, and 0.51 SLSs, α is 6.66, 6.73, and 6.91 meV/kbar, respectively (from the three-SLS common run). It is not clear whether the excitons in the SLSs are free or bound to a donor.^{3,9} However, since $\alpha_{\text{free}} \cong \alpha_{\text{donor bound}}$ in ZnSe, as is seen in Table V, this uncertainty is not very significant. Therefore, α for ZnSe may be obtained either from the average for light- and heavy-hole free excitons in the thin epilayer (α_{free}) or from $\alpha_{\text{donor bound}}$ for bulk ZnSe. Consequently, $\alpha = 6.70$ meV/kbar is used for comparison. Using Eq. (12), the expected differences due to strain changes in the SLS are presented in Table IV assuming alloy bulk moduli determined from $1/a^{3.6}$ scaling or from the measurements on the wurtzite alloys. Within experimental error, the small differences between the SLS α 's are consistent with predictions, though each measured α is low by ~ 0.2 meV/kbar relative to the predicted value in Table IV. It will be seen that this difference may in part be related to the pressure dependence of the confinement and exciton binding energies.

These results are consistent with type-I band alignment for each SLS throughout the pressure range where violet PL is observable. More significant deviations of α from α_{ZnSe} would be expected for type-II alignment at ambient pressure. For example, using Eq. (15), a difference $a_{v1} - a_{v2}$ of 0.2 eV would yield deviations on the order of 0.5–1.0 meV/kbar for the three superlattices. Furthermore, $\alpha_1 > \alpha_2$ (Table V) implies that α_{II} is likely $< \alpha_{\text{ZnSe}}$, exclusive of strain effects, and that α_{II} should decrease with x , which are contrary to the current results. Moreover, a

TABLE V. Band parameters for ZnSe ($x=0$) and $\text{Zn}_{1-x}\text{Mn}_x\text{Se}$ using Eq. (1). Since $\alpha = (a_v - a_c)/B$, the temperature dependence of B can lead to differences in measured values of α (and β) for ZnSe.

x	E_0 (eV)	α (meV/kbar)	β (meV/kbar ²)	Sample type	Measurement (T)	Reference
0.0	2.7980	6.70	-0.014	bulk	PL donor bound exciton (9 K)	21
0.0	2.8041	6.79	-0.011	epilayer/GaAs	PL hh free exciton (9 K)	21
0.0	2.8166	6.58	-0.018	epilayer/GaAs	PL lh free exciton (9 K)	21
0.0	...	6.48	-0.007	epilayer/GaAs	PR hh free exciton (80 K)	22
0.0	...	6.33	-0.012	epilayer/GaAs	PR lh free exciton (80 K)	22
0.0	2.688	7.12	-0.015	bulk	band-edge transmission (295 K)	19
0.1	2.648	6.7	-0.017	bulk	band-edge transmission (295 K)	26
0.15	2.675	6.30	-0.018	bulk	band-edge transmission (295 K)	26
0.25	2.756	6.34	-0.027	bulk	band-edge transmission (295 K)	26

large negative value of β would also suggest type-II alignment because $|\beta_2| > |\beta_1|$ (Table V); however, the values of β measured here are close to that for ZnSe, which is again consistent with type-I behavior.

For $x > \sim 0.2$ in $\text{Zn}_{1-x}\text{Mn}_x\text{Se}$, E_0 increases and α decreases with increasing x (Table V). Therefore, $\alpha_1 > \alpha_2$, even though $(E_0)_1 < (E_0)_2$. Since $\alpha_1 > \alpha_2$ and $B_1 > B_2$ imply that $(a_{v1} - a_{c1})/(a_{v2} - a_{c2}) > B_1/B_2 > 1$ (with $a_v > 0$, $a_c < 0$), adding pressure to a type-I structure will decrease either the conduction- or valence-band offset, or both of them. This could lead to a crossover of the valence or conduction bands. Further, with increasing pressure the ZnMnSe band gap eventually becomes smaller than that of ZnSe. For $x=0.25$, the band gaps are equal at 50 kbar (including the quadratic terms) for unstrained material at 295 K, while the gaps are equal at 77 kbar when the effects of strain and quantum confinement in the SLS are included at 9 K. This implies that an initially type-I ZnSe/ $\text{Zn}_{0.75}\text{Mn}_{0.25}\text{Se}$ SLS should become type II at a pressure no higher than 77 kbar. As is seen in this subsection and in Sec. III D, this is not inconsistent with the observations for the $x=0.23$ SLS. No direct comparison is possible for the other SLSs.

Additional effects of pressure on the PL energy include the pressure dependence of the quantum confinement energies for electrons and holes, and of the exciton binding energy (Rydberg energy). These include the effects of pressure on the well width, barrier height, effective masses,³⁷ dielectric constant,³⁸ and the 3D-2D dimensionality of the exciton.³⁹

Confinement energies scale as n^2/mL^2 , where n is the quantum number, m is the appropriate effective mass, and L is the well width. In PL, only the $n=1$ levels are important. The change in $\alpha = dE/dp$ due to the decreasing well width with p is $\sim +0.02$ meV/kbar, while that due to the increasing effective mass,³⁷ which is associated with the increasing band gap with p , is estimated to be ~ -0.06 meV/kbar (-0.04 and -0.02 meV/kbar for the electrons and light holes, respectively).

The exciton binding energy E_x will also change with p . The binding energy of the exciton varies as $-(1/\epsilon r) f(L/a_B)$, where ϵ is the dielectric constant, r is the exciton radius, and $f(x)$, which weights the 3D-2D dimensionality of the binding energy, is a function of the well width L in

units of the Bohr radius a_B .³⁹ Changes to α due to the pressure dependence of ϵ (Ref. 38) and r are estimated to be ~ -0.006 and ~ -0.07 meV/kbar, respectively. Finally, as the well width decreases, the exciton becomes less three dimensional in character and more two dimensional, according to df/dp . This perturbs α by $\sim +0.025$ meV/kbar.³⁹ The binding energy of the exciton E_x will therefore increase overall by ~ -0.05 meV/kbar assuming that band offsets do not change with pressure.

Therefore, the net effect of pressure on confinement and exciton binding decreases α by ~ 0.1 meV/kbar. This change in α may explain why α for the $x=0.23$ SLS is smaller than that for bulk ZnSe. Inclusion of small perturbations due to band offset changes should not change this observation. Anyway, note that these corrections are relatively small and within the experimental error.

Band offsets do, however, change with pressure. The ZnSe well in the $x=0.23$ SLS is thin enough that the biexciton feature is resolved from the exciton.⁹⁻¹¹ With added pressure it merges into the free-exciton peak at a (relative) rate of 0.16 meV/kbar. As with the exciton, the binding energy of the biexciton depends on pressure-dependent quantities, such as the effective masses and the well width. In particular, reduced dimensionality due to thinner ZnSe layers with increased p would suggest increased biexciton binding energy E_{xx} and increased splitting of the exciton and biexciton;^{11,40} however, exactly the opposite behavior is seen, which suggests that offset variations with p result in a net reduction of two-dimensional confinement. This is reasonable because $\alpha_2 < \alpha_1$, which means that the sum of the conduction- and valence-band offsets decreases with pressure. As a result, both the exciton and biexciton binding energies, E_x and E_{xx} , in fact decrease with pressure.

C. Intraionic Mn^{2+} transitions

At ambient pressure, PL from ZnMnSe films and bulk material is predominantly in the yellow (~ 2.1 eV), due to intraionic transitions in the Mn^{2+} ions, while PL due to electron/hole recombination is weak. The "yellow" PL seen here can be attributed to the ${}^4T_1 \rightarrow {}^6A_1$ Mn^{2+} transition, as has been previously proposed.^{8,27} Since GaAs becomes indirect above 41.3 kbar,⁴¹ the yellow PL does not come from the GaAs substrate.

As seen in Fig. 4, the energy of the yellow PL decreases

with pressure, with a slope of -3.2 meV/kbar for each SLS at 9 K (Table III), which is insensitive to x . The data presented by Arora *et al.*²⁷ on the yellow PL from bulk $\text{Zn}_{0.67}\text{Mn}_{0.33}\text{Se}$ also shows a negative pressure dependence for this $\text{Mn}^{2+} {}^4T_1 \rightarrow {}^6A_1$ transition with a coefficient ~ -3 meV/kbar at 295 K. According to crystal-field theory,⁴² the transition energy between the 4T_1 state (which comes from the 4G state for free $\text{Mn}^{2+} 3d^5$) and the ${}^6A_1({}^6S)$ ground state is⁴²

$$E({}^4T_1) - E({}^6A_1) = 10\tilde{B} + 5\tilde{C} - 10\tilde{D}q, \quad (16)$$

where $\tilde{B}$ and $\tilde{C}$ are the Racah parameters and $\tilde{D}q$ is the crystal-field value.

In the absorption study by Ves *et al.*,²⁶ the transition energy of ${}^4A_1, {}^4E \leftarrow {}^6A_1$ in bulk $\text{Zn}_{1-x}\text{Mn}_x\text{Se}$ was found to have the negative linear pressure coefficients -2.0 and -2.25 ± 0.2 meV/kbar for $x=0.15$ and 0.25 , respectively, at 295 K. The splitting of these two levels is⁴²

$$E({}^4A_1, {}^4E) - E({}^6A_1) = 10\tilde{B} + 5\tilde{C}. \quad (17)$$

In Ref. 26, the pressure derivative of this relation was used to determine that $d\tilde{B}/dp = -0.065$ meV/kbar by assuming that $\tilde{C}/\tilde{B} = 4.5$.

Using Eqs. (16) and (17), the pressure derivative of the energy difference between the $({}^4A_1, {}^4E)$ and 4T_1 states is $10 d(\tilde{D}q)/dp$. Since in a point ion model $\tilde{D}q \sim 1/R^5$, where R is the radial distance,⁴²

$$10 \frac{d(\tilde{D}q)}{dp} = \frac{50}{3} \frac{\tilde{D}q}{B}, \quad (18)$$

where B is the bulk modulus. With $B=577$ kbar and $\tilde{D}q=0.045$ eV,⁶ this difference is 1.3 meV/kbar, which agrees with the experimental difference of 1 meV/kbar using the current data and that from Ref. 26. Similar confirmations of Eq. (18) have been seen for Mn^{2+} intraionic transitions in CdMnTe (Ref. 43) and ZnMnTe .⁴⁴ The biaxial strain present in these SLSs and the differences in measurement temperatures in the different cited experiments should have little effect on this analysis.

D. Intensity changes and phase transitions

In the $x=0.51$ SLS, the intensities of both the violet and yellow PL decrease rapidly above ~ 67 kbar. For the $x=0.33$ SLS, the violet PL decreases rapidly near ~ 75 kbar, but the yellow PL remains strong until $> \sim 82$ kbar. For the $x=0.23$ SLS, the violet PL decreases rapidly near 85 kbar, but the yellow PL remains strong up to the maximum pressure 88 kbar. These abrupt decreases may be due to phase transitions or to changes in the band alignment.

Ves *et al.*²⁶ found that bulk $\text{Zn}_{1-x}\text{Mn}_x\text{Se}$ (zinc-blende structure) undergoes a phase transition at a pressure that decreases with x from ~ 135 kbar for $x=0$ (ZnSe) to ~ 92 kbar for $x=0.25$. This suggests that at elevated pressures a phase transition may be occurring in the alloy layers, which could either hinder the creation of electron/hole pairs in the ZnSe layers or the observation of band-gap PL from the ZnSe. Also, a phase transition in the ZnMnSe could affect the Mn^{2+} ions and perturb (and quench) the

yellow PL. If both the violet and yellow PL were affected this way, the intensities of both signals would abruptly decrease at the same pressure. This is clearly seen for the $x=0.51$ SLS, but is not seen for the other two SLSs. Using a linear fit to extrapolate the data in Ref. 26 to higher Mn^{2+} concentrations, phase transition pressures of 96 , 78 , and 47 kbar are predicted for the $x=0.23$, 0.33 , and 0.51 zinc-blende alloys, respectively. For the $x=0.51$ SLS, the changes occur at p much higher than the extrapolated phase transition pressure. This is not surprising since Weinstein *et al.*^{45,46} have shown that in a heterostructure composed of two semiconductors, the semiconductor with the lower phase transition pressure in the bulk phase can be superpressed beyond that transition pressure because of the energy competition between misfit dislocations and interfacial strain.

The decrease of yellow PL intensity at the phase transition is consistent with the studies by Ves *et al.*,²⁶ who saw absorption attributed to the ${}^4A_1, {}^4E \leftarrow {}^6A_1$ intraionic transition from ~ 10 – 15 kbar up to only ~ 6 kbar below the phase transition, which was noted by the sample becoming opaque. They saw no absorption at ambient pressure. Although yellow PL was seen at 1 bar in the three SLSs examined here (and also by Arora *et al.*),²⁷ Fig. 6 shows that it is relatively weak below 20 kbar. Note also that the $x=0.51$ SLS became opaque at the same ~ 67 kbar pressure at which the violet and yellow PL vanished.

Alternately, this sudden decrease in violet PL intensity with pressure could be explained by a valence- or conduction-band crossover from type-I $\rightarrow$ II alignment. Since the band gap in ZnMnSe is expected to eventually be smaller than that in ZnSe at high enough pressure, as was discussed in Sec. III B, this mechanism is a distinct possibility. The intensity of yellow PL would not be expected to decrease in this mechanism, unless the upper Mn^{2+} level also crossed with the ZnSe or ZnMnSe valence band. The rapid decrease of the violet PL in the $x=0.23$ and 0.33 SLSs near 85 and 75 kbar, respectively, may be due to such a band crossing, while the decrease in yellow PL near 82 kbar in the latter sample may be due to a phase transition in the alloy layers.

IV. CONCLUDING REMARKS

The results of the photoluminescence experiments conducted here are consistent with type-I band alignment in $\text{ZnSe}/\text{ZnMnSe}$ strained-layer superlattices at ambient pressure, with electron and hole confinement in the ZnSe layers. Type-I alignment occurs for pressures up to at least 65 kbar for each SLS studied. At even higher pressures there is evidence of phase transitions in the ZnMnSe layers and of band crossings.

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