PHYSICAL REVIEW B VOLUME 46, NUMBER 20 15 NOVEMBER 1992-II

Exciton photoluminescence in strained and unstrained ZnSe under hydrostatic pressure

Judah A. Tuchman, Sangsig Kim, Zhifeng Sui, and Irving P. Herman
Department of Applied Physics, Columbia University, New York, New York 10027

(Received 13 May 1992; revised manuscript received 30 July 1992)

Near-band-gap photoluminescence (PL) from exciton recombination in bulk crystalline ZnSe and in strained and strain-relaxed ZnSe epilayers grown on GaAs substrates is examined for pressures up to 80 kbar at 9 K in a diamond-anvil cell. The small sublinear dependence of PL energy with pressure for bulk ZnSe is attributed to the pressure dependence of the bulk modulus. In the strained ZnSe film, the change in biaxial strain with pressure is seen by the changing separation of the heavy- and light-hole exciton peaks. The heavy-hole exciton energy goes from being 12.5 meV below that of the light hole (1 bar), to the same energy as the light hole (~ 29 kbar), to relatively higher enegy (>29 kbar) as pressure is increased, which shows that the strain in the ZnSe film has been tuned from being compressive to tensile. In contrast, PL suggests that strain-relaxed films slip when pressure is applied. The hydrostatic deformation potential for near-band-gap transitions in ZnSe is $a = -4.37$ eV, while $|a|$ is unexpectedly larger for transitions associated with deep levels. There is evidence that the tetragonal deformation potential b is a function of either volume deformation or strain.

I. INTRODUCTION

The electronic structure and vibrational properties of ZnSe-based semiconductor heterostructures have been studied in great detail, in part because these structures are potential active media in optical devices involving blue light emission.[1,2] The interesting properties of these heterostructures come from band-gap engineering through the use of strains, dopants, and quantum confinement. This study examines the effects of strain on the electronic properties of ZnSe by studying changes in band-edge photoluminescence (PL) that occur with the application of hydrostatic pressure. Three contrasting types of ZnSe structures are examined: strained and strain-relaxed epilayers of ZnSe on GaAs, and bulk crystalline ZnSe. This appears to be the first investigation of band-edge photoluminescence in bulk and thin-film ZnSe under pressure.

Epilayers of ZnSe have been grown commensurately and incommensurately on GaAs substrates by using molecular-beam epitaxy (MBE). Commensurate growth has been achieved for thicknesses up to ~ 0.15 μm.[3–6] Elastic strains due to the 0.25% lattice mismatch are accommodated up to this critical thickness. However, for larger thicknesses misfit dislocations lower the total energy of the system and incommensurate growth ensues.[3,5,6] Photoluminescence has been used to characterize epilayer strains by their effect on band-edge emission.[5,7,8]

The three samples considered here represent three contrasting conditions of initial strain. For the bulk ZnSe sample there is no lattice mismatch, and therefore no net strain is present at ambient pressure. In the second sample, the ZnSe epilayer is thinner than the critical thickness for misfit dislocation formation (~ 1500 Å). The film is therefore commensurately grown to the GaAs substrate, and is under compressive strain of $\sim 0.25\%$. Finally, in the third sample, the ZnSe epilayer is greater than the critical thickness, and is therefore incommensurately grown. As a result, at ambient pressure there is no biaxial strain in the film at the growth temperature (~ 320 °C). There is, however, net biaxial tension in the film at room temperature and at the 9-K temperature of these measurements, since the thermal expansion coefficient is larger for the epilayer than for the substrate.[5,6,8]

The biaxial strain in the ZnSe layers causes a shift in the band-gap energy, as well as a splitting between the heavy- and light-hole valence bands, which are otherwise degenerate at $\mathbf{k}=0$. In the strained layer, the application of hydrostatic pressure not only increases the net hydrostatic component of strain, but also changes the nonhydrostatic component because of the differences in the compressibilities of ZnSe and GaAs.[9] The separation in the lh and hh exciton PL peaks indicates this changing strain. In particular, in this paper the crossover from initially compressive to tensile strain is demonstrated to occur near 29 kbar for the strained ZnSe epilayer at 9 K.

Previous studies on the application of hydrostatic pressure to ZnSe have primarily focused on bulk material. These have included absorption,[10,11] donor-acceptor pair,[12] and self-activated luminescence experiments[13] at various temperatures, which have measured the linear slope of the band-gap energy E with pressure p in the range 6.0–7.5 meV/kbar. Ves *et al.*[11] have shown a sublinear relationship between the ZnSe band-gap energy and pressure by transmission, and have provided a fit to their data to quadratic order.

A preliminary report of this work described PL in these ZnSe structures up to 25 kbar.[14] To our knowledge there had been no previous study of the pressure dependence of the near-band-gap photoluminescence in either bulk or epilayer ZnSe systems. During the course of the current work, two related investigations of the effect of pressure on strains in ZnSe epilayers on GaAs have appeared. Cui *et al.*[15] have studied this system using Raman scattering. Rockwell *et al.*[16] have examined ZnSe epilayers at 80 K by using photoreflectance, and have concluded that the tetragonal deformation potential b depends on pressure.

II. EXPERIMENTAL PROCEDURE AND RESULTS

Photoluminescence measurements were made on 0.082-μm- (strained) and 2.1-μm- (strain relaxed) thick ZnSe epilayers grown on GaAs (001) by molecular-beam epitaxy, which are labeled the thin and thick films, respectively, and on bulk crystalline ZnSe that was grown by zone melting. Experiments were conducted at $T=9$ K and at pressures up to 80 kbar, which is below the pressure for phase transitions in ZnSe (137 kbar) and GaAs (172 kbar).

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. 17, and was placed within a closed cycle cryostat. Samples were inserted together with ruby chips, for pressure calibration,[18] within a gasketed liquid argon bath to obtain near-hydrostatic conditions. While the cell design allows for pressure tuning at low temperature, it was found that near-hydrostatic conditions could not be obtained this way. Pressure was therefore added at room temperature.

ZnSe photoluminescence was excited using the 4067-Å or the multiline uv lines (3375–3564 Å) from a krypton ion laser, and detected using a 0.85-m double spectrometer, and a cooled photomultiplier tube or intensity-enhanced diode array. Photon counting electronics were interfaced to an IBM AT for A/D data conversion, storage, and analysis.

PL spectra for each of the three samples are presented at ambient pressure in Figs. 1–3. For the bulk crystalline sample (Fig. 1) the following identifications have been made. The dominant feature at 2.7970 eV (I_{20}) is associated with a neutral bound donor exciton, attributed to either an In or Ga impurity. A neutral bound acceptor accounts for the exciton feature at 2.7924 eV (I_1). The feature at 2.7827 eV (I_1^D) is commonly attributed to deep Cu acceptors or Zn vacancies, or to an exciton bound to an impurity complex which involves Cu. The phonon replica $I_1^{D\text{-LO}}$ is found 31.6 meV lower in energy than I_1^D. Finally, two weak features higher in energy than I_{20} are due to the excited state ($n=2$) of a donor bound exciton at 2.8014 eV (I_{2D}) and the free exciton transition at 2.8039 eV (FE).

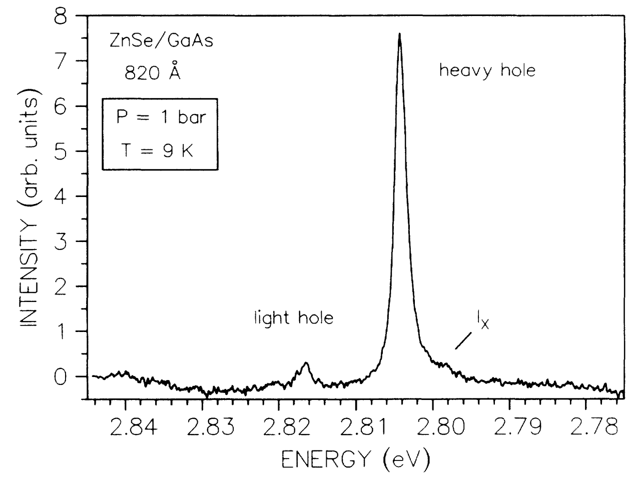

FIG. 2. The PL spectrum of a strained ZnSe layer on GaAs at ambient pressure at 9 K.

The two main peaks observed in the PL spectrum of the thin film (Fig. 2) correspond to the ground-state free exciton transition for heavy holes (2.8041 eV), and, higher in energy by 12.5 meV, to that for light holes (2.8166 eV). An additional but very small peak is found near 2.7998 eV (I_x), which is usually attributed to a neutral bound exciton.

For the thick film (Fig. 3), a total of six features are identified. Two of the features correspond to the $n=1$ light-hole FE (2.8006 eV), which is the largest peak, and

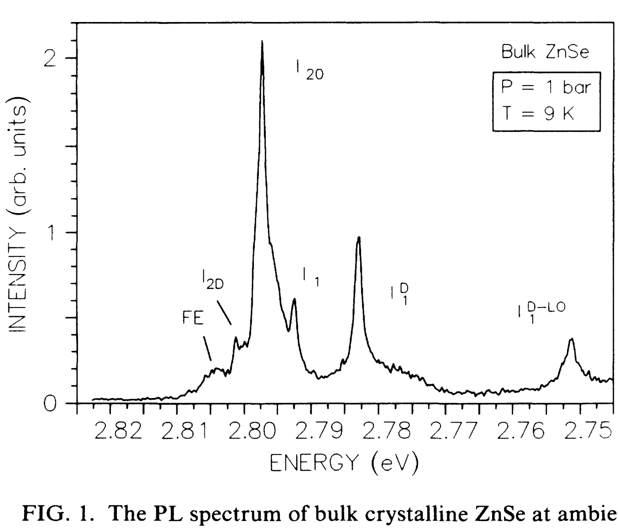

FIG. 1. The PL spectrum of bulk crystalline ZnSe at ambient pressure at 9 K.

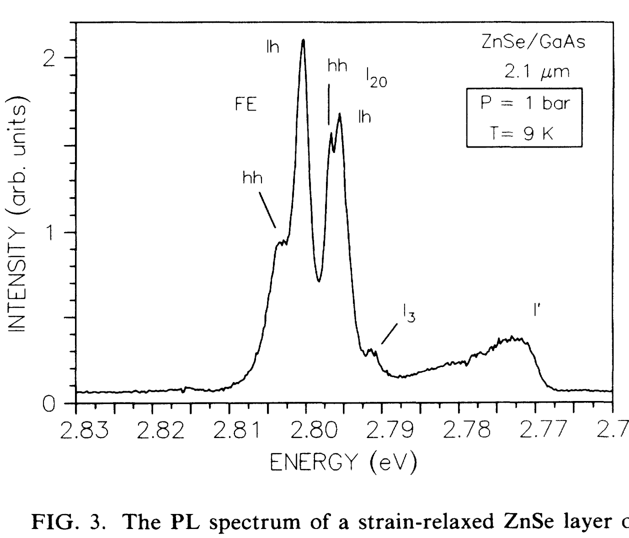

FIG. 3. The PL spectrum of a strain-relaxed ZnSe layer on GaAs at ambient pressure at 9 K.

the heavy-hole FE (2.8034 eV), which is the small shoulder on the high-energy side of the lh peak. The (I_{20}) neutral donor bound exciton also accounts for two peaks corresponding to the heavy-hole feature at 2.7969 eV and the light hole at 2.7959 eV. The remaining two features correspond to an ionized donor (I_3) at 2.7915 eV and an unidentified peak (I') at 2.7726 eV.

Photoluminescence is monitored with increasing pressure for each of the three samples, with representative PL spectra shown in Figs. 4(a)–6(a). For each, the PL energies of various excitonic features are obtained by deconvoluting and fitting the peaks, and are plotted as a function of pressure [Figs. 4(b)–6(b)]. These are fit by

$$E(p)=E_0(1\text{ bar})+\alpha p+\beta p^2 \qquad (1)$$

with α and β listed in Table I. Typical experimental errors in PL energy are $\sim\pm0.5$ meV and in pressure are $\sim\pm1$ kbar.

One feature of these measurements is the large α for the deeper excitonic peaks. Specifically, for bulk ZnSe, the I_1^D feature increases at a faster rate than the I_{20} peak, and the two peaks merge at ~55 kbar [Fig. 4(a)].

For the thin epilayer, the prominent feature is the decrease in the energy difference between the heavy-hole and light-hole exciton features with pressure. These merge near $p=29$ kbar, and then begin to separate again [Fig. 5(a)]. The heavy-hole peak is lower in energy at low pressures, while the lower-energy feature at high pressures is identified as the light hole. This is confirmed by the change in the ratio of peak intensities through crossover. The difference between the hh and lh energies is not linear with p [Fig. 5(b)].

III. DISCUSSION

Hydrostatic pressure shifts the conduction- and valence-band edges of a semiconductor by changing the volume, while uniaxial pressure also splits these bands by changing crystal symmetry.[19–21] For ZnSe with its direct band gap at Γ, the conduction band is only subject to the hydrostatic components of strain.[22] In addition to the net shift of the valence bands (Γ_8) due to hydrostatic strain, tetragonal distortion (biaxial and uniaxial strain) splits the fourfold-degenerate $P_{3/2}$ multiplet into heavy-

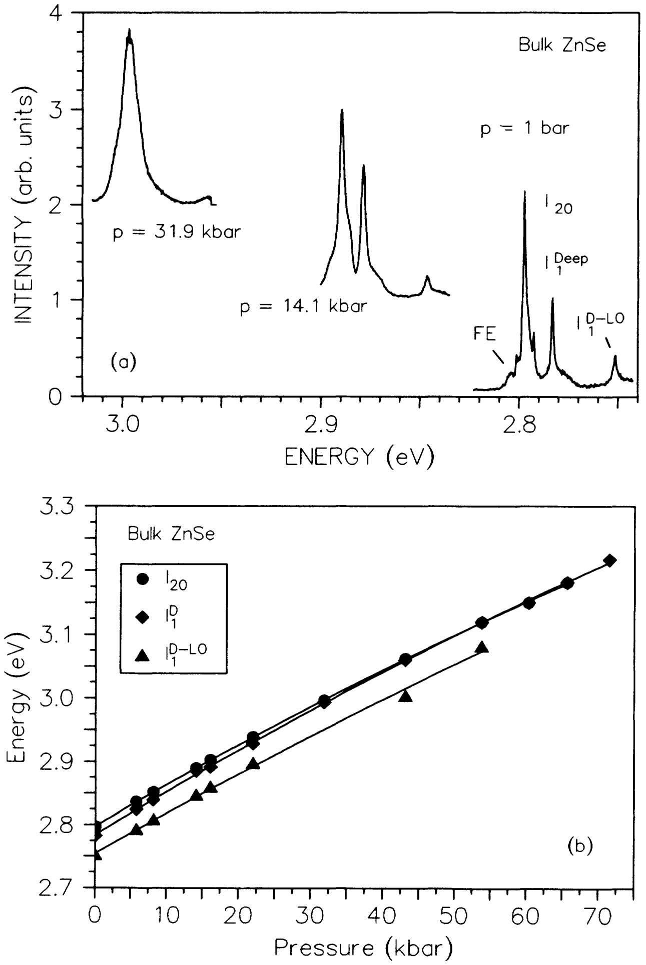

FIG. 4. Representative PL traces for bulk ZnSe at various pressures in (a), with the energy dependence of the I_{20}, I_1^D and $I_1^{D\text{-LO}}$ peaks vs pressure at 9 K in (b).

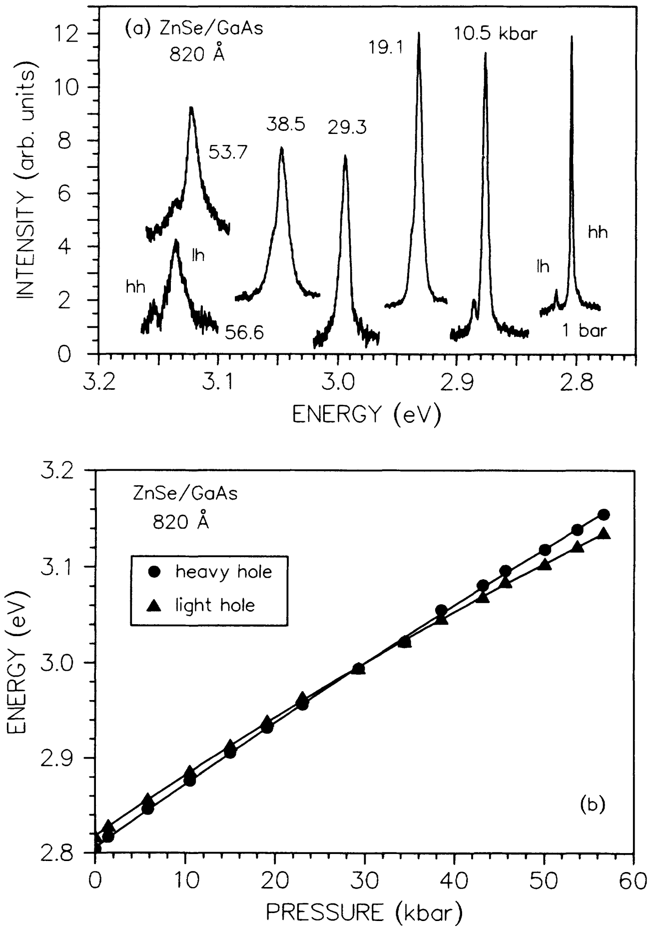

FIG 5. Representative PL traces for the thin ZnSe layer at various pressures in (a), with the energy dependence of the light-hole and heavy-hole peaks vs pressure at 9 K in (b).

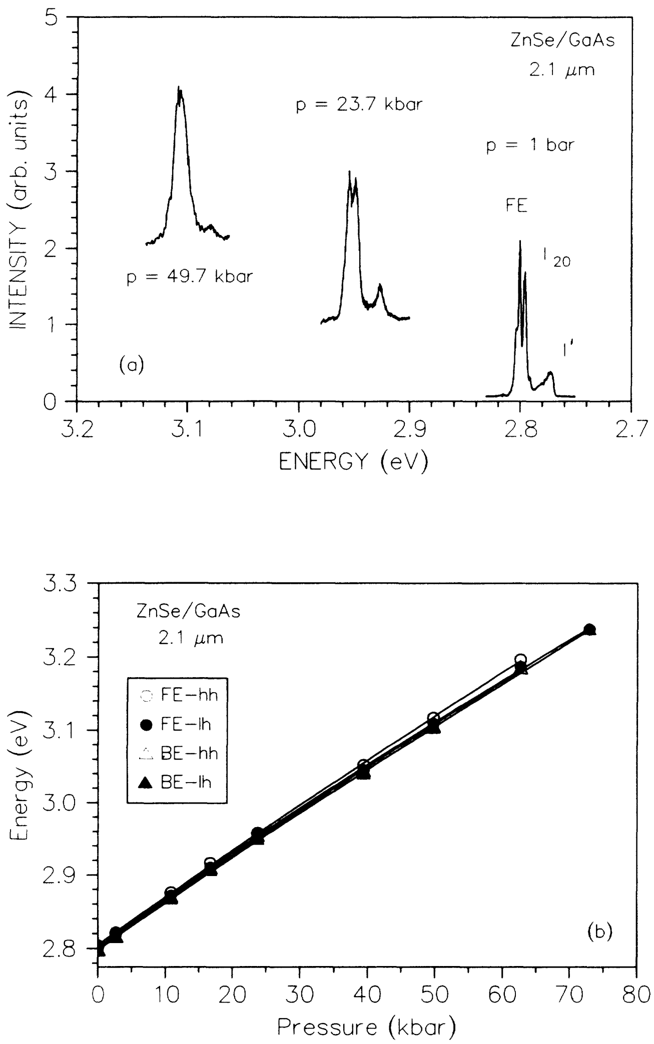

FIG. 6. Representative PL traces for the thick ZnSe layer at various pressures in (a), with the energy dependence of the free exciton (FE) light- and heavy-hole peaks and the I_{20} bound-exciton (BE) light- and heavy-hole peaks vs pressure at 9 K in (b).

TABLE I. Parameter fits for ZnSe PL energy vs pressure.

	Feature	α (meV/kbar)	β (meV/kbar^2)
Bulk	I_{20}	6.70±0.2	−0.014±0.003
	I_1^D	6.94±0.2	−0.013±0.003
	$I_1^{D\text{-LO}}$	6.49±0.2	−0.010±0.004
Thin epilayer	FE hh	6.79±0.2	−0.011±0.003
	FE lh	6.58±0.2	−0.018±0.003
Thick epilayer	FE hh	6.55±0.2	−0.005±0.003
	FE lh	6.61±0.2	−0.008±0.003
	I_{20} hh	6.56±0.2	−0.007±0.003
	I_{20} lh	6.42±0.2	−0.005±0.003
	I_3	6.55±0.2	−0.008±0.004
	I'	6.90±0.2	−0.016±0.004

hole (hh: $J=\frac{3}{2}$, $m_J=\pm\frac{3}{2}$) and light-hole (lh: $J=\frac{3}{2}$, $m_J=\pm\frac{1}{2}$) bands.

Including the relative shifts of the conduction band and the average of the valence bands under hydrostatic deformation ($\Delta\Omega/\Omega$) to second order, the band gap for unstrained bulk ZnSe varies as

$$E_{\text{bulk}}(\Omega)=E_0(\Omega_0)+a\frac{\Delta\Omega}{\Omega}+\delta\left[\frac{\Delta\Omega}{\Omega}\right]^2 , \tag{2}$$

where Ω is the volume, Ω_0 is the volume at 1 bar, and $\Delta\Omega=\Omega-\Omega_0$. $a=a_c-a_v$ and $\delta=\delta_c-\delta_v$, where a_c and a_v are the (linear) hydrostatic deformation potentials for the conduction and valence bands, respectively, and δ_c and δ_v are the quadratic dependences of the conduction- and valence-band Γ-point energies on volume, respectively.

At zone center, the three valence bands split due to spin-orbit coupling and uniaxial deformations by[20]

$$\Delta E_{v,\text{hh}}=\tfrac{1}{3}\Delta_0-\tfrac{1}{2}\delta E_{001} , \tag{3}$$

$$\Delta E_{v,\text{lh}}=-\tfrac{1}{6}\Delta_0+\tfrac{1}{4}\delta E_{001}+\tfrac{1}{2}[\Delta_0^2+\Delta_0\delta E_{001}+\tfrac{9}{4}(\delta E_{001})^2]^{1/2} , \tag{4}$$

$$\Delta E_{v,\text{so}}=-\tfrac{1}{6}\Delta_0+\tfrac{1}{4}\delta E_{001}-\tfrac{1}{2}[\Delta_0^2+\Delta_0\delta E_{001}+\tfrac{9}{4}(\delta E_{001})^2]^{1/2} , \tag{5}$$

where Δ_0 is the spin-orbit splitting and $\delta E_{001}=2b(\varepsilon_{zz}-\varepsilon_{xx})$ is the strain splitting, with b the tetragonal or shear uniaxial deformation potential. To first order, δE_{001} depends on pressure, while Δ_0 does not.

Using Eqs. (2)–(4), the heavy-hole and light-hole band gaps are

$$E_{\text{hh}}=E_0+a\left[\frac{\Delta\Omega}{\Omega}\right]+\delta\left[\frac{\Delta\Omega}{\Omega}\right]^2+b(\varepsilon_{zz}-\varepsilon_{xx}) , \tag{6}$$

$$E_{\text{lh}}=E_0+a\left[\frac{\Delta\Omega}{\Omega}\right]+\delta\left[\frac{\Delta\Omega}{\Omega}\right]^2-b(\varepsilon_{zz}-\varepsilon_{xx})-2\frac{b^2(\varepsilon_{zz}-\varepsilon_{xx})^2}{\Delta_0} . \tag{7}$$

Since $\Delta_0=430$ meV for ZnSe and $\delta E_{001}\sim 10$ meV for the strained layers, Eq. (4) has been expanded assuming $\Delta_0 \gg \delta E_{001}$ to give Eq. (7).

A. Bulk ZnSe

For bulk ZnSe the band gap E can be expressed in terms of volume Ω, as in Eq. (2), or pressure p, as in Eq. (1). These expressions can be related by expanding Murnaghan's equation of state[23]:

$$\Omega(p)=\Omega(1\text{ bar})\left[1+p\frac{B'}{B}\right]^{-1/B'} , \tag{8}$$

where B is the bulk modulus of ZnSe and $B'=dB/dp$. The linear terms are related by

$$\alpha_{\text{bulk}}=-\frac{a}{B} , \tag{9}$$

while the quadratic terms are related by

$$\beta_{\text{bulk}}=\frac{[(1+B')a+2\delta]}{2B^2}\ . \tag{10}$$

One could obtain a and δ from α and β by using Eqs. (9) and (10). However, when Eq. (8) is expanded in orders of pB'/B, it becomes clear that analysis of any parameter in terms of pressure can be inaccurate when p approaches even a fraction of B/B' ($=130$ kbar). Instead, either several terms of higher order in p must be included in the fit or all the data must be expressed in terms of $\Delta\Omega/\Omega$ by using Murnaghan's equation before analysis.

The pressure dependence of the data in Fig. 4(b) was changed to a dependence on volume by using Eq. (8) with the ZnSe parameters $B=642$ kbar and $B'=4.77$.[11,24] B was obtained at 9 K by extrapolating the ZnSe bulk modulus at 300 K [610 kbar, which is an average of two published values, 595 (Refs. 15 and 25) and 624 kbar (Refs. 11 and 24)] using the reported temperature dependence of bulk modulus down to 77 K.[26] From the quadratic fit of the data for the I_{20} exciton, which is expected to track the band edge, one obtains the hydrostatic deformation potentials $a=-4.37$ eV and $\delta=+5.21$ eV. These can be compared to $a=-4.30$ eV and $\delta=+6.63$ eV, which are obtained from α and β by using Eqs. (9) and (10) and are therefore less accurate.

Ves *et al.*[11] analyzed their transmission data as a quadratic fit of energy versus linear deformation ($-\Delta a/a$). Their linear and quadratic coefficients $a'=14.4$ eV and $\delta'=6.2$ eV can be compared to $a'=13.1$ eV and $\delta'=30.3$ eV for the current data analyzed in terms of $-\Delta a/a$. δ' measured for bulk ZnSe here is significantly larger than that in Ref. 11, but is consistent with that measured in ZnSe epilayers both here (Sec. III B) and in Ref. 16.

Pressure is seen to increase the peak associated with the deep level (I_1^D) faster than it increases the peak for the shallow neutral donor bound exciton (I_{20}). Typically, a deep level is expected to have a weaker pressure dependence than the band edge[27] due to its increased localization. However, an exciton bound to a deep acceptor is expected to track the band edge since the pressure coefficient of the valence band is relatively small and the electron is bound to the hole via Coulomb attraction (as for a shallow donor). The increased pressure dependence seen here suggests reduced Coulomb attraction due to the complex nature of the defect.

Finally, because the LO phonon energy increases by ~ 0.04 meV/kbar,[15] α for the phonon replica ($I_1^{D\text{-LO}}$) should be smaller than that for I_1^D by this amount. It is not clear why the measured difference is even larger.

B. Strained ZnSe epilayers

In ZnSe epilayers biaxial strain results from the lattice mismatch between the epilayer and the substrate. The degree of lattice mismatch in a coherently grown ZnSe epilayer leads to the nonhydrostatic strain components:

$$\varepsilon_{xx}^{(b)}=\varepsilon_{yy}^{(b)}=\frac{a_G(p)-a(p)}{a(p)}=\varepsilon(p)\ , \tag{11}$$

$$\varepsilon_{zz}^{(b)}=-\frac{2C_{12}}{C_{11}}\varepsilon_{xx}^{(b)}\ , \tag{12}$$

where a_G is the GaAs lattice constant, which is the in-plane lattice parameter for the ZnSe strained layer, a is the unstrained lattice parameter for ZnSe, and C_{11} and C_{12} are elastic constants for ZnSe [$B=(C_{11}+2C_{12})/3$].

The pressure dependence of the lattice parameter for bulk material is obtained from Eq. (8):

$$a(p)=a(1\ \text{bar})\left[1+p\frac{B'}{B}\right]^{-1/3B'}\ , \tag{13}$$

where $B'=dB/dp$.

Externally applied hydrostatic pressure modifies biaxial strain through the pressure dependences of Eqs. (11) and (12):

$$\varepsilon(p)=\frac{a_G}{a}\left[\frac{1-\dfrac{p}{3B_G}}{1-\dfrac{p}{3B}}\right]-1 \tag{14}$$

in the low-pressure regime. B_G is the bulk modulus for GaAs (794 kbar at 9 K, also $B'=4.67$).[28] Since $B>B_G$ while $a<a_G$, pressure decreases the magnitude of the strain in the ZnSe epilayer initially. Use of the exact expression for ε instead of the linearized form will decrease $d\varepsilon/dp$ slightly.[9]

Pressure also leads to additional hydrostatic strain components:

$$\varepsilon_{xx}^{(h)}=\varepsilon_{yy}^{(h)}=\varepsilon_{zz}^{(h)}=\frac{1}{3}\left[\left[1+\frac{B'}{B}p\right]^{-1/B'}-1\right]\ . \tag{15}$$

Each component of the total strain is composed of a hydrostatic and biaxial component, $\bar{\varepsilon}_{ij}=\varepsilon_{ij}^{(h)}+\varepsilon_{ij}^{(b)}$.

Using Eqs. (11)–(15), at low p the fractional change in volume (Ω) can be written as

$$\frac{\Delta\Omega}{\Omega}=\bar{\varepsilon}_{xx}+\bar{\varepsilon}_{yy}+\bar{\varepsilon}_{zz}=-\frac{p}{B}+2(1-C_{12}/C_{11})\varepsilon(p)\ . \tag{16}$$

Keeping only the linear terms in Eqs. (6) and (7)

$$E_{\substack{hh\\lh}}=E_0-\frac{a}{B}p+\left[2a\left[1-\frac{C_{12}}{C_{11}}\right]\mp b\left[1+\frac{2C_{12}}{C_{11}}\right]\right]\varepsilon\ . \tag{17}$$

In the thin layer the heavy-hole level is higher than the light hole ($\varepsilon<0$), while the light-hole level is higher in the thick film ($\varepsilon>0$). Using Eqs. (9) and (17)

$$\alpha_{\substack{hh\\lh}}=\alpha_{\text{bulk}}+\left[2a\left[1-\frac{C_{12}}{C_{11}}\right]\mp b\left[1+\frac{2C_{12}}{C_{11}}\right]\right]\frac{d\varepsilon}{dp}\ , \tag{18}$$

where

$$\frac{d\varepsilon}{dp}=\frac{1}{3}\frac{a_G}{a}\left[\frac{1}{B}-\frac{1}{B_G}\right]\ . \tag{19}$$

By examining at ambient pressure the splitting of the heavy and light holes and the blueshift of their average energy relative to bulk ZnSe, a and b may be determined with Eq. (17), as was done in Ref. 4. Using $C_{11}/C_{12}=0.6$, one obtains $a=-4.74$ eV and $b=-1.14$ eV, which are close to the values -4.87 and -1.05 eV, respectively, reported in Ref. 4.

Equation (19) is valid when the ZnSe film does not slip on the GaAs substrate as pressure is applied, i.e., if the in-plane lattice constant of the ZnSe film follows the lattice constant of GaAs. This is expected to be true for the commensurate thin film. Equations (18) and (19) predict that $\alpha_{\mathrm{lh}}<\alpha_{\mathrm{hh}}<\alpha_{\mathrm{bulk}}$, and that the magnitude of the biaxially compressive strain should decrease with increasing pressure, become zero near 26 kbar, and then become increasingly tensile as pressure increases. Therefore, below ~26 kbar the lh exciton is expected to be higher in energy than the hh, while above this crossover pressure the hh exciton should be higher. Exact analysis[9] of strains using Murnaghan's equation also predicts a crossover, but at pressure of 31 kbar.

This pressure tuning of strain and the reversal of the lh and hh features have been confirmed for the thin epilayer, as is seen in Fig. 5. When data at 29.3 and 34.4 kbar, where the lh and hh PL features cannot be resolved, are excluded from analysis, the crossover from initially compressive to tensile strain is seen to occur at 28.8 kbar. Inclusion of these points, with the assumption that $E_{\mathrm{lh}}=E_{\mathrm{hh}}$ at these two pressures, leads to crossover at 30.8 kbar.

The deformation potentials can also be determined by analyzing E_{lh} and E_{hh} at elevated p by using Eqs. (6) and (7). The average of the light-hole and heavy-hole free exciton energies can be plotted versus volume deformation to help obtain the hydrostatic deformation potentials. This assumes that biaxial strain symmetrically splits the lh and hh energies, as in Eq. (17). The resulting values for a and δ are -4.56 and $+5.18$ eV, respectively. These are consistent with the values obtained in the preceding section for shallow levels in bulk crystalline ZnSe, which is expected because both free excitons and excitons bound to a shallow level are pinned to the band edge. The variation of the exciton binding energy with applied hydrostatic pressure is estimated to be only on the order of -0.07 meV/kbar, and is not very significant.

Equation (17) shows that b may be determined from the light-hole to heavy-hole energy difference at each pressure, as was already done at ambient pressure. The resulting deformation potential is plotted at each pressure in Fig. 7(a), which suggests that b decreases with pressure as $b\ (\mathrm{eV})=-1.02-0.037p$ (kbar). A similar experimental observation has been reported by Rockwell *et al.*[16] by using photoreflectance; they also modeled b as a decreasing function of pressure. By comparing the data fits using a constant and pressure-dependent tetragonal deformation potential in Fig. 7(b) (as in Figs. 6 and 9 of Ref. 16) it is seen that the assumption of a constant b leads to a very poor fit.

It is possible that the nonlinear separation of the lh and hh peaks may be explained by higher-order terms in the Hamiltonian, such as those of order $\varepsilon^2[\sim(\varepsilon_{zz}-\varepsilon_{xx})^2]$ or $\varepsilon(\Delta\Omega/\Omega)\ [\sim(\varepsilon_{zz}-\varepsilon_{xx})p]$, or by improved analysis of biaxial strain. While it is seen that the use of Murnaghan's equation to determine biaxial strain in ZnSe, instead of a linear approximation, predicts the downward curvature seen in Fig. 5(b), even with a constant value of b, it alone does not explain the increased splitting with pressure. This conclusion is in accord with Ref. 16.

The terms that are linear in biaxial strain in Eqs. (6) and (7) are $\pm b(p)\ (\varepsilon_{zz}-\varepsilon_{xx})$, which can be expressed as $\pm(b_0+b_1p)(\varepsilon_{zz}-\varepsilon_{xx})$ or as $\pm b_0(\varepsilon_{zz}-\varepsilon_{xx})$ $\pm\eta(\varepsilon_{zz}-\varepsilon_{xx})(\Delta\Omega/\Omega)$, where $\eta=-b_1B$. For $b_1=-0.037$ eV/kbar, which is determined here, one finds that $\eta=23.75$ eV. Rockwell *et al.*[16] suggested a correlation between the pressure-dependent tetragonal deformation potential and the general linear decrease of b among semiconductors with decreasing lattice constant, as determined from tight-binding calculations.[29] When expressed as a change of b with volume, this trend suggests that b decreases by 3.97 eV per $\Delta\Omega/\Omega$ decrease of

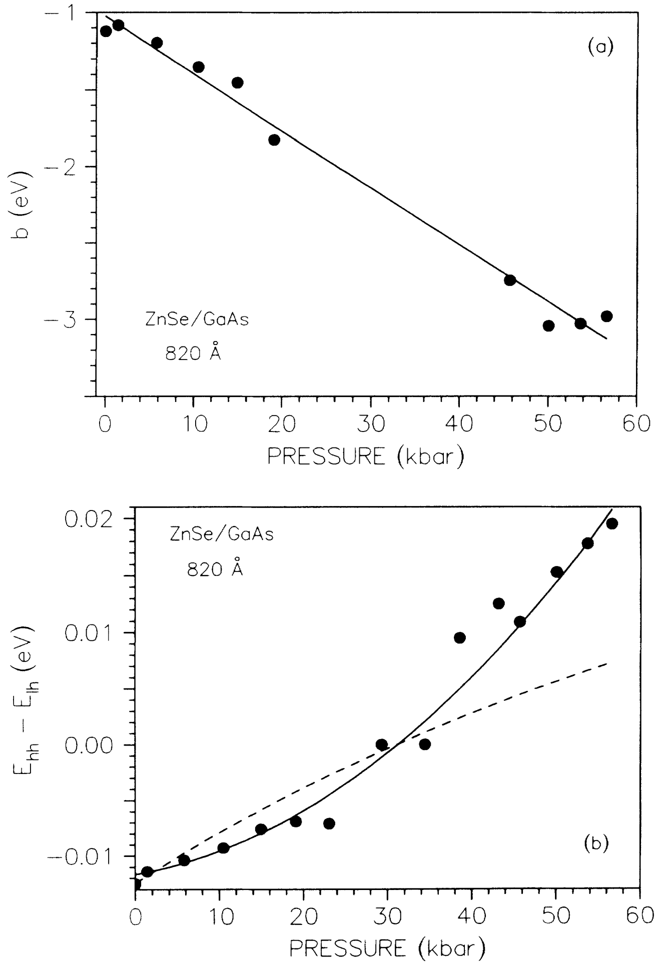

FIG. 7. The fit for the tetragonal deformation potential b from the thin-film data of Fig. 5 in (a), and the experimental heavy- and light-hole energy difference from Fig. 5 in (b), which is compared to the models with either the pressure-independent value of b (-1.14 eV) (dashed curve) or the pressure-dependent relation for b (solid curve) from (a).

semiconductor volume, which is smaller than η. It is not clear whether such a comparison is very meaningful.

When the effect of biaxial strain on volume deformation [Eq. (16)] is considered, the $(\Delta\Omega/\Omega)^2$ expressions in Eqs. (6) and (7) are seen to have a term of order εp, namely, $4\varepsilon(1-C_{12}/C_{11})p/B$, which could explain this apparent pressure dependence of b. However, the magnitude of this term is small ($\sim 3\times10^{-4}$ at 50 kbar, corresponding to a perturbation of 1.6 meV) and anyway, it does not affect the lh/hh splitting.

The energy difference $E_{\rm hh}-E_{\rm lh}$ was also modeled by using a pressure-independent value for b plus an additional term $\kappa\varepsilon^2$. One physical mechanism for this latter term is the light-hole/spin-orbit split band mixing seen in Eq. (7). This fit is plotted versus strain ε in Fig. 8, with the parameters $b=-2.23$ eV and $\kappa=1880$ eV and with strain determined by using Murnaghan's equation. This large value for κ may suggest that the $\kappa\varepsilon^2$ term is not physically significant. By using Eq. (7), κ would be expected to be ~ 120 eV, which is much smaller in magnitude than the model fit for κ.

The change in the weak feature on the high-energy side of the hh peak with pressure-induced strain proves that it is due to the light-hole FE, and that it is not the $n=2$ hh FE, as has been suggested.[30] This identification is also confirmed by the ratio of the intensities of these two peaks at pressures below and above the pressure p_c at which crossover to strain-free conditions occurs.

The transition rate for electron/hole recombination varies as $m_r^{3/2}$, where m_r is the electron/hole reduced mass.[31] Therefore, the ratio of the peak intensities I for lh and hh free exciton recombination is

$$\frac{I_{\rm lh}}{I_{\rm hh}}=\left[\frac{m_{\rm rl}}{m_{\rm rh}}\right]^{3/2}\exp(-\Delta E/kT)\ , \qquad (20)$$

where ΔE is the hh/lh separation, which is >0 at ambient pressure. Consider the PL spectrum at two pressures $p_1<p_c$ and $p_2>p_c$, for which ΔE is δE (>0) and $-\delta E$, respectively. If the ratio of the intensity of the weaker, higher-energy peak to the stronger, lower-energy peak R is R_1 at p_1(i.e.,$I_{\rm lh}/I_{\rm hh}$) and R_2 at p_2(i.e.,$I_{\rm hh}/I_{\rm lh}$), then Eq. (20) gives $\mathcal{R}=R_2/R_1=(m_{\rm rh}/m_{\rm rl})^3$ for any δE. It is clear from Fig. 5(a) that R is much larger for tensile ZnSe films ($p>29$ kbar) than for compressive films ($p<29$ kbar). Also from this figure $\mathcal{R}\sim4$, which is close to the 4.8 ratio that is expected from theory, using $m_c=0.16m_e$, $m_{\rm lh}=0.149m_e$, and $m_{\rm hh}=0.86m_e$ for ZnSe.[26]

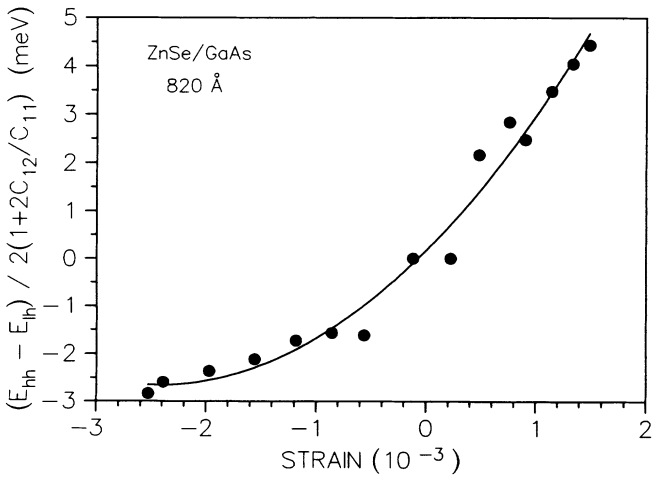

FIG. 8. The normalized heavy-hole–light-hole splitting plotted vs biaxial strain ε, where strain is determined by using Murnaghan's equation. The model fit includes a pressure-independent value for b and a $\kappa\varepsilon^2$ term.

C. Unstrained ZnSe epilayers

Using the values of a and b derived for the thin epilayer, in the thick ZnSe film the redshift from the corresponding energies in bulk ZnSe and the lh/hh splitting both correspond to a slight tensile strain of 0.06% at ambient pressure, which has been attributed[5,6,8] to the difference in the thermal expansion coefficients for ZnSe (6.8×10^6/K; 300 K) and GaAs (5.8×10^6/K; 300 K).[32]

If there were no slippage of the thick ZnSe film as pressure is applied, then α for the dominant light-hole feature would be ~0.67 meV/kbar below that of the bulk, and the lh and hh splitting would increase by ~0.48 meV/kbar. Since α is much closer to the bulk value than this prediction and since the hh and lh features follow each other closely for both free and neutral donor bound exciton PL [Fig. 6(b)], there appears to be much slippage as pressure is applied. This is in agreement with the Raman studies by Cui *et al.*[15] who found that applied hydrostatic pressure changes the optical phonon frequency in a thick incommensurate ZnSe film and bulk ZnSe at exactly the same rate. However, because the light- and heavy-hole PL features are still split, there still appears to be some residual biaxial strain, even at elevated pressure. Also note that the free exciton and I_{20} peaks track each other with pressure.

IV. CONCLUDING REMARKS

Pressure tuning of biaxial strain in ZnSe epilayers is clearly seen by the shifting and eventual reversal in energy of the photoluminescence peaks due to light- and heavy-hole exciton recombination. No such strain tuning is seen for incommensurate ZnSe layers. The hydrostatic deformation potential is approximately the same for free excitons and those bound to a shallow donor, but is larger in magnitude for excitons associated with a deep level. Though the tetragonal deformation potential obtained from the epilayer studies seems to depend on pressure (or volume), the actual physical mechanism for this is not clear.

ACKNOWLEDGMENTS

The authors would like to thank R. L. Gunshor, L. A. Kolodziejski, D. A. Cammack, and M. Shone for providing the samples studied here. We also wish to thank D. Olego, K. Shazhad, R. D. Hong, and A. Zunger for interesting discussions, and B. Weinstein for sending us a copy of Ref. 15 prior to publication. This work was supported by the Joint Services Electronics Program under Contract No. DAAL03-91-C-0016 and by the Office of Naval Research.

[1] M. A. Haase, J. Qiu, J. M. DePuydt, and H. Cheng, Appl. Phys. Lett. **59**, 1272 (1991).

[2] H. Jeon, J. Ding, W. Patterson, A. V. Nurmikko, W. Xie, D. C. Grillo, M. Kobayashi, and R. L. Gunshor, Appl. Phys. Lett. **59**, 3619 (1991); H. Jeon, J. Ding, A. V. Nurmikko, W. Xie, D. C. Grillo, M. Kobayashi, R. L. Gunshor, G. C. Hua, and N. Otsuka, *ibid.* **60**, 2045 (1992).

[3] J. Kleiman, R. M. Park, and S. B. Qadri, J. Appl. Phys. **61**, 2067 (1987).

[4] R. L. Gunshor, L. A. Kolodziejski, M. R. Melloch, M. Vaziri, C. Choi, and N. Otsuka, Appl. Phys. Lett. **50**, 200 (1987).

[5] T. Yao, Y. Okada, S. Matsui, K. Ishida, and I. Fujimoto, J. Cryst. Growth **81**, 518 (1987).

[6] J. Petruzzello, B. L. Greenberg, D. A. Cammack, and R. Dalby, J. Appl. Phys. **63**, 2299 (1988).

[7] K. Mohammed, D. A. Cammack, R. Dalby, P. Newbury, B. L. Greenberg, J. Petruzzello, and R. N. Bhargava, Appl. Phys. Lett. **50**, 37 (1987).

[8] K. Shazhad, Phys. Rev. B **38**, 8309 (1988).

[9] J. A. Tuchman and I. P. Herman, Phys. Rev. B **45**, 11 929 (1992).

[10] A. L. Edwards, T. E. Slykhouse, and H. G. Drickamer, J. Phys. Chem. Solids **11**, 140 (1959).

[11] S. Ves, K Strossner, N. E. Christensen, C. K. Kim, and M. Cardona, Solid State Commun. **56**, 479 (1985).

[12] G. L. House and H. G. Drickamer, J. Chem. Phys. **67**, 3221 (1977).

[13] P. Jaszczyn-Kopec, B. Canny, G. Syfosse, and G. Hamel, Solid State Commun. **49**, 795 (1984).

[14] J. A. Tuchman, Z. Sui, I. P Herman, R. L. Gunshor, L. A. Kolodziejski, D. A. Cammack, and M. Shone, in *Properties of II-VI Semiconductors,* edited by F. J. Bartoli, H. F. Schaake, and J. F Schetzina, MRS Symposia Proceedings No. 161 (Materials Research Society, Pittsburgh, 1990), p. 471.

[15] L. J. Cui, U. D. Venkateswaran, B. A. Weinstein, and B. T. Jonker, Bull. Am Phys. Soc. **36**, 621 (1991); L. J. Cui, U. D. Venkateswaran, B. A. Weinstein, and B T. Jonker, Phys. Rev. B **44**, 10 949 (1991).

[16] B. Rockwell, H. R. Chandrasekhar, M. Chandrasekhar, A. K. Ramdas, M. Kobayashi, and R. L. Gunshor, Phys. Rev. B **44**, 11 307 (1991).

[17] D. J. Dunstan and W. Scherrer, Rev. Sci Instrum. **59**, 627 (1988).

[18] G. J. Piermarini and S. Block, Rev. Sci. Instrum. **46**, 973 (1975).

[19] G. L. Bir and G. E. Pikus, in *Symmetry and Strain-Induced Effects in Semiconductors,* edited by D. Lourish (Wiley, New York, 1974).

[20] C. G. Van de Walle, Phys. Rev. B **39**, 1871 (1989); F. H. Pollak and M. Cardona, Phys. Rev. **172**, 816 (1968).

[21] F. H. Pollak, in *Semiconductors and Semimetals,* edited by Thomas P. Pearsall (Academic, Boston, 1990), Vol. 32, p. 17.

[22] T. B. Bahder, Phys. Rev. B **41**, 11 992 (1990). The conduction band is also subject to uniaxial strain, but to a lesser degree.

[23] F. D. Murnaghan, Proc. Natl. Acad. Sci. **30**, 244 (1944).

[24] B. H. Lee, J. Appl. Phys. **41**, 2988 (1970).

[25] D. Berlincourt, H. Jaffe, and L. R. Shiozawa, Phys. Rev. **129**, 1009 (1963).

[26] *Numerical Data and Functional Relationships in Science and Technology,* edited by O. Madelung, M. Schultz, and H. Weiss, Landolt-Börnstein, New Series, Group III, Vol. 17b (Springer-Verlag, Berlin, 1982), pp. 129 and 144.

[27] R. D. Hong, D. W. Jenkins, S. Y. Ren, and J. D. Dow, Phys. Rev. B **38**, 12 549 (1988).

[28] H. J. McSkimin, A. Jayaraman, and P. Andreatch, Jr., J. Appl. Phys. **38**, 2362 (1967); J. R. Drabble, in *Semiconductors and Semimetals,* edited by R. K. Willardson and A. C. Beer (Academic, New York, 1966), Vol. 2, p. 75; C. W. Garland and K. C. Park, J. Appl. Phys. **31**, 1426 (1960).

[29] A. Blacha, H. Presting, and M. Cardona, Phys. Status Solidi B **126**, 11 (1984).

[30] J. Gutowski, N. Presser, and G. Kudlek, Phys. Status Solidi A **120**, 11 (1990).

[31] J. I. Pankove, *Optical Processes in Semiconductors* (Dover, New York, 1971), p. 125.

[32] S. I. Novikova, in *Semiconductors and Semimetals,* edited by R. K. Willardson and A. C. Beer (Academic, New York, 1966), Vol. 2, p. 33; S. S. Mitra and N. E. Massa, in *Handbook on Semiconductors,* edited by T. S. Moss (North-Holland, Amsterdam, 1986), Vol. 1, p. 96; N. Shibata, A. Ohki, S. Zembutsu, and A. Katsui, Jpn. J. Appl. Phys. **27**, L487 (1988).