

Effects of Pressure on the Zn Vacancy in ZnSe: Essential Role of Lattice Relaxation for a Basic C_{3v} Defect

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The photoluminescence (PL) and PL excitation (PLE) spectra of the isolated Zn vacancy (V_{Zn}) in ZnSe are measured under hydrostatic pressure to 50 kbar at 7 K. The PL band shifts with pressure, roughly 30% faster than the band gap. Compression decreases the Stokes shift, reflecting a reduction in the C_{3v} lattice relaxation around the V_{Zn}^- site. Defect-molecule calculations show that this arises from the dominance of spring-constant stiffening over increased Jahn-Teller coupling. We determine the V_{Zn} configuration-coordinate diagram at high pressure. Compression deepens the energy of the V_{Zn}^- thermal level. [S0031-9007(98)07699-6]

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Stokes-shifted photoluminescence (PL) bands resulting from recombination at strongly lattice-relaxed defects are common in semiconductors [1]. In ZnSe, such bands arise from, e.g., isolated Zn vacancies (V_{Zn}) [2], donor-vacancy complexes (A centers) [1], and Se-site acceptors [3]. Although pressure experiments have been reported for a number of deep PL transitions [4,5], the results can be difficult to interpret in the presence of strong lattice relaxation [6]. Often, the pressure shifts of deep PL peaks are slower than that of the material's direct band gap [7], in agreement with the insensitivity to compression predicted for localized states by either Brillouin zone averaging [8] or tight binding models [9]. In contrast, recent experiments reveal that the deep PL bands in ZnSe due to P_{Se} , As_{Se} and the A centers of Ga and Cl shift with pressure *substantially faster* (~ 2 to 6 meV/kbar faster) than the band gap [10,11].

This rapid pressure shift suggests that the pertinent deep levels [acceptors ~ 0.3 – 0.7 eV above the valence band edge (VBE)] become more shallow with pressure, a result that bears on p -type doping problems in II-VI materials [12,13]. However, the possible explanations of this behavior are problematic. Either (i) the VBE moves rapidly to higher absolute energy with pressure—in disagreement with theory [14]; (ii) the deep acceptor states shift rapidly to lower energy (in fact, faster than the VBE by ~ -2 to -6 meV/kbar)—despite strong localization; or (iii) the lattice relaxation at defect sites decreases with pressure—*counterintuitive* to the expected increase in electron-phonon coupling due to enhanced orbital overlap.

To resolve these issues, we perform experiments and calculations that explore the influence of lattice relaxation on the pressure behavior of the PL and PL excitation (PLE) spectra of the V_{Zn} center in ZnSe. This deep defect is prototypical. In the standard tight binding picture, the V_{Zn} levels are delimiters for the bound states of deep defects on the Zn sublattice [7,9]. Its V_{Zn}^- charge state is subject to a strong C_{3v} Jahn-Teller distortion [2]. We present pressure data on the V_{Zn} optical levels that can

be understood only by taking explicit account of *lattice relaxation changes*. Considering the delimiting nature of the V_{Zn} levels, our findings bear on a wide range of cation-substitutional localized defects in large band-gap II-VI materials.

PL and PLE spectra were measured at pressures up to 50 kbar ($T = 7$ K), using a ruby calibrated diamond-anvil cell with ^4He pressure medium. A 50 W (cw) Xe arc lamp, dispersed by a $3/4$ m (1200 g/mm) monochromator, served as the tunable excitation source in the PLE measurements. Both this source (at fixed sub-band-gap frequencies), and the 364 nm Ar^+ laser line (~ 1 mW cw focused into a 50 μm spot) were used for excitation in the PL studies. A 1 m double monochromator (1800 g/mm) was operated in scanning or fixed frequency mode to record the PL or PLE spectra, respectively. The ZnSe samples studied were cleaved from the same electron-irradiated (to enhance the V_{Zn} density) material studied extensively by Watkins and co-workers [2]; they were n type with $N_d - N_a \sim 9 \times 10^{16}$ cm^{-3} .

The T_d ground state of the Zn vacancy in n -type ZnSe is doubly ionized, $V_{Zn}^{=}$ [2,13]. Optical excitation and emission occur via the transitions:

$$\begin{aligned} V_{Zn}^{=} + \gamma(2.51 \text{ eV}) &\rightarrow V_{Zn}^- + e; \\ e_d + V_{Zn}^- &\rightarrow V_{Zn}^{=} + \gamma(1.72 \text{ eV}). \end{aligned} \quad (1)$$

The hole trapped at V_{Zn}^- localizes on one of the four Se dangling bonds, leading to a C_{3v} Jahn-Teller distortion. At low temperature, the photoionized electron is captured by a residual shallow donor, and PL proceeds by a donor-acceptor-pair (DAP) process with a 0.79 eV Stokes shift. Our samples also exhibit a second PL band (2.01 eV at 1 atm.) due to DAP transitions involving A centers [1].

The measured PL spectra of the V_{Zn} and A -center bands (excited at the absorption edge by the Xe lamp), and the shallow-donor bound exciton I_2 line (excited at 364 nm), are shown for several pressures in Fig. 1. The two lowest traces compare the present 1 atm data to a spectrum from Ref. [2] recorded under similar conditions on freshly electron-irradiated material. In the present

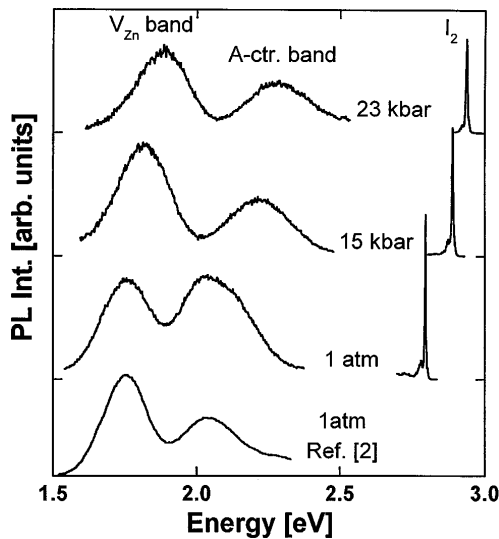


FIG. 1. Pressure PL spectra for the ZnSe sample studied here, and 1 atm data from Ref. [2] for a similar sample after fresh electron irradiation.

data, the A-center band is shifted by $\sim +0.1$ eV and broadened, reflecting the expected slow diffusion of V_{Zn} to form additional A centers. However, the V_{Zn} related PL is still strong, indicating the continued presence of a substantial density of isolated V_{Zn} centers in our sample.

Figure 2 displays the V_{Zn} PLE spectra at several pressures, and the A-center PLE spectrum at 1 atm (observed at their respective PL maxima). The broad low-energy band in the V_{Zn} spectra corresponds to the direct optical excitation of V_{Zn}^- described in Eq. (1) [2]. Although this band is weaker than reported in Ref. [2], it is clearly observable above background, confirming that the annealing of isolated V_{Zn} sites in our shelf-aged sample is incomplete. The sharper PLE peak at 2.75 eV (1 atm) arises from geminate recombination mediated by band edge states. For the A center, only the latter PLE peak is observed.

This difference in the two PLE spectra is exploited to better obtain the direct V_{Zn} PLE band. At each pressure, the sharp A-center PLE peak is fit to a Lorentzian line shape. This profile (rescaled to match the analogous near-edge V_{Zn} peak) is then subtracted from the V_{Zn} PLE spectrum to give the broad low-energy bands shown in Fig. 2.

Figure 3 shows that all the observed PL and PLE peak positions shift to higher energy with compression [15]. The I_2 pressure shift is 6.2 ± 0.2 meV/kbar, very close to that of the ZnSe band gap (6.5 ± 0.2 meV/kbar) [16]. The faster-than-gap shifts of the V_{Zn} (8.4 ± 0.5 meV/kbar) and A-center (10.4 ± 0.5 meV/kbar) PL bands suggest that the deep acceptor states (optical levels) involved in these DAP transitions become more shallow with pressure. This is similar to our findings for other deep acceptors in ZnSe [10,11]. In contrast, the slower-than-gap shift of the V_{Zn} direct PLE band (3.9 ± 0.8 meV/kbar) indicates

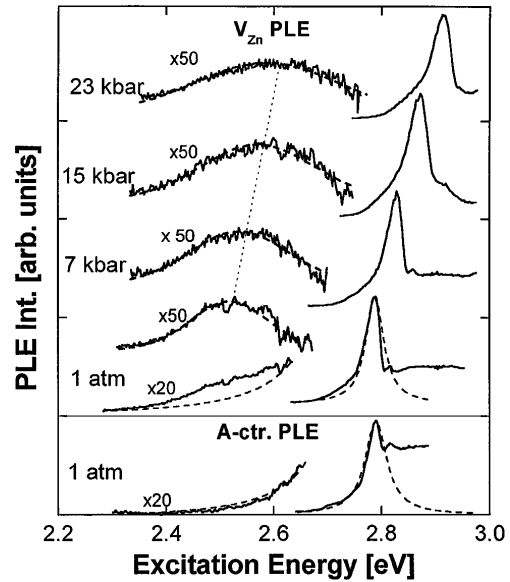


FIG. 2. Pressure PLE spectra for the direct (low-energy), and the band-edge excitation peaks of V_{Zn} . Dashed curves illustrate fitting of the band-edge A-center PLE, and analysis of the V_{Zn} data using this fitted line shape.

that the corresponding V_{Zn} PLE optical level becomes deeper with pressure. We conclude that the Stokes shift between the V_{Zn} PL and PLE transitions *decreases* with pressure, or, equivalently, that compression *reduces* the lattice relaxation responsible for this Stokes shift.

To investigate the origins of this behavior, we determine the V_{Zn} configuration coordinate (CC) diagram at high pressures, by means of a semiempirical defect-molecule calculation fitted to our PL and PLE results.

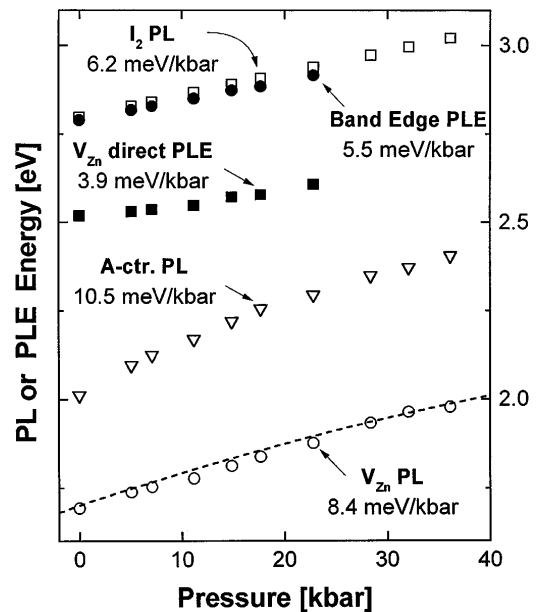


FIG. 3. Pressure shifts of the band maxima for the observed PL and PLE features. Labels give the best-fit linear pressure coefficients. Dashed curve shows the result of our defect-molecule calculation.

Jeon *et al.* established a realistic 1 atm CC diagram for the V_{Zn} center by considering the energy levels of four Se dangling bonds (directed toward V_{Zn}) subject to couplings

$$H_t = \begin{bmatrix} a_1 & t_{2x} & t_{2y} & t_{2z} \\ 3J & 0 & 0 & -V_1 Q \\ 0 & -J + V_2 Q/\sqrt{3} & 0 & 0 \\ 0 & 0 & -J + V_2 Q/\sqrt{3} & 0 \\ -V_1 Q & 0 & 0 & -J - 2V_2 Q/\sqrt{3} \end{bmatrix} \quad (2)$$

where a_1 , t_{2x} , t_{2y} , and t_{2z} are orthogonal combinations [with z parallel to $(\bar{1}\bar{1}\bar{1})$] of Se sp^3 dangling orbitals, $4J$ is the T_d crystal-field splitting, and the deformation potentials V_1 and V_2 describe the linear coupling to a C_{3v} distortion of amplitude Q along the z axis. After including a harmonic restoring force, good agreement with 1 atm optical data was obtained for $J = -0.11$ eV, $V_1 = V_2 = -1.26$ eV, a phonon frequency of $\omega_0 = 90$ cm^{-1} , and $Q_0 = 0.39$ Å for the relaxation amplitude [2]. The solid curves in Fig. 4 show the V_{Zn} CC-diagram at 1 atm.

We treat the effects of pressure by calculating J , V_1 , and V_2 in Eq. (2) as functions of the atomic positions in a cluster extending to second neighbors around the V_{Zn} site. The a_1 and t_2 basis states are constructed from the $4s$ and $4p$ Se atomic orbitals tabulated by Herman and Skillman [17]. The full Hamiltonian contains (beside kinetic energy) a sum of (i) the Herman-Skillman atomic Se potentials on nearest-neighbor (NN) sites ($+6e/\epsilon R$ is used outside each Se core), (ii) $+2e/\epsilon R$ on Zn second neighbors, and (iii) $-e/R$ on the vacancy to account for the net charge localized at V_{Zn}^- . We compute the matrix elements of this Hamiltonian, and their variation under trigonal displacement of the NN-Se atoms (*in order to obtain the deformation potentials V_1 and V_2*), via an adaptive algorithm iterated to 1% precision or better. All matrix elements are normalized by the appropriate overlap integrals.

Table I summarizes the calculated results. The known 1 atm CC diagram can be reproduced by allowing the NN-Se atoms to undergo a breathing expansion of 0.45 Å around the V_{Zn}^- site, and by choosing a local-mode frequency of $\omega_0 = 138$ cm^{-1} (with $m_{\text{eff}} = m_{\text{Se}}$). We do not assume $V_1 = V_2$ (as Jeon *et al.*), but calculate each matrix element separately; their average is in accord with the effective V reported in Ref. [2]. Undue weight should not be given to the large breathing expansion [13]. Its value results from a one-time (at 1 atm) adjustment, which is not expected to strongly affect trends in the pressure variation of the V_{Zn} CC diagram.

Next, we determine the effects of pressure by recalculating J , V_1 , and V_2 for a new set of atomic positions, in which the cluster atoms are displaced isotropically inward from the 1 atm breathing-relaxed configuration. A softer lattice is simulated near V_{Zn} by moving the NN-Se atoms rigidly with the second neighbor Zn shell. This gives a factor of 1.4 increase in local compressibility

by both a T_d crystal field, and a C_{3v} Jahn-Teller distortion [2]. The eigensolutions for the electron degrees of freedom are found from the interaction Hamiltonian,

χ_L . At each pressure, we input the measured PLE energy and the calculated values of J , V_1 , and V_2 . The local-phonon frequency ω is then adjusted to match the observed PL energy. The pressure dependence of ω obtained in this way corresponds to the Gruneisen constant, $\gamma \equiv 1/\chi_L \partial \ln \omega / \partial P = +1.15$. This best-fit γ is physically realistic (close to unity), and could easily result from a superposition of ZnSe lattice modes. (If the bulk compressibility is used, $\gamma = 1.6$ is found—still reasonable.) The adjustment of $\omega(P)$ is very sensitive; γ variations exceeding $\pm 25\%$ cannot be accommodated by our data.

The dashed curves in Fig. 4 show our result for the V_{Zn} CC-diagram at 35 kbar. The origin of the rapid PL pressure shift, and of the decreasing Stokes shift, is immediately clear. The C_{3v} Jahn-Teller distortion Q_0 decreases with compression, causing the PL energy to gain from the quadratic falloff with Q of the V_{Zn}^- ground state, as well as from the energy “upshift” of the V_{Zn}^- excited state. The calculated coupling constants V_1 and V_2 increase (*in magnitude*) with pressure (Table I). However, their increase is not sufficient to offset the change in the restoring force ($-m\omega^2 Q$) driven by γ . Thus, no counterintuitive situation exists: The decrease in lattice relaxation results from stiffening of

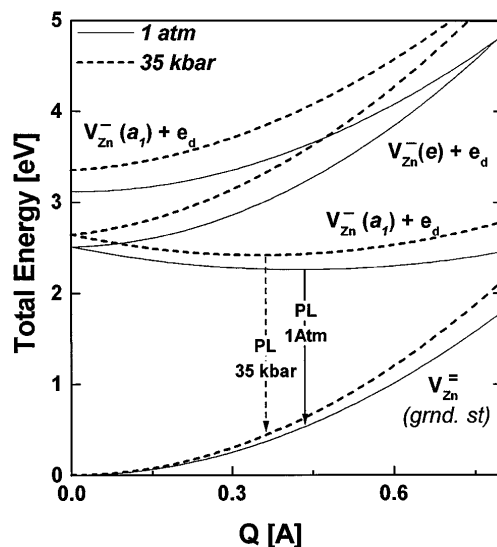


FIG. 4. CC diagrams at 1 atm and 35 kbar for V_{Zn} in ZnSe calculated via the defect-molecule model, adjusted to fit the present pressure data and the 1 atm results of Ref. [2]. Note decrease in V_{Zn}^- relaxation at high pressure.

TABLE I. Results of the defect-molecule calculation for V_{Zn} in ZnSe, corresponding to the 1 atm CC diagram in Ref. [2] and the average values of $\partial E_{PLE}/\partial P$ and $\partial E_{PL}/\partial P$ measured in the present work.

J (eV)	dJ/dP (eV/kbar)	V_1 (eV/A)	dV_1/dP (eV/kbar A)	V_2 (eV/A)	dV_2/dP (eV/kbar A)	$\{dE_{opt}/dP\}_{PL}$ (eV/kbar)	$\{dE_{opt}/dP\}_{PLE}$ (eV/kbar)	E_{therm} (eV)	dE_{therm}/dP (eV/kbar)
-0.15	-7.3×10^{-4}	-0.41	-6.0×10^{-3}	-1.6	-1.8×10^{-2}	-2.2×10^{-3}	$+2.3 \times 10^{-3}$	0.7	$+1.2 \times 10^{-3}$

harmonic forces, *not* from weakening of the Jahn-Teller coupling.

It is now possible to decide whether the isolated V_{Zn} defect becomes a deeper or a more shallow hole trap with compression. Also appearing in Table I are our findings for the pressure coefficients of the optical (PL and PLE) and thermal levels of V_{Zn} relative to the VBE. Although pressure causes the optical level involved in the PL transition to become more shallow, both the PLE and the thermal levels deepen—the latter at the average rate of 1.2 meV/kbar. Thus, the V_{Zn} center in *n*-type ZnSe becomes a deeper acceptor under pressure. Note that, based solely on the faster-than-gap PL pressure shift, one might *wrongly* predict a *deep-to-shallow* transition for this defect.

Similar stiffening-induced decreases in lattice relaxation may explain the faster-than-gap pressure shifts observed in ZnSe for the PL bands arising from deep P_{Se} and A_{Se} acceptors, and from $[Ga-V_{Zn}]$ and $[Cl-V_{Zn}]$ A centers [10,11]. However, in order to settle this issue, and to decide whether these defects will undergo pressure-induced deep-to-shallow transitions, the shifts of their PLE spectra with pressure *must* also be measured. Very recent experiments by the authors suggest that the direct PLE transition of P_{Se} differs from that of V_{Zn} in that it follows the band gap with pressure. This means that the P_{Se} thermal level becomes more *shallow*, but the deduced shift of -1.1 meV/kbar relative to the VBE is too slow for this level to cross the VBE prior to the α - β phase change (138 kbar) in ZnSe.

Using *ab initio* calculations that include lattice relaxation, Park and Chadi predict pressure shifts of similar sign and magnitude (-1.6 to -1.3 meV/kbar) for the thermal levels of the A^+ (broken bond) defects of P_{Se} and A_{Se} in ZnSe [18]. Although the tight-binding treatment of Hong *et al.* does not explicitly include lattice relaxation, it, likewise, predicts pressure coefficients of ~ -1 meV/kbar for Se-site acceptors having levels in the lower half of the ZnSe gap (appropriate for P_{Se} and A_{Se}) [9]. The latter theory also finds that the t_2 state of V_{Zn} should deepen with pressure at a rate of $\sim +1$ meV/kbar, in accord with our result (Table I) for the *thermal* level of this defect. However, the direction of pressure shift predicted in Ref. [9] for the V_{Zn} PL level would be opposite to that observed. This again points out the need to explicitly consider lattice relaxation when analyzing pressure-PL results.

The present PL and PLE experiments on the V_{Zn} center in ZnSe establish the effects of pressure on the energy levels of a prototypical deep defect. Calculations

show that the observed decrease in Stokes shift is due to stiffening of harmonic forces. We find that the technologically important issue of whether compressive strain (or analogous bond-length variation in alloys) drives this defect toward a deep-to-shallow transition depends strongly on *changes* in lattice relaxation. In view of the delimiting character of the V_{Zn} levels, it is likely that the present results are relevant to many other cation-substitutional localized acceptors.

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- [1] P. J. Dean, Phys. Status Solidi (a) **81**, 625 (1984).
- [2] D. Y. Jeon, H. P. Gislason, and G. D. Watkins, Phys. Rev. B **48**, 7872 (1993); K. M. Lee, Ph.D. thesis, Lehigh University, 1983.
- [3] A. R. Reinberg, W. C. Holton, M. De Wit, and R. K. Watts, Phys. Rev. B **3**, 410 (1971).
- [4] H. G. Drickamer, in *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic, NY, 1965), Vol. 17, pp. 2–33; B. A. Weinstein, Philos. Mag. B **50**, 709 (1984).
- [5] T. Suski, P. Perlin, H. Teisseyre, M. Leszczynski, I. Grzegory, J. Jun, M. Bockowski, S. Porowski, and T. D. Moustakas, Appl. Phys. Lett. **67**, 2188 (1995).
- [6] C. P. Slichter and H. G. Drickamer, Phys. Rev. B **22**, 4097 (1980).
- [7] H. P. Hjalmarson, P. Vogl, D. J. Wolford, and J. D. Dow, Phys. Rev. Lett. **44**, 810 (1980).
- [8] D. J. Chadi and K. J. Chang, Phys. Rev. Lett. **61**, 873 (1988).
- [9] R. Hong, D. W. Jenkins, S. Y. Ren, and J. D. Dow, Phys. Rev. B **38**, 12549 (1988).
- [10] M. Ming Li, D. J. Strachan, T. M. Ritter, M. Tamargo, and B. A. Weinstein, Phys. Rev. B **50**, 4385 (1994).
- [11] T. M. Ritter, B. A. Weinstein, R. M. Park, and M. C. Tamargo, Phys. Rev. Lett. **76**, 964 (1996).
- [12] D. J. Chadi, Annu. Rev. Mater. Sci. **24**, 45 (1994).
- [13] D. B. Laks, C. G. Van de Walle, G. F. Neumark, P. E. Blochl, and S. T. Pantelides, Phys. Rev. B **45**, 10965 (1992).
- [14] C. G. Van de Walle, Phys. Rev. B **39**, 1871 (1989).
- [15] For the broad bands, the positions of the maxima are found by fitting to Gaussian profiles after correcting for the monochromator response.
- [16] J. A. Tuchman, M. Kim, Z. Sui, and I. P. Herman, Phys. Rev. B **46**, 13371 (1992).
- [17] F. Herman and S. Skillman, in *Atomic Structure Calculations* (Prentice-Hall, Englewood Cliffs, NJ, 1963).
- [18] C. M. Park and D. J. Chadi, J. Phys. Chem. Solids **56**, 585 (1995).