

Shallow to deep transformation of Se donors in GaSb under hydrostatic pressure

H. Navarro-Contreras, F. de Anda-Salazar, and J. Olvera-Hernández

Instituto de Investigación en Comunicación Óptica, Universidad Autónoma de San Luis Potosí, Alvaro Obregón 64, San Luis Potosí, S.L.P., Mexico 78000

Leonardo Hsu and M. D. McCluskey

Department of Physics, University of California, Berkeley, California 94720

and Center for Advanced Materials, Materials Science Division, Lawrence Berkeley National Laboratory, Berkeley, California 94720

E. E. Haller

Center for Advanced Materials, Materials Science Division, Lawrence Berkeley National Laboratory, Berkeley, California 94720

and Department of Material Science and Mineral Engineering, University of California, Berkeley, California 94720

(Received 13 August 1998; revised manuscript received 9 October 1998)

We have observed that highly doped GaSb:Se, which is opaque to far IR radiation, becomes transparent at hydrostatic pressures above 9.8 ± 2 kbar. We discuss how this behavior may be explained by the transformation of Se shallow donors into Se-DX (where DX is the unknown donor or X donor) centers in GaSb. Under this assumption the position of the Se-DX energy level at zero pressure is calculated to lie 80 ± 30 meV above the conduction band at atmospheric pressure. The onset of transparency allowed us to observe several multiphonon absorbance features. We assign six of them to two-phonon absorptions. From the measured pressure dependence of the TO phonon, the Grüneisen parameter for this compound is calculated to be $\gamma_{\text{TO}} = 1.23 \pm 0.18$. No persistent photoconductivity is observed for these Se-DX centers, a fact that may be explained by the expectation that the optical energy necessary to transform them back into the shallow form is larger than the band-gap energy of GaSb at all pressures examined, although it may be also an indication that the Se shallow donors change to deep donors associated with the L_1 minima of ionization energy larger than 90 meV. [S0163-1829(99)02211-0]

The study of the behavior of shallow impurities, both donors and acceptors, under hydrostatic pressure has recently received considerable attention.^{1,2} Much of this interest has originated from the fact that many of these shallow impurity states in binary III-V compounds transform into unknown donor or X-donor (DX) centers under applied pressures above a certain threshold value.

The DX center is a deep-level defect found in many n -type compound semiconductors and their alloys. DX centers were first discovered in GaAs_{1-x}P_x by Craford *et al.*,³ and have been studied extensively in Si-doped n -type Al_xGa_{1-x}As for $x > 0.22$.⁴ In addition, some shallow substitutional donors in binary compound semiconductors such as Si in GaAs and S in InP are known to transform into DX centers under hydrostatic pressure.^{5,6} These experiments demonstrated that DX centers are related to substitutional donors⁷ whose shallow electronic level become deep under certain conditions of alloying or hydrostatic pressure. DX centers are characterized by several unusual properties, including a large difference between their thermal and optical ionization energies, small electron capture cross sections, and persistent photoconductivity.

In addition to the examples mentioned above, DX centers have also been observed to form in Te-doped GaSb at hydrostatic pressures larger than 27.8 kbar.⁸ Deep-level transient spectroscopy measurements of sulfur-doped GaSb have shown that the S donor coexists as a shallow donor and as a DX-like deep level at atmospheric pressure and low temperatures.^{9,10} These results, combined with the sugges-

tion that DX centers might be a general phenomenon in all III-V compounds,¹¹ prompted the question of the existence of Se-DX centers in GaSb.

At atmospheric pressure, the L_1 conduction band (CB) minima in GaSb are only 0.08 eV above the absolute conduction-band minimum at the Brillouin zone center (Γ_1). The X_1 minima near the (100) zone boundaries lie about 0.43 eV above the Γ_1 minimum.¹² Upon application of hydrostatic pressure, the Γ_1 and L_1 minima move upwards and the X_1 minima move downwards in energy with respect to the valence band, as illustrated in Fig. 1. Because the Γ_1 conduction-band minimum has a larger pressure coefficient than the L_1 minima, the L_1 minima become lower in energy than the Γ_1 point above roughly 10 kbar. At still higher applied pressures (above 50 kbar) the X_1 conduction-band minima fall below the L_1 valleys in energy, and thereafter are the absolute minima. The pressure dependencies of the binding energies of two group VI elements that form donors in GaSb, Se, and Te have been studied previously by observing the changes in resistivity at liquid helium temperatures, and at pressures as high as 50 kbar.^{13,14} In those studies it was thought that the increase in resistivity above 10 kbar in GaSb:Se was due to the greater effective mass of the Se shallow donor associated with the L_1 minima.¹⁴ However, it has more recently been suggested that these observations may indicate the formation of DX centers.¹⁵

Here we report on the observation of the freezing out of free carriers in GaSb:Se at liquid helium temperature and hydrostatic pressures above 9.8 ± 2 kbar, when the L_1 valleys have replaced the Γ_1 minimum as the absolute CB minima.

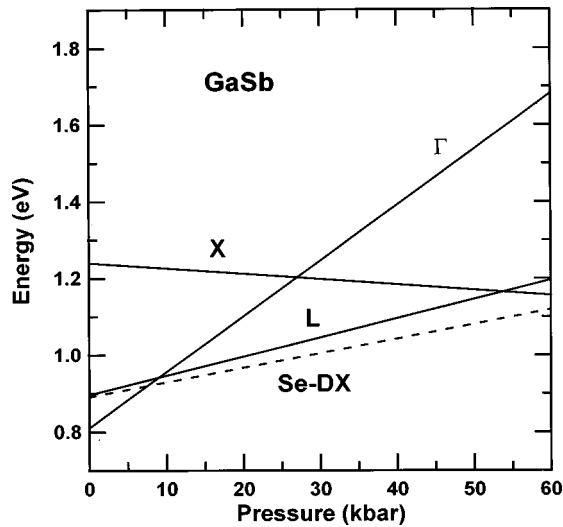


FIG. 1. Plot of the energies of the local conduction-band minima at various symmetry points for GaSb as a function of pressure. Energies are relative to the top of the valence band.

We discuss how this freezing out of the carriers may be due to two different possibilities: either the carriers bind to a deeper form of the Se donors associated with the L_1 minima after the replacement of absolute CB minima takes place, or the shallow donors transform to DX centers. However, in contrast to the transformations of Te donors into DX centers in GaSb, no persistent photoconductivity was observed for the transformation of the Se donors in this compound as discussed below. We also report the observation of several multiphonon absorbance features in this compound after the sample becomes transparent.

The samples used in these experiments were GaSb:Se grown by liquid-phase epitaxy (LPE). They had free-carrier concentrations of $6 \times 10^{17} \text{ cm}^{-3}$ and were 32–36- μm thick. Prior to growth, the substrates were cleaned with a solution of 0.25:2.56:0.74 mol of HF, H_2O_2 , and $\text{C}_4\text{H}_6\text{O}_6$ (tartaric acid). The GaSb:Se layer was grown at 450 °C in flowing high-purity hydrogen, which had been diffused through palladium silver. The dew point of the hydrogen is less than –90 °C. Sapphire boats were used to minimize the introduction of unintended impurities during the growth. In preparing the samples to be used in diamond anvil cells, the substrate was eliminated by thinning down the material to a film approximately 30 μm in thickness, so that the only remaining material was the LPE-grown GaSb:Se. This film was then cut into small disks 300 μm in diameter using an ultrasonic grinder as described elsewhere.¹

Hydrostatic pressure was applied to the sample using a modified Merrill-Basset diamond anvil cell with liquid nitrogen as the pressure medium. The far-infrared transmission of the sample was measured with a Digilab FTS-80E vacuum Fourier transform spectrometer using a small Ge:Ga photoconductive detector mounted directly behind the pressure cell. The radiation was incident normal to the (100) face of the sample. We measured the pressure inside the cell at room temperature by means of the pressure dependence of the wavelength of the R_1 and R_2 fluorescence lines of the Cr^{3+} ion in ruby. The low-temperature pressure, at which the measurements were made, was estimated from a calibration previously obtained using the pressure dependence of the ν_3

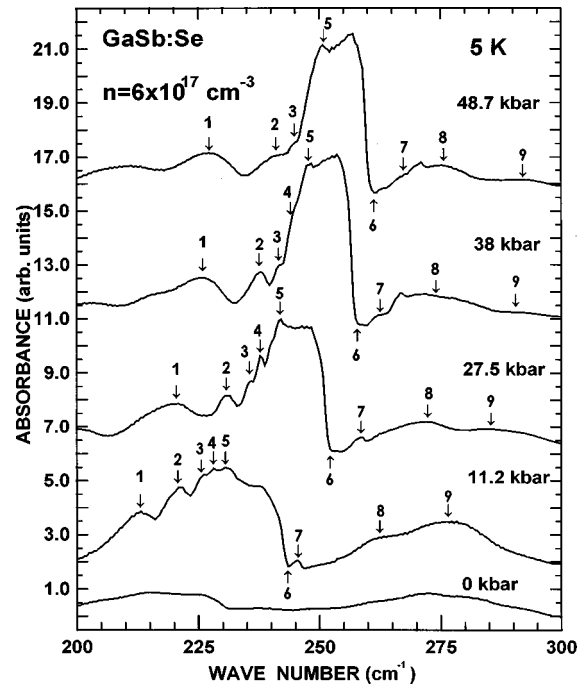


FIG. 2. Absorbance spectra of GaSb:Se under various hydrostatic pressures. The vertical lines point to pressure-dependent, phonon, or multiphonon features.

vibrational mode of CO_2 at 4.2 K.¹⁶ The uncertainty in the applied pressures is estimated to be ± 2 kbar. All spectra were recorded at 5 K.

In Fig. 2 the absorbance spectra of the GaSb:Se at various pressures and at a temperature of 5 K are shown. In the first spectrum, taken at atmospheric pressure when the sample was opaque, we see that the absorption spectrum is flat and nearly featureless. At low pressures the Se donors are all in the shallow donor state. This spectrum results from stray light, which passes around the sample.

At such high-doping levels, the shallow impurity band has broadened and merged with the conduction band. Hence, all of the donor electrons from Se behave like free carriers and the sample is opaque to far-infrared radiation (FIR) due to free-carrier absorption. When the sample is subjected to hydrostatic pressures of 9.8 ± 2 kbar or above, however, the Se shallow donors transform into a deeper form. In what follows we will discuss the case when these donors transform into DX centers. In this case, upon cooling, the carriers become trapped at the deeper DX levels and the sample becomes transparent to FIR. In some other wider band-gap semiconductors the DX centers may be converted back into their shallow configuration by shining light on the sample of energy greater than the optical energy E_0 , that is typically of the order of 1 eV or larger. At low temperatures, a thermal barrier prevents these shallow donors from returning to their deep DX configuration. This behavior gives rise to the phenomenon of persistent photoconductivity (PPC). The sample is opaque in this condition. In those compounds the shallow donor-to-DX center transition pressure is taken to be the pressure at which the sample shows this persistent photoconductivity. However, the absence of this PPC could be explained if the Se donors in GaSb have an optical transition energy larger than 1 eV, i.e., larger than the band gap of this

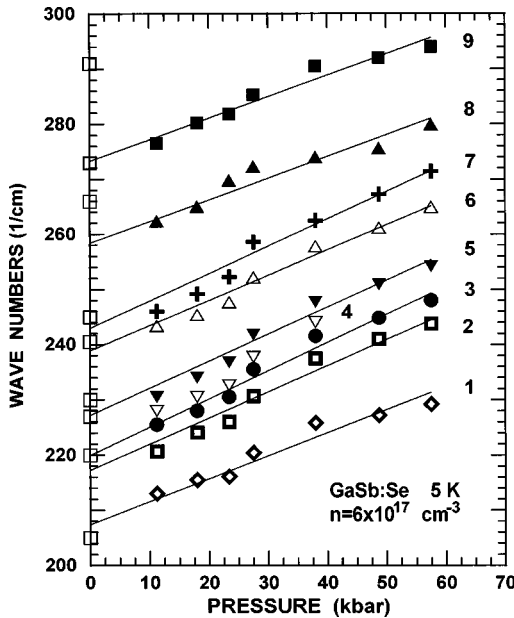


FIG. 3. Pressure dependence of the absorbance features in Se-doped GaSb. Squares at zero pressure: expected positions of the phonon or multiphonon absorption process at liquid-helium temperatures. Straight lines: least squares (linear) fits.

compound at all pressures examined. Then the required photons cannot penetrate the crystal and there will be no PPC. We discuss below how indeed this assumption may be the case for the Se donors in GaSb.

Under hydrostatic pressures larger than 11.2 kbar the sample is transparent and the reflectance of the reststrahlen band (visible as an absorption), as well as some multiphonon absorptions of GaSb are visible below 250 cm^{-1} . Spectra recorded at 8.3 kbar indicate that the sample is still almost completely opaque. Therefore, we choose the threshold hydrostatic pressure value for this transformation of the Se donors as the value halfway between these two pressures, i.e., at 9.8 ± 2 kbar.

If indeed the transformation of Se shallow donors into Se-DX centers is the explanation for the onset of the freezing of the CB carriers observed in this paper, then we can estimate the energy of the Se-DX level in GaSb at zero pressure relative to the conduction-band minimum, from the transition value of 9.8 ± 2 kbar, in analogy to the case of the sulfur DX center in InP.⁶ Following Chadi and Chang,¹⁷ who proposed that as the DX level is deep, its pressure derivative is the same as that of the conduction band averaged over all k space, the average is estimated using the expression proposed by those authors¹⁷

$$dE_{CB}/dP = [dE(\Gamma)/dP + 3dE(X)/dP + 4dE(L)/dP]/8.$$

We use $dE(\Gamma)/dP = 14.5 \pm 0.3 \text{ meV/kbar}$, $dE(X)/dP = -1.4 \pm 0.6 \text{ meV/kbar}$,¹⁸ and $dE(L)/dP = 5 \pm 0.3 \text{ meV/kbar}$,¹⁹ to obtain $dE_{CB}/dP = 3.8 \pm 0.4 \text{ meV/kbar}$. This implies that the DX level approaches the conduction band minimum at Γ at the rate of $dE(\Gamma)/dP - dE_{CB}/dP = 10.7 \pm 0.7 \text{ meV/kbar}$. This results in a zero-pressure DX level energy position of $105 \pm 30 \text{ meV}$ above the conduction band. If a correction of 25 meV is subtracted, as suggested in Ref. 20 as the position of the DX level below the shallow

level to yield the sample 90% transparent, we get as a position of the Se-DX level $80 \pm 30 \text{ meV}$ above the conduction band at zero pressure.

A theoretical calculation by Park and Chadi,²¹ predicts that Se, as well as S and Te should form DX centers in GaSb. This result is expected from two models: the broken-bond DX (BB-DX) of C_{3v} symmetry model and a new model, called cation-cation bonded DX (CCB-DX), which they claim applies to the sulfur DX donors in this compound. S and Te are predicted to form CCB-DX centers with calculated binding energies of -60 and 210 meV . Within the BB-DX model the binding energies for S and Te are predicted to be 10 and 70 meV, respectively. The binding energy of Te DX centers has been experimentally measured to be $300 \pm 70 \text{ meV}$,⁸ which suggests a CCB-DX character for this center.²¹ Very similar binding energies in both models for the Se-DX in GaSb, 90 and 80 meV above the conduction band, respectively, are calculated. Therefore, the estimated experimental result of $80 \pm 30 \text{ meV}$, is not conclusive to the Se DX character.

The optical energy of the sulphur S-DX center is calculated to be 1.25 eV in GaAs and 0.95 eV in GaSb.²¹ The optical energy of the Se-DX donor required to transform it into a shallow donor is larger than that of S-DX and it has been calculated to be 1.34 eV for the CCB-DX and 1 eV for the BB-DX configurations in GaAs.²¹ Therefore, it is reasonable to expect that the optical energy of the Se-DX might be also larger than that of sulphur in GaSb, i.e., $>1 \text{ eV}$ for both DX configurations. Indeed, the sulfur donor has been observed to coexists in the shallow and the DX form at zero pressure and presents a quenching behavior of the PPC phenomenon that reflects the fact that the incoming photons are absorbed in its majority by band-gap transitions.²¹ If indeed the optical energy of the Se donor fulfills the condition $>1 \text{ eV}$, then no PPC is expected for these donors since the band-gap energy of the GaSb remains $\leq 1 \text{ eV}$ for almost all the applied pressures in this paper as can be observed from Fig. 1.

As mentioned before, as the $L1$ minima become the absolute minima at a pressure close to 10 kbar, $L1$ associated donors are expected to form at this and at larger pressures, competing with the DX as another structure available to the Se donors. $L1$ donors are expected to give rise to considerable absorption at such high-doping levels. However, no IR absorption continuum is observed at all wave numbers observed up to 700 cm^{-1} , or $\approx 90 \text{ meV}$. Therefore, if donors associated with the $L1$ band are responsible for the observed onset of transparency after 10 kbar, then they have to have an ionization energy larger than this value. However, these donors are expected theoretical,²² to have an ionization energy of 18 meV. Experimentally there exists a previous report stating that this ionization energy has to be $\approx 50 \text{ meV}$.²³ If $L1$ associated donors are indeed responsible for the observed behavior of Se donors reported in this paper, it would mean that the Hall experiments from which the result of Ref. 23 was obtained would have to be revised.

In Fig. 2, one can follow at least eight features that shift to higher energies with increasing pressures. These include seven peaks that we have assigned to phonon or multiphonon absorptions, and the absorbance minimum to the right of the reststrahlen band that corresponds to the phonon LO energy.

TABLE I. Phonons and low-energy multiphonon processes that may be expected in GaSb. The multiphonon assignments differ in some cases from those in Ref. 24.

No.	Phonon combinations at 5 K	Calculated values (cm^{-1})	Extrapolated values to zero pressure (cm^{-1})	Observed pressure dependence ($\text{cm}^{-1}/\text{kbar}$)
1	LA(L)+TA(L)	204	207.4 ± 1.2	0.42 ± 0.07
2	LA(WL)+TA(WL)	220	217.3 ± 1.2	0.47 ± 0.07
3	LA(X)+TA(X)	227	219.9 ± 1.2	0.51 ± 0.07
5	TO(Γ)	230	227.2 ± 1.2	0.51 ± 0.07
6	LO(Γ)	240.5	238.8 ± 1.2	0.48 ± 0.07
7	TO(L)+TA(L)	245	243.0 ± 1.2	0.47 ± 0.07
8	LO(L)+TA(L)	266	258.4 ± 1.2	0.39 ± 0.07
9	TO(X)+TA(X)	273	273.3 ± 1.2	0.39 ± 0.07
	LO(X)+TA(X)	273		

The values used for one-phonon frequencies are taken from Ref. 25.

The WL-line phonon frequencies TA=80 cm^{-1} and LA=140 cm^{-1} are from Ref. 26.

The values for TO[L], TO[Γ], and LO[Γ], 197, 230, and 240.5 cm^{-1} , are respectively, from Ref. 24.

The excitation of a LO mode is IR forbidden in diamond or zinc-blende compounds. In some cases we observe a ninth very small unidentified peak.

In Fig. 3, a plot of the pressure dependence of these absorbance features is shown. No other consistent features were observed outside of the spectral region of this figure. The solid lines are linear fits. The values of these absorptions extrapolated to atmospheric pressure are listed in Table I, where they are compared to absorptions expected from various multiphonon excitations. Some multiphonon absorptions in GaSb have been reported in the literature.²⁴ However, we observe some additional multiphonon absorptions and our assignments differ in two cases from those made in Ref. 24.

The values used for the transverse acoustic (TA) and longitudinal acoustic (LO) phonons are those of Farr, Taylor, and Sinha²⁵ for TA[L], LA[L], TA[X], and LA[X], TO[X], LO[X], and LO[L] phonons, which are 48, 156, 59, 168, 215, 215 and 207 cm^{-1} , respectively. These values are higher than those normally quoted in the literature by 2–3 cm^{-1} to account for the small stiffening of the modes at low temperatures. The calculations of Giannozzi and Gironcoli²⁶ were used to find the locations of the peaks in the phonon density of states, determined to lie midway along the (WL) line at the zone boundary (i.e., TA[WL]=80 cm^{-1} and LA[WL]=140 cm^{-1}). The energies of the TO[L], TO[Γ], and LO[Γ] phonons (197, 230, and 240.5 cm^{-1}) are from Ref. 24, as their values provide better fits to the restrahlen reflection at room temperature and to our extrapolated value for the TO(L)+TA(L) multiphonon absorption.

In Table I the pressure dependence of the phonon-absorption processes observed are listed in the last column. All of the slopes range from 0.39 to $0.51 \pm 0.07 \text{ cm}^{-1}/\text{kbar}$. Based on our data, the pressure dependence of the TO phonon is $d\omega_{\text{TO}}/dP = 0.49 \pm 0.07 \text{ cm}^{-1}/\text{kbar}$. From this value, we can estimate the Grüneisen parameter (used to describe the response of the lattice vibrations to applied pressure or equivalently, to isothermal compression) as

$$\gamma = B/\omega_{\text{TO}}(\partial\omega_{\text{TO}}/\partial P)_T = (\partial \ln \omega_{\text{TO}}/\partial \ln V)_T = 1.23 \pm 0.18,$$

where $B = 5.79 \times 10^5 \text{ bar}$ is the isothermal bulk modulus of GaSb at 4.2 K.⁸ This value is close to that of $\gamma = 1.10 \pm 0.22$,²⁷ derived from the pressure dependence of TO phonons in GaSb measured by Raman scattering.

In summary, we have observed the freezing out of carriers from Se shallow donors in GaSb into a deeper form of this donor at pressures of $9.8 \pm 2 \text{ kbar}$ and above. At higher pressures, the sample becomes transparent at low temperatures allowing us to observe several additional absorbance peaks, which we have identified as multiphonon absorptions. A shallow to a deep DX Se donor transformation may be responsible for this freezing out of carriers under applied hydrostatic pressures. In this case the energy position of the Se-DX center at zero pressure may be calculated to lie $80 \pm 30 \text{ meV}$ above the conduction band. If replacement of the shallow donors by L_1 associated donors is responsible for this phenomenon, our results indicate that these donors have to be deeper in energy than 90 meV. From the observed pressure dependence of the GaSb TO phonon, the Grüneisen parameter for this compound is calculated to be $\gamma_{\text{TO}} = 1.23 \pm 0.18$, a figure that is close to the value derived from the pressure dependence of Raman scattering by TO phonons in GaSb of $\gamma_{\text{TO}} = 1.10 \pm 0.22$.

This work was partially supported by the U.S.A.-México Scientific Collaboration Program NSF-CONACYT, spring promotion 1995, CONACYT research project under Contract No. 4851005-0690PE, Fondo de Apoyo a la Investigación de la Universidad Autónoma de San Luis Potosi (FAI-UASLP) and the USNSF, the Director, Office of Energy Research, Office of Basic Energy Sciences, Materials Science Division of the U.S. Department of Energy under Contract No. DE-AC03-76SF0098. H.N. wishes to acknowledge the warm hospitality of the research group of E. E. Haller at LBNL and UCB.

- ¹L. Hsu, S. Zehender, E. Bauser, and E. E. Haller, Phys. Rev. B **55**, 10 515 (1997). See also, Leonard Hsu, Ph.D. thesis, University of California, Berkeley, 1997; University of California Lawrence Berkeley National Laboratory Report No. LBNL-40583, 1997 (unpublished).
- ²J. A. Wolk, M. L. Thewalt, W. Walukiewicz, and E. E. Haller, Phys. Rev. Lett. **68**, 3619 (1992).
- ³M. G. Craford, G. E. Stillman, J. A. Rossi, and N. Holonyak, Phys. Rev. **168**, 867 (1968).
- ⁴D. V. Lang and R. A. Logan, Phys. Rev. Lett. **39**, 635 (1977).
- ⁵M. Mizuta, M. Tachikawa, H. Kukimoto, and S. Minomura, Jpn. J. Appl. Phys. **24**, L143 (1985).
- ⁶J. A. Wolk, M. B. Kruger, J. N. Heyman, W. Walukiewicz, R. Jeanloz, and E. E. Haller, Phys. Rev. Lett. **66**, 774 (1991).
- ⁷Y. Takeda, X. C. Gong, Yu Zhu, and A. Sasaki, Jpn. J. Appl. Phys. **26**, L273 (1987).
- ⁸H. Navarro-Contreras, F. de Anda-Salazar, L. Hsu, and E. E. Haller, Phys. Rev. B **57**, 12 169 (1998).
- ⁹As suggested by K. Khachatryan, E. R. Weber, and M. Kaminska, Mater. Sci. Forum **38-41**, 1067 (1989).
- ¹⁰I. Poole, M. E. Lee, I. R. Cleverly, A. R. Peaker, and K. E. Singer, Appl. Phys. Lett. **57**, 1645 (1990).
- ¹¹P. S. Dutta, K. S. R. Koteswara Rao, K. S. Sangunni, and H. L. Bhat, Appl. Phys. Lett. **65**, 1412 (1994).
- ¹²D. E. Aspnes, C. G. Olson, and D. W. Lynch, Phys. Rev. B **14**, 4450 (1976).
- ¹³B. B. Kosicki and W. Paul, Phys. Rev. Lett. **17**, 246 (1966).
- ¹⁴B. B. Kosicki, A. Jayaraman, and W. Paul, Phys. Rev. **172**, 246 (1966).
- ¹⁵K. J. Malloy, and K. Khachatryan, in *Imperfections in III/V Materials, Semiconductor and Semimetals* edited by R. K. Williardson and A. C. Beer (Academic, New York, 1993), Vol. 38, p. 235.
- ¹⁶M. D. McCluskey, L. Hsu, L. Wang, and E. E. Haller, Phys. Rev. B **54**, 8962 (1996).
- ¹⁷D. J. Chadi and K. J. Chang, Phys. Rev. Lett. **61**, 873 (1988).
- ¹⁸J. F. Tsay, S. S. Mitra, and B. Bendow, Phys. Rev. B **10**, 1476 (1974).
- ¹⁹A. K. Walton and S. F. Metcalfe, J. Phys. C **9**, 3855 (1976).
- ²⁰W. Walukiewicz, J. Lagowski, L. Jastrzebski, P. Rava, M. Lichtensteiger, C. H. Gatos, and H. C. Gatos, J. Appl. Phys. **51**, 2659 (1980).
- ²¹C. H. Park and D. J. Chadi, Phys. Rev. B **54**, R14 246 (1996).
- ²²The $L1$ donor Rydberg can be calculated to be 18.8 meV, using the $L1$ density-of-states mass $1/m_{op} = (2/m_{\parallel} + 1/m_{\perp})^{1/3} = 0.34$, $m_{\parallel} = 1.2m_0$, and $m_{\perp} = 0.14m_0$, and $\epsilon_0 = 15.7$.
- ²³K. Hoo and W. M. Becker, Phys. Rev. B **14**, 5372 (1976).
- ²⁴I. V. Skryabinskii and Yu. I. Ukhanov, Fiz. Tverd. Tela (Leningrad) **14**, 3629 (1972) [Sov. Phys. Solid State **14**, 3041 (1973)].
- ²⁵M. K. Farr, J. G. Taylor, and S. K. Sinha, Phys. Rev. B **11**, 1587 (1975).
- ²⁶P. Giannozzi and S. Gironcoli, Phys. Rev. B **43**, 7231 (1991).
- ²⁷F. Cerdeira, C. J. Buchenauer, H. F. Pollak, and M. Cardona, Phys. Rev. B **5**, 580 (1972).