

## Structural properties and polarization charge densities of InSb

D. Singh and Y. P. Varshni

*Department of Physics, University of Ottawa, Ottawa, Ontario K1N 6N5, Canada*

(Received 28 May 1985)

Polarization charge densities and structural properties of zinc-blende InSb, calculated using an *ab initio* pseudopotential scheme, are reported, both at the free volume and a reduced volume near the semiconductor-metal phase transition. These are discussed in relation to previous calculations on other covalent solids and to experimental data.

### I. INTRODUCTION

Indium antimonide is an interesting material with potentially important applications. Over a relatively narrow range of pressures and temperatures it is found to occur in a number of structures,<sup>1</sup> including a metastable rocksalt structure.<sup>2</sup> The extent of this polymorphism may be interpreted as suggesting that InSb is in some sense a borderline material with a near instability in its bonding. It seems reasonable to expect that worthwhile information regarding the nature of the covalently bonded solids may be obtained from the study of such materials and their similarities with and differences from prototypical materials such as silicon. Motivated by this and a recent x-ray scattering study,<sup>3</sup> we recently reported valence charge densities for zinc-blende-structure InSb at its free volume and at a reduced volume for which the semiconducting phase is unstable.<sup>4</sup> These charge densities were calculated with an *ab initio* method,<sup>5</sup> making use of a published set of norm-conserving pseudopotentials.<sup>6</sup> The conclusion of that study was that under pressure the behavior of the valence charge density in InSb is qualitatively very similar to that in silicon<sup>7</sup> and InAs.<sup>8</sup> Here polarization charge densities and energies associated with various zone-center phonons are reported for zinc-blende-structure InSb at its free volume, the polarizations being discussed in relation to the corresponding polarizations in other covalent materials.<sup>9-11</sup> In view of the above-mentioned x-ray scattering study<sup>3</sup> it was felt that it would be desirable to perform similar calculations at a reduced volume, and thereby further to test the view that the high-pressure semiconductor-metal phase transition is not caused by an instability in the covalent bonds, but rather is related to the competition between the covalent bonding energy and the Ewald interactions which are expected to strengthen under pressure.<sup>4,7</sup> The importance of this x-ray scattering study is that it can be interpreted as evidence for the existence of large fluctuations near the transition volume, such fluctuations not normally being associated with such a strongly first-order phase transition.

### II. METHOD

The phonon energies and charge densities reported here were calculated using the method of Ihm, Zunger, and Cohen<sup>5</sup> with the Ceperley-Alder exchange correlation en-

ergy<sup>12</sup> and the pseudopotentials tabulated in Ref. 6. A basis of about 530 plane waves was used for the calculations presented here and the same number of Fourier components were retained in the charge densities. In order to test the convergence of the calculation the bulk modulus and charge densities at several volumes were calculated using a basis of 725 plane waves and were found to be negligibly different (see Table I) from the results obtained with the smaller basis in view of the other uncertainties in the calculation. The Brillouin-zone averages were evaluated using a set of two special points<sup>13,14</sup> in the irreducible wedge for the fcc structure, yielding five points for trigonal distortions and three for tetragonal distortions. While the convergence of the calculation with respect to the number of special points was not checked, we note that this set has been found to yield accurate charge densities and phonon energies in a number of semiconductors.<sup>15</sup>

In the calculation spin-orbit interactions were neglected. While this approximation could certainly not be justified for a calculation of the band structure of a material such as InSb where spin-orbit splittings can be larger than the band gap,<sup>16</sup> it is expected to be reasonable in the present context because we are concerned with averaged properties, i.e., charge densities and total energies, and thus not the properties of states in a specific band at a specific point in the Brillouin zone. Recent relativistic calculations on SnTe and PbTe (Ref. 17) tend to support the use of this approximation. Moreover, energy-minimization calculations of the surface structure of InSb using a tight-binding method have indicated that the structure of InSb surfaces is not affected very much by spin-orbit interactions.<sup>18</sup> Errors resulting from this approximation are probably largest in the calculation of anharmonic force constants, which are expected to be more dependent on the details of the band structure than harmonic quantities.

### III. RESULTS AND DISCUSSION

#### A. Total-energy calculations

In Table I the equilibrium lattice constant  $a_0$ , bulk modulus  $B$ , and its pressure derivative  $B'$ , obtained by fitting total energies calculated at a variety of volumes  $\Omega$  to Murnaghan's equation of state<sup>21</sup> are presented. The shear elastic constant  $2c_s = c_{11} - c_{12}$ ,  $c_{44}$ , and the internal strain

TABLE I. Structural properties of zinc-blende InSb. The experimental elastic constants are from the data of Ref. 19. The pressure derivative  $B'$  is from Ref. 20. The size of the basis is given by  $n$ .

| Property              | $\Omega/\Omega_0$ | This study |         | Experiment |
|-----------------------|-------------------|------------|---------|------------|
|                       |                   | $n=531$    | $n=725$ |            |
| $a_0$ (Å)             |                   | 6.34       | 6.34    | 6.49       |
| $B$ (GPa)             |                   | 50         | 50.7    | 48.31      |
| $B'$                  |                   | 4.7        | 4.9     | 4.91       |
| $c_{44}$ (GPa)        | 1.000             | 35         |         | 31.32      |
|                       | 0.935             | 34         |         |            |
| $c_{11}-c_{12}$ (GPa) | 1.000             | 36         |         | 31.30      |
|                       | 0.935             | 38         |         |            |
| $\zeta$               | 1.000             | 0.43       |         |            |
|                       | 0.935             | 0.55       |         |            |

parameter  $\zeta$ , calculated both at the experimental free volume  $\Omega_0$  and at a reduced volume for which the zinc blende structure is unstable, are also presented. (In InSb the semiconductor-metal transition occurs at about  $\Omega/\Omega_0=0.945$ .) The shear constant  $c_s$  was calculated from the total energy changes associated with homogeneous tetragonal distortions in which one of the cube axes was stretched or compressed by small amounts ( $\sim 1\%$ ) while the other two axes were also changed in order to keep the volume of the unit cell constant.

The internal strain parameter  $\zeta$  and  $c_{44}$  were calculated from the energy changes associated with homogeneous trigonal distortions, relative displacements of the anion and cation sublattices along a [111] direction, and combinations of these. The values of  $c_s$  and  $c_{44}$  were found to change somewhat as the volume was reduced to  $\Omega/\Omega_0=0.935$  from  $\Omega_0$ . However, in view of the probable accuracy of this calculation it is difficult to attach much significance to these changes. The theoretical elastic constants are compared with the 0-K elastic constants of Ref. 19. It may be noted that the agreement between the experimental and theoretical results is reasonable although not quite as good as obtained for some other materials using similar methods.<sup>22</sup> The internal strain parameter ( $\zeta=0.43$ ) obtained here is somewhat lower than experimental values for Si [ $\zeta=0.74$  (Ref. 23),  $\zeta=0.72$  (Ref. 24)], Ge [ $\zeta=0.72$  (Ref. 25)], and GaAs [ $\zeta=0.764$  (Ref. 26)], but comparable to previous *ab initio* calculations on these materials.<sup>27,28</sup> As noted in Ref. 27 the discrepancy is probably outside the limits of the theoretical uncertainty and may be due to the assumption of overlapping spherical atoms in the analysis of the experimental data and anharmonicity due to finite strains. In fact the Fourier component of the valence charge density obtained in this calculation is  $\rho_v(600)=0.05$  at zero strain and increases by about 6% under a 1% strain. More importantly we find that the transverse optical phonon becomes highly anharmonic under stress as discussed below.  $\zeta$  increases as the volume is reduced, reflecting the expected weakening of bond-bending forces relative to bond-stretching forces. In Table II calculated frequencies  $\omega_{\text{TO}}(\Gamma)$  of the zone-center transverse optical phonon and the corresponding anharmonic force constant  $k_{xyz}$  defined by

TABLE II. Frequency of the transverse optical phonon,  $\omega_{\text{TO}}(\Gamma)$  and anharmonic force constant  $k_{xyz}$  for zinc-blende InSb. The experimental value is from Ref. 29.

| $\Omega/\Omega_0$ | $\omega_{\text{TO}}(\Gamma)$<br>( $10^{13}$ s $^{-1}$ ) | $k_{xyz}$<br>(eV/Å $^3$ ) |
|-------------------|---|---------------------------|
| 1.000             | 3.50  | -38                       |
| 0.985             | 3.56  | -42                       |
| 0.935             | 3.74  | -44                       |
| 0.892             | 3.93  | -58                       |
| 0.847             | 4.12  | -71                       |
| 1.000 (expt)      | 3.48  |                           |

$$\Delta E_{\text{tot}}(u) = ku^2 + 8k_{xyz} \left[ \frac{u}{\sqrt{3}} \right]^3 \quad (1)$$

are presented. Here  $\Delta E_{\text{tot}}(u)$  is the change in total energy per unit cell for a relative displacement between the two sublattices of  $2u$ .  $\omega_{\text{TO}}(\Gamma)$  and  $k_{xyz}$  were calculated with the distortions used for  $c_{44}$  and  $\zeta$ . It will be noted that at the free volume the experimental and theoretical frequencies are in excellent agreement. The frequency and anharmonic force constant increase smoothly over the entire volume range including the range where the zinc-blende structure is unstable and can be well described by a Grüneisen parameter  $\gamma_{\text{TO}}(\Gamma)=0.97$ . The corresponding parameters for InP and InAs have been measured to be 1.44 (Ref. 30) and 1.2 (Ref. 31), respectively. Thus the present results would seem to suggest that InSb follows the chemical trend. However, a recent state-of-the-art Raman scattering study<sup>32</sup> has yielded  $\gamma_{\text{TO}}(\Gamma)=1.41$ . Although the frequency  $\omega_{\text{TO}}(\Gamma)$  obtained in Ref. 32 does not agree to within the stated errors with a previous neutron scattering measurement,<sup>29</sup> it seems unlikely that the discrepancy in the Grüneisen parameter can be explained by an experimental error. We do not understand the source of the discrepancy. In any case the present results do show that neither  $\omega_{\text{TO}}(\Gamma)$  nor  $k_{xyz}$  display any exceptional behavior near the transition volume.

In Table III the anharmonic force constant  $k_{xyz}$  is given for [111] strains of 0.5% and 1%. The phonon frequency  $\omega_{\text{TO}}(\Gamma)$  remained unchanged under these strains to within the accuracy of our calculation and thus is not shown. Under strain  $k_{xyz}$  changes sign and the anharmonicity increases dramatically. Assuming that other zinc-blende- and diamond-structure materials show similar behavior, this result suggests that the experimental determinations of the internal strain parameters in those materials may have been affected by anharmonic effects as suggested by Nielsen and Martin.<sup>27</sup> This might also be related to a re-

TABLE III. Anharmonic force constant as a function of (111) strain,  $e_{12}=e_{23}=e_{13}=e$  at  $\Omega=\Omega_0$ .

| $e$   | $k_{xyz}$ (eV/Å $^3$ ) |
|-------|------------------------|
| 0     | -38                    |
| 0.005 | 0                      |
| 0.010 | 214                    |

cently reported anisotropic stress-sensitive anomaly in the temperature dependence of the lattice constant of silicon,<sup>33</sup> although it is not possible to make a more definite statement based on this data.

### B. Valence charge densities

In Fig. 1, (110) (a) valence charge densities, (b) polarization charge densities for a frozen TO( $\Gamma$ ) phonon, and (c) polarization charge densities for a homogeneous tetragonal distortion are shown for zinc-blende-structure InSb both at the free volume and a reduced volume,  $\Omega/\Omega_0=0.935$ . For the polarization charge densities a 1% stretch of the [111] bonds was used for the optical phonon whereas a 1% stretch of the  $z$  axis and a compensating compression of the other two axes was used for the tetragonal distortion. In order to make the redistribution more

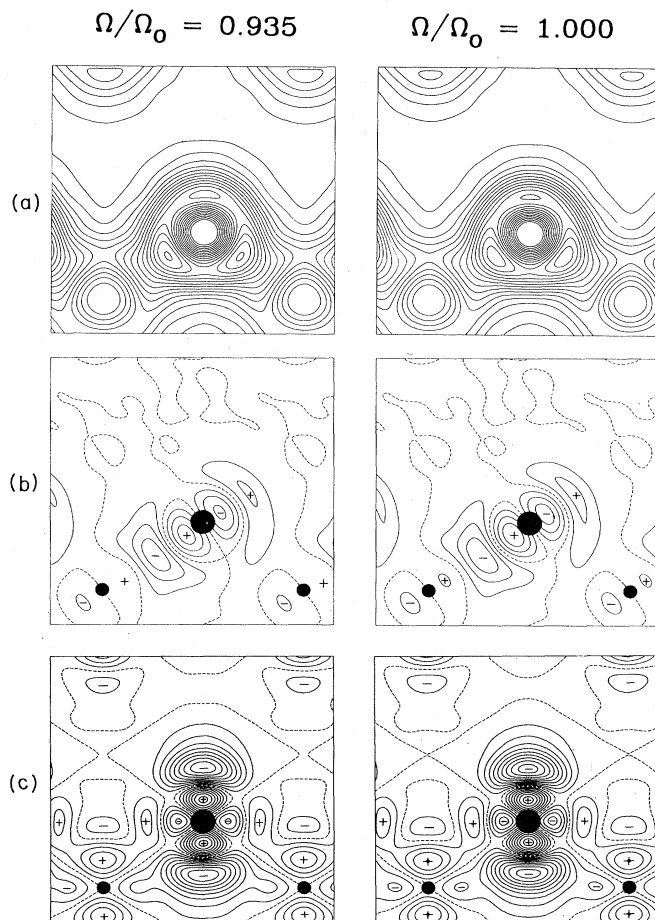


FIG. 1. (110) Charge densities and polarization for InSb. The charge densities are in the top row, (a); the polarization associated with a TO phonon is in the middle row, (b); and the polarization associated with a tetragonal distortion is in the bottom row, (c). Adjacent contours are separated by 2, 0.2, and 0.04 electrons/cell in (a), (b), and (c), respectively. The dashed contours are set at 0.

evident for this distortion the component corresponding to a rigid homogeneous distortion has been eliminated.

As discussed in Ref. 4 the valence charge densities at the two volumes are very similar, the apparent difference consisting of a small movement of the bond-charge maximum away from the anion under pressure. This is consistent with Raman scattering measurements which indicate that the difference  $\omega_{LO}(\Gamma) - \omega_{TO}(\Gamma)$  decreases under pressure in most zinc-blende materials<sup>31,32,34-38</sup> corresponding to a reduction in the effective charge  $e_T^*$ . It is interesting to note that similar reductions are observed at high temperatures,<sup>39</sup> perhaps reflecting the similar natures of the high-pressure and high-temperature (melting) phase transitions.<sup>40</sup> As for the charge density, it will be noted from Fig. 1 that both the polarization charge of the transverse optical phonon and perhaps surprisingly that of the tetragonal shear distortion are, under pressure, very similar to the corresponding quantities at the free volume. This may be expected for the TO phonon for which the forces are dominated by ion-ion interactions,<sup>41</sup> but the result for the tetragonal distortion lends further support to the conclusion of Yin and Cohen<sup>7</sup> and Ref. 4 that the semiconductor-metal high-pressure phase transition is not caused by an instability in the electron distribution but rather a competition between the covalent energy and the Ewald interactions.

The polarization charges for the TO( $\Gamma$ ) phonons contain a strong dipolelike contribution corresponding to a rigid displacement of the bond charge with the anion. There is also a small charge transfer from the stretched bond to the compressed bonds. This transfer is slightly off center in that the charge tends to flow to the region of the compressed bonds furthest from the stretched bond. The dominance of the dipolelike contribution in InSb is very similar to the polarization in ZnSe (Refs. 10 and 11) and quite unlike that in Si (Ref. 9) and Ge (Ref. 10) despite the fact that InSb is much less ionic than ZnSe, having a Phillips ionicity of 0.321 compared to 0.63 in ZnSe. This indicates that even for covalent materials with moderate ionicities the bond charge is strongly associated with the anions.

The polarization charge densities for the tetragonal distortion consist of small movements of the valence electrons toward the ions between bonds for which the bond angle is reduced and conversely a redistribution away from the ions between bonds where the angle is increased. The total amount of bond charge is not changed much by this distortion.

To summarize, charge densities, polarizations, and structural properties of zinc-blende InSb have been calculated, with reasonable agreement with experimental data being obtained. It is found that the valence electrons behave almost identically under high pressures, for which the zinc-blende structure is unstable, as at the free volume.

The fact that the covalent bonds are found to be undistorted under pressure may be qualitatively understood by making use of some of Phillips's ideas<sup>42</sup> and noting the strengthening of the pseudopotential in the bonding region as the volume is reduced. This arises because under pressure the minima in the indium pseudopotentials move to

wards the bond charges which are located near the minima of the antimony pseudopotentials. (The minimum in the antimony pseudopotential is about 1.7 a.u. from the anion sites while at the free volume the minimum in the indium is about 3.7 a.u. away. The bond charge maximum is located about 1.85 a.u. from the anion.) This also helps to account for the movement of the bond charges away from the anions as the crystal is compressed since as the anion-cation distance is reduced the bond charge may be expected to be influenced to a greater extent by the cations.

It would be of interest to compliment this study with

calculations on the  $\beta$ -Sn-like high pressure phase or the metastable rocksalt phase under pressure. We have not done this as it would no doubt require consideration of spin-orbit effects. However, in this regard we note that Mele and Joannopoulos,<sup>43</sup> using a somewhat different technique, have calculated the band-structure and valence charge density of rocksalt structure InSb at its free volume. They found that in the rocksalt structure there is a large charge transfer of about  $0.9e$  from the cations to the anions, suggesting that this structure and possibly the high-pressure phases are stabilized by both ionic and metallic bonding.

- <sup>1</sup>S.-C. Yu, I. L. Spain, and E. F. Skelton, *J. Appl. Phys.* **49**, 4741 (1978).
- <sup>2</sup>K. Asoumi, O. Shimomura, and S. Minomura, *J. Phys. Soc. Jpn.* **41**, 1630 (1976).
- <sup>3</sup>D. R. Yoder-Short, R. Colella, and B. A. Weinstein, *Phys. Rev. Lett.* **49**, 1438 (1982).
- <sup>4</sup>D. Singh and Y. P. Varshni, *Phys. Rev. B* **31**, 8252 (1985).
- <sup>5</sup>J. Ihm, A. Zunger, and M. L. Cohen, *J. Phys. C* **12**, 4409 (1979).
- <sup>6</sup>G. B. Bachelet, D. R. Hamann, and M. Schluter, *Phys. Rev. B* **26**, 4199 (1982).
- <sup>7</sup>M. T. Yin and M. L. Cohen, *Phys. Rev. Lett.* **50**, 1172 (1983).
- <sup>8</sup>D. Singh and Y. P. Varshni, *Solid State Commun.* **55**, 549 (1985).
- <sup>9</sup>B. N. Harmon, W. Weber, and D. R. Hamann, *J. Phys. (Paris)* **42**, C6-628 (1981).
- <sup>10</sup>R. Resta, *Phys. Rev. B* **27**, 3620 (1983).
- <sup>11</sup>R. Resta and A. Baldereschi, *J. Phys. (Paris)* **42**, C6-661 (1981).
- <sup>12</sup>D. M. Ceperley and B. J. Alder, *Phys. Rev. Lett.* **45**, 566 (1980); J. Perdew and A. Zunger, *Phys. Rev. B* **23**, 5048 (1981).
- <sup>13</sup>A. Baldereschi, *Phys. Rev. B* **7**, 5212 (1973).
- <sup>14</sup>D. J. Chadi and M. L. Cohen, *Phys. Rev. B* **8**, 5747 (1973).
- <sup>15</sup>See, for example, P. Bendt and A. Zunger, *Phys. Rev. B* **26**, 3114 (1982).
- <sup>16</sup>M. Cardona, K. L. Shaklee, and F. H. Pollack, *Phys. Rev.* **154**, 699 (1967).
- <sup>17</sup>K. M. Rabe and J. D. Joannopoulos, *Bull. Am. Phys. Soc.* **30**, 466 (1985).
- <sup>18</sup>D. J. Chadi, *Phys. Rev. B* **19**, 2074 (1979).
- <sup>19</sup>L. J. Slutsky and C. W. Garland, *Phys. Rev.* **113**, 167 (1959).
- <sup>20</sup>I. O. Bashkin and G. I. Peresada, *Sov. Phys.—Solid State* **16**, 2058 (1975) [*Fiz. Tverd. Tela (Leningrad)* **16**, 3166 (1974)].
- <sup>21</sup>F. D. Murnaghan, *Proc. Nat. Acad. Sci. U.S.A.* **3**, 244 (1944); F. D. Murnaghan, *Finite Deformation of an Elastic Solid* (Wiley, New York, 1951).
- <sup>22</sup>S. G. Louie, in *Electronic Structure, Dynamics and Quantum Structural Properties of Condensed Matter*, edited by J. T. Devreese and Piet van Camp (Plenum, New York, 1985), and references therein.
- <sup>23</sup>H. D'Amour, W. Denner, H. Schulz, and M. Cardona, *J. Appl. Crystallogr.* **15**, 148 (1982).
- <sup>24</sup>C. S. G. Cousins, L. Gerward, J. Staun Olsen, B. Selsmark, and B. J. Sheldon, *J. Appl. Crystallogr.* **15**, 154 (1982).
- <sup>25</sup>C. S. G. Cousins, L. Gerward, K. Nielsen, J. Staun Olsen, B. Selsmark, B. J. Sheldon, and G. E. Webster, *J. Phys. C* **15**, L651 (1982).
- <sup>26</sup>C. N. Koumelis, G. E. Zardas, C. A. Landos, and D. K. Leventuri, *Acta Crystallogr. Sect. A* **32**, 84 (1975).
- <sup>27</sup>O. H. Nielsen and R. M. Martin, *Phys. Rev. Lett.* **50**, 697 (1983); R. M. Martin and O. H. Nielsen, in Ref. 22, *Electronic Structure, Dynamics and Quantum Structural Properties of Condensed Matter*.
- <sup>28</sup>B. N. Harmon, W. Weber, and D. R. Hamann, *Phys. Rev. B* **25**, 1109 (1982).
- <sup>29</sup>D. L. Price, J. M. Rowe, and R. M. Nicklow, *Phys. Rev. B* **3**, 1268 (1971).
- <sup>30</sup>R. Trommer, H. Muller, M. Cardona, and P. Vogl, *Phys. Rev. B* **21**, 4869 (1980).
- <sup>31</sup>A. Jayaraman, V. Swaminathan, and B. Batlogg, *Pramana* **23**, 405 (1984).
- <sup>32</sup>K. Aoki, E. Anastassakis, and M. Cardona, *Phys. Rev. B* **30**, 681 (1984).
- <sup>33</sup>Y. Soejima, K. Inoue, T. Kawahara, N. Ohama, and A. Okazaki, *J. Phys. C* **18**, 2431 (1985).
- <sup>34</sup>B. A. Weinstein and G. J. Piermarini, *Phys. Rev. B* **12**, 1172 (1975).
- <sup>35</sup>B. A. Weinstein, J. B. Renucci, and M. Cardona, *Solid State Commun.* **9**, 1651 (1971).
- <sup>36</sup>S. S. Mitra, O. Brafman, W. B. Daniels, and R. K. Crawford, *Phys. Rev.* **186**, 942 (1969).
- <sup>37</sup>R. Trommer, E. Anastassakis, and M. Cardona, in *Light Scattering in Solids*, edited by M. Balkanski, R. C. C. Leite, and S. P. S. Porto (Flammarion, Paris, 1976), p. 396.
- <sup>38</sup>This is not observed for AlSb; C. J. Buchenauer, F. Cerdeira and M. Cardona, in Ref. 37, *Light Scattering in Solids*, p. 280.
- <sup>39</sup>See, for example, E. Liarokapis and E. Anastassakis, *Phys. Rev. B* **30**, 2270 (1984).
- <sup>40</sup>N. H. March and F. Flores, *Solid State Commun.* **49**, 649 (1984).
- <sup>41</sup>H. Wendel and R. M. Martin, *Phys. Rev. Lett.* **40**, 950 (1978).
- <sup>42</sup>J. C. Phillips, *Bonds and Bands in Semiconductors* (Academic, New York, 1973).
- <sup>43</sup>E. J. Mele and J. D. Joannopoulos, *Phys. Rev. B* **24**, 3145 (1981).