

## Theoretical study of cubic versus tetragonal structures of defect zinc-blende semiconductors: $\text{CdIn}_2\text{Se}_4$

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The structural properties of  $\text{CdIn}_2\text{Se}_4$  are calculated from first principles with use of the local-density approximation and norm-conserving pseudopotentials. Particular attention has been paid to the relative stability of the tetragonal and cubic spinel phases. We find that (i) the tetragonal phase is the most stable at zero pressure, (ii) this phase actually is a pseudocubic one ( $c/a=1$ ), (iii) the combined effect of the lower symmetry and of the presence of defects induces distortions in the anion sublattice, and (iv) a transition to the spinel phase occurs under an applied pressure of  $\sim 10$  kbar. The electronic properties of the two phases are also discussed in terms of the electron charge-density distribution and density of states.

### I. INTRODUCTION

The defect zinc-blende semiconductor  $\text{CdIn}_2\text{Se}_4$  belongs to a family of ternary compounds which have been extensively investigated in the last decade,<sup>1</sup> mainly because of their potential nonlinear-optics applications. The most common crystal structure of  $\text{CdIn}_2\text{Se}_4$  is a tetragonal (actually pseudocubic) phase in which each cation is tetrahedrally coordinated by four anions and each anion is in turn coordinated by two Cd ions, one In ion, and one vacancy. The presence of an ordered array of vacancies has recently prompted extensive theoretical investigations<sup>2,3</sup> directed to clarify the effect of these vacancies on the structural and electronic properties of the crystal. In particular, it has been found that lone-pair Se dangling orbitals exist which span a variety of orientations and an energy range of about 3 eV at the top of the valence band. It has also been suggested on the basis of a critical analysis of the available experimental information and of the Jaffe-Zunger<sup>4</sup> model that the observed departures of the anion sublattice from a perfect cubic close-packed arrangement are merely a manifestation of the tendency of covalent bonds to attain their ideal tetrahedral value.

It is the purpose of the present paper to supplement the aforementioned analysis with detailed first-principles total-energy calculations in both the tetragonal and a less common cubic structure. In fact, a noteworthy feature of  $\text{CdIn}_2\text{Se}_4$  is that it can also be grown in a cubic spinel phase where the cations are distributed between octahedral and tetrahedral sites. This material is therefore a useful benchmark for studying the relative stability of octahedral versus tetrahedral cation site distribution. This

problem, besides being of fundamental importance for understanding the physics of ternary compounds, is also technologically relevant in connection with stability of chalcogenide-based photoelectrochemical cells.<sup>5</sup> Our attention is also focused on the relative stability of the spinel and tetragonal phases and its dependence upon the applied pressure; a phase transition between the tetragonal and the cubic spinel phase is predicted at an applied pressure of  $\sim 10$  kbar in fair agreement with the experimental findings (18 kbar).<sup>6</sup>

This work is organized as follows. The crystal structures are discussed in Sec. II; the computational details are given in Sec. III; our results for the structural and electronic properties are reported in Secs. IV and V, respectively; finally, Sec. VI contains our discussion and conclusions.

### II. CRYSTAL STRUCTURE

The tetragonal phase of  $\text{CdIn}_2\text{Se}_4$  can be found in three polytypes<sup>7</sup> which are usually referred to as  $\alpha$ ,  $\beta$ , and  $\gamma$  and which only differ in their cation arrangement. We will focus our attention on the  $\alpha$  phase which is the simplest and best known: its crystalline structure is pseudocubic with space group  $D_{2d}^{11}$ . As shown in Fig. 1, the pseudocubic cell contains one chemical formula; four anions are located at the corners of a fcc lattice, while the three cations are distributed among the four tetrahedral sites of a zinc-blende structure. Since experimental<sup>8</sup> and theoretical<sup>2,9</sup> investigations on  $\text{CdIn}_2\text{Se}_4$  suggest that its electronic properties are rather sensitive to the details of the crystal structure, we have optimized the unit shape and internal positions with respect to all the symmetry-

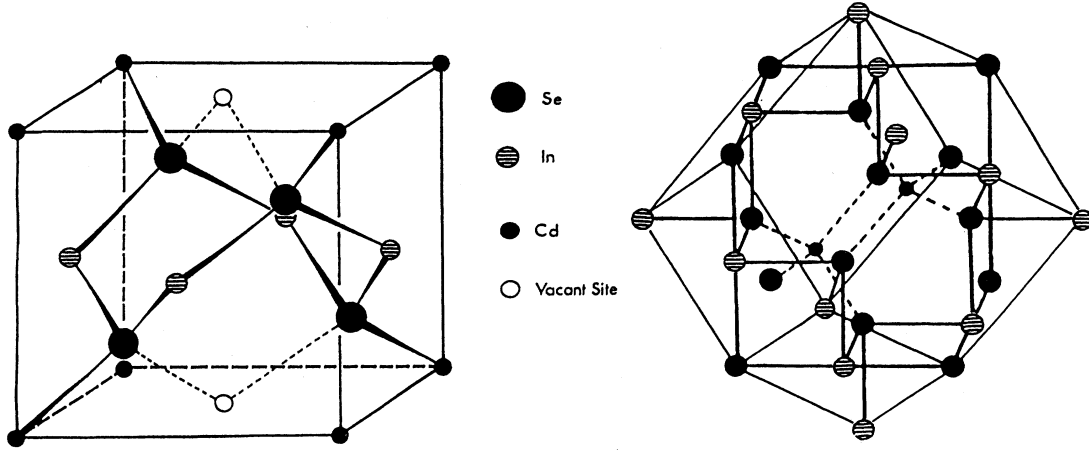


FIG. 1. Unit cell of  $\text{CdIn}_2\text{Se}_4$  in the tetragonal (left), and in the spinel phase (right).

conserving distortions. To this end, we consider the tetragonal compression along the  $c$  axis and two internal anion relaxations,  $\epsilon$  and  $\delta$ , which correspond to displacements perpendicular and parallel to the  $c$  axis, respectively. Table I gives the atomic positions of  $\alpha\text{-CdIn}_2\text{Se}_4$  as a function of  $c/a$  and of the distortion parameters  $\epsilon$  and  $\delta$ . We reiterate that the undistorted structure is characterized by  $c/a = 1$ ,  $\epsilon = 0.25$ , and  $\delta = 0.25$ .

The spinel structure of  $\text{CdIn}_2\text{Se}_4$  is much less common and is not usually considered as one of its stable crystalline phases, though it was discovered almost 20 years ago.<sup>6,10</sup> This phase can be prepared by a pressure reaction and possibly it escaped attention because of some difficulties in the preparation method.<sup>6,10</sup> The atomic arrangement in the spinel structure is described in Ref. 11 and studied in the particular case of the related  $\text{MgIn}_2\text{S}_4$  compound. The unit cell contains 14 atoms whose lattice positions are reported in Table II. When the value of the so-called *internal distortion parameter*  $u$  is  $\frac{3}{8}$ , the anions lie on an ideal fcc lattice. The symmetry of the crystal is cubic, space group  $O_h^7 (Fd\bar{3}m)$ , independent of the value of  $u$ . According to experiment<sup>6</sup> we have assumed a normal cation distribution, which corresponds to all the In atoms located in octahedral sites and all the Cd ones in tetrahedral sites. The unit cell of the spinel structure contains two molecules.

### III. COMPUTATIONAL METHOD

We have performed our calculations using the Kohn-Sham local-density approximation (LDA) to the

Hohenberg-Kohn density-functional theory<sup>12</sup> and norm-conserving pseudopotentials.<sup>13</sup> This technique is by now a well-established means for obtaining accurate information about the electronic ground-state properties of solids. As input for the LDA we take the electron-gas data from Ceperley and Alder<sup>14</sup> as interpolated by Perdew and Zunger.<sup>15</sup> We have used norm-conserving pseudopotentials from Ref. 16, assuming the Cd  $4d$  states to be frozen in the core (i.e., we assume the valence charge of Cd to be  $Z_v = 2$ ). The inclusion of Cd  $4d$  states in the valence shell would certainly improve the accuracy of it, but would also make the calculation impractical within the present plane-wave pseudopotential method. The electronic wave functions have been expanded into a plane-wave basis set up to a kinetic energy cutoff of 9 Ry. This choice leads to a convergence error for the energy differences of about 0.001 Ry, which is sufficient for obtaining accurate results for all the properties we have computed. The Brillouin-zone (BZ) integrations have been performed using the Baldereschi special-points technique.<sup>17</sup> For the spinel structure, we used two Chadi-Cohen points which are enough for obtaining well-converged values for the quantities we have calculated. This set of points, when used in the tetragonal phase, gives rise to six inequivalent points in an irreducible wedge of the BZ. We have verified that the kinetic ener-

TABLE I. Atomic positions in the unit cell, in units of the lattice parameter  $a_0$ , for tetragonal phase of  $\text{CdIn}_2\text{Se}_4$ .

	Cd	In	Se
1	(0,0,0)	$(\frac{1}{2}, 0, \frac{1}{2}c/a)$	$(\epsilon, \epsilon, \delta c/a)$
2		$(0, \frac{1}{2}, \frac{1}{2}c/a)$	$(-\epsilon, -\epsilon, \delta c/a)$
3			$(\epsilon, -\epsilon, -\delta c/a)$
4			$(-\epsilon, \epsilon, -\delta c/a)$

TABLE II. Atomic positions in the unit cell, in units of the lattice parameter  $a_0$ , for normal spinel phase of  $\text{CdIn}_2\text{Se}_4$ .

	Cd	In	Se
1	(0,0,0)	$(\frac{5}{8}, \frac{5}{8}, \frac{5}{8})$	$(-u, -u, u)$
2	$(\frac{1}{4}, \frac{1}{4}, \frac{1}{4})$	$(\frac{7}{8}, \frac{7}{8}, \frac{5}{8})$	$(u, u, u)$
3		$(\frac{5}{8}, \frac{7}{8}, \frac{7}{8})$	$(-u, u, -u)$
4		$(\frac{7}{8}, \frac{5}{8}, \frac{7}{8})$	$(u, -u, -u)$
5			$(\frac{1}{4} + u, \frac{1}{4} + u, \frac{1}{4} - u)$
6			$(\frac{1}{4} - u, \frac{1}{4} - u, \frac{1}{4} - u)$
7			$(\frac{1}{4} + u, \frac{1}{4} - u, \frac{1}{4} + u)$
8			$(\frac{1}{4} - u, \frac{1}{4} + u, \frac{1}{4} + u)$

gy cutoff and the number of special points are sufficient for obtaining well-converged results for all the properties we have computed. In our calculations we have minimized the total crystal energy with respect to the volume for both tetragonal and normal spinel phases. For each volume, we have calculated the equilibrium values of the distortion parameters through an accurate determination of the forces acting on the anions, the forces on cations vanishing by symmetry. In this way it has been possible to obtain much more accurate values for the distortion parameters than it was possible to obtain in Ref. 2. For the tetragonal phase, we have also studied the dependence of the total energy on  $c/a$ .

#### IV. STRUCTURAL PROPERTIES

Our results for the main structural properties are summarized in Table III. As has been already remarked in the previous section, the equilibrium values of the internal distortion parameters  $\epsilon$  and  $\delta$  of the tetragonal phase are different from the ones reported in Ref. 2 since the latter have been obtained without the computation of the interatomic forces. The agreement between theoretical and experimental values is satisfactory. In fact, the most noticeable discrepancy, namely an equilibrium lattice constant for the tetragonal phase which is 5% less than the corresponding experimental value, can be safely ascribed to our neglect of the Cd  $4d$  orbitals.<sup>3</sup> In fact our value for the In—Se bond length is 2.63 Å, to be compared with an experimental value of 2.62 Å, while the Cd—Se theoretical bond length is 2.45 Å against an experimental value of 2.61 Å.

The most relevant energetically favored distortion for the tetragonal phase is the one corresponding to anion relaxations parallel to the  $c$  axis. In particular, we found that the coordinates of the anions in the plane perpendicular to the  $c$  axis differ only slightly from their ideal values, while the equilibrium value of  $c/a$  is 1, thus indicating that the tetragonal structure actually is a pseudocubic one. The equilibrium value of  $c/a$  has been determined for several values of the molecular volume by minimizing the energy with respect to  $c/a$  and to the

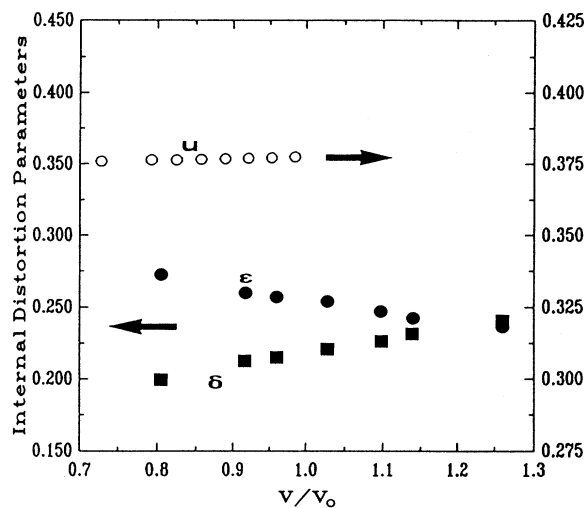


FIG. 2. Distortion crystallographic parameters, in units of the lattice constant, as a function of the molar volume of  $\text{CdIn}_2\text{Se}_4$ . The left scale refers to the tetragonal phase ( $\epsilon$  and  $\delta$ ), while the right scale refers to the spinel phase ( $u$ ).  $V_0$  is the equilibrium volume of the tetragonal phase.

internal distortions  $\epsilon$  and  $\delta$ . For all the volumes we have examined, the minimum energy is always attained at  $c/a = 1$ . The experimental<sup>7,18</sup> and theoretical<sup>2,3</sup> values of internal distortion parameters for the tetragonal phase indicate an almost undistorted structure.

The variation of the distortion parameters as a function of the volume is displayed in Fig. 2. In the pseudocubic phase the equilibrium values of both  $\delta$  and  $\epsilon$  vary almost linearly with the volume. On the contrary, the equilibrium value of  $u$  in the spinel structure is practically independent of the volume.

Figure 3 reports the total energy per molecule as a function of the volume. The curve has been obtained by fitting our numerical results to the Murnaghan equation of state.<sup>19</sup> The equilibrium energy per molecule of the spinel phase is slightly higher than for the tetragonal

TABLE III. Calculated structural properties of tetragonal and spinel phase of  $\text{CdIn}_2\text{Se}_4$ :  $a_0$  is the lattice parameter,  $B_0$  the bulk modulus;  $c/a$ ,  $u_0$ ,  $\epsilon_0$ , and  $\delta_0$  are the internal distortion parameters as described in text.

	$a_0$ (a.u.)	$B_0$ (Mbar)	$c/a$	$u_0$	$\epsilon_0$	$\delta_0$
Tetragonal	10.53	0.49	1.0		0.255	0.218
Expt.	10.99 <sup>a</sup>		1.0		0.275	0.227
Bernard and Zunger <sup>b</sup>	10.99		1.0		0.272	0.234
Spinel	20.25	0.86		0.377		
Expt.	21.44 <sup>c</sup> –21.55 <sup>d</sup>			0.383 <sup>c</sup>		

<sup>a</sup>From Ref. 18.

<sup>b</sup>From Ref. 3.

<sup>c</sup>From Ref. 6.

<sup>d</sup>From Ref. 10.

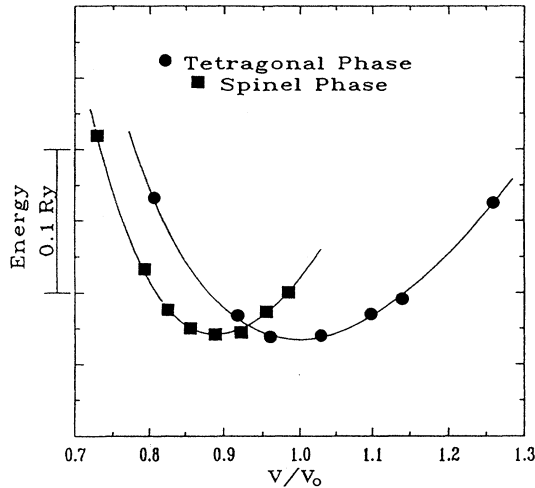


FIG. 3. Energy per molecule as a function of the volume for the tetragonal and spinel phase of  $\text{CdIn}_2\text{Se}_4$ .  $V_0$  is the equilibrium volume of the tetragonal phase.

phase ( $\sim 0.005$  Ry), in agreement with the empirical fact that the tetragonal phase is the more common of the two. It is interesting to note that the internal distortions play an important role in stabilizing the pseudocubic phase. In fact, if we do not allow anions to relax, i.e., if we fix the selenium atoms in their ideal positions for both tetragonal and spinel phases, then the latter structure is more stable by  $\sim 0.008$  Ry/molecule.

Finally, we have studied the relative stability of the two phases of our compound as a function of the applied pressure. Figure 4 shows the variation of the volume as a function of the pressure for both phases of  $\text{CdIn}_2\text{Se}_4$ . We found a phase transition between the two structures at a

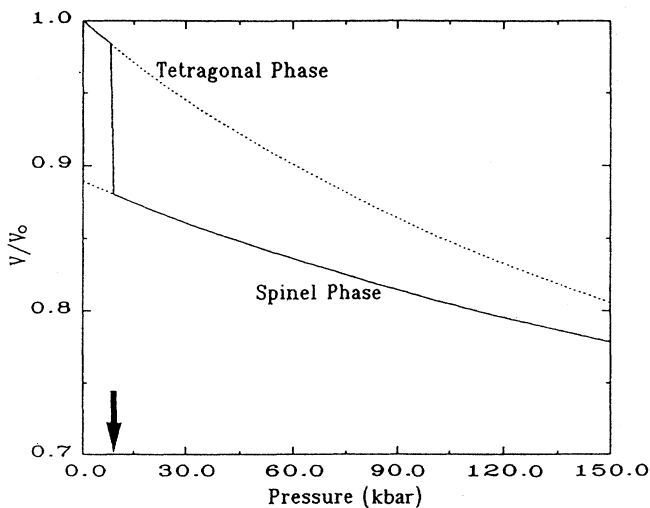


FIG. 4. Volume per molecule as a function of the applied pressure for the spinel and tetragonal phases of  $\text{CdIn}_2\text{Se}_4$ .  $V_0$  is the equilibrium volume of the tetragonal phase.

pressure of  $\sim 10$  kbar, to be compared with an experimental value of 18 kbar.<sup>6</sup> The relative variation of the volume is 10% in good agreement with experiment<sup>6</sup> (7.3%).

## V. ELECTRONIC PROPERTIES

In Fig. 5 we report our calculated valence density-of-states (DOS) curves for  $\text{CdIn}_2\text{Se}_4$  both in the tetragonal and spinel phases. These have been obtained by diagonalizing the self-consistent Hamiltonian at a large number of special points in the Brillouin zone including point  $\Gamma$  (10 and 18 for spinel and tetragonal form, respectively) and smearing the resulting histogram with a Gaussian convolution of width  $\Delta = 0.3$  eV. We checked that the qualitative features of the density of states are independent of the number of special points and of  $\Delta$ . From Fig. 5 we see that both structures show an intraband gap due to the energy difference between the anion  $4s$  atomic states and the other atomic states involved in the chemical bonds. The relevant features of our theoretical DOS are compared with the photoemission data<sup>8</sup> (only available for the tetragonal phase) in Table IV, where we also report

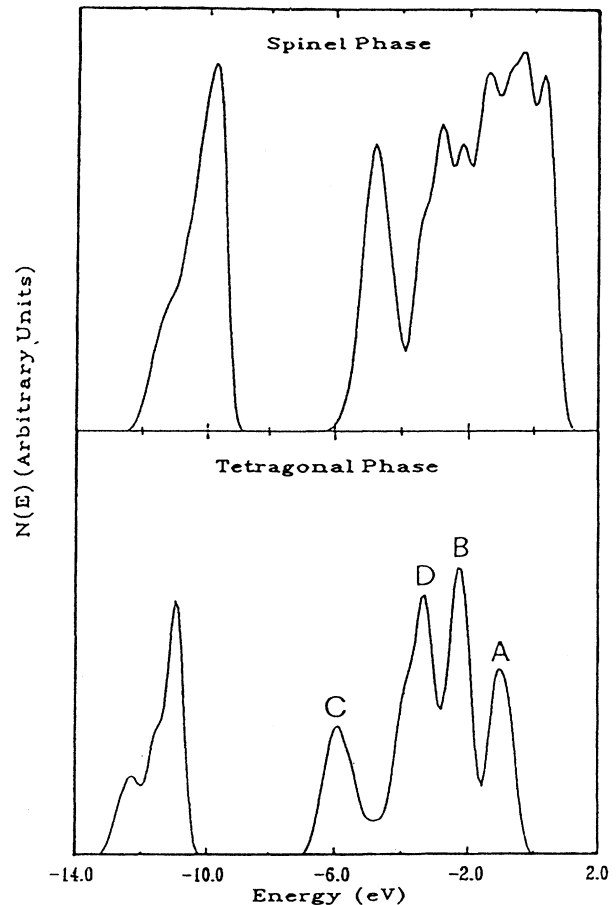


FIG. 5. Valence density of states of the spinel and tetragonal phases of  $\text{CdIn}_2\text{Se}_4$ . The energy is measured from the top of the valence band of the tetragonal structure.

TABLE IV. Energy (eV) of the main peaks (above the intraband gap) of the density of states for tetragonal phase of CdIn<sub>2</sub>Se<sub>4</sub>. The zero of energy corresponds to the top of the valence band. See Fig. 5 for identification of peaks.

	$E_A$	$E_B$	$E_C$	$E_D$
Present work	-1.1	-2.1	-3.1	-6.0
Baldereschi <i>et al.</i> <sup>a</sup>	-0.5	-2.0		-4.7
Expt. <sup>b</sup>	-1.1	-1.8		-6.1

<sup>a</sup>From Ref. 20.

<sup>b</sup>From Ref. 8.

the results of a previous semiempirical pseudopotential band-structure calculation.<sup>20</sup> The main features of the experimental spectrum are well reproduced by our calculation. In particular, the position of the *A*, *B*, and *D* peaks are predicted by our calculation with remarkable accuracy, as is the width of the upper valence band. Our calculations, however, predict a fourth peak (marked *C* in the figure) which is not observed experimentally. The improvement on previous semiempirical pseudopotential calculations<sup>20</sup> is sensible. In particular, the previous calculations underestimated the width of the upper valence band by  $\sim 1.5$  eV, missed the positions of the main photoemission peaks by several tenths of eV, and also predicted a gap between the *A* and *B* peaks which is not observed experimentally, nor predicted by the present calculation. We also point out that the high-lying part of the valence band (near the band edge) is clearly different for the two structures. In fact, there is a peak in the case of the tetragonal phase (labeled *A* in the lower part of Fig. 5) which is absent in the DOS of the spinel phase. This is consistent with the interpretation of this peak made in Ref. 8, according to which it corresponds to *4p* selenium atomic orbitals oriented toward the vacant site direction.

A distinctive feature of the valence band of CdIn<sub>2</sub>Se<sub>4</sub> is the occurrence (Refs. 20 and 9) of two (not always nonzero) intraband energy gaps, which we shall call  $E_g^1$  and  $E_g^2$  (the lower and upper one, respectively). Table V reports the values of  $E_g^1$  and  $E_g^2$ , as well as of the total and upper valence-band widths ( $\Delta_{\text{val}}^1$  and  $\Delta_{\text{val}}^2$ , respectively) for three sets of calculations, namely the present one, the semiempirical pseudopotential calculation by Baldereschi *et al.*,<sup>20</sup> and the all-electron self-consistent calculation by Bernard and Zunger.<sup>3</sup> Table V clearly shows that the two sets of first-principles results are quite close to each other while in sensible disagreement with the

TABLE V. Total and upper valence-band widths ( $\Delta_{\text{val}}^1$  and  $\Delta_{\text{val}}^2$ ) and lower and upper intraband energy gaps ( $E_g^1$  and  $E_g^2$ ), in eV.

	$\Delta_{\text{val}}^1$	$E_g^1$	$\Delta_{\text{val}}^2$	$E_g^2$
Present work	12.2	4.3	5.9	0.0
Bernard and Zunger <sup>a</sup>	12.5	6.0	5.3	0.0
Baldereschi <i>et al.</i> <sup>b</sup>	15.4	9.0	4.0	0.4

<sup>a</sup>From Ref. 3.

<sup>b</sup>From Ref. 20.

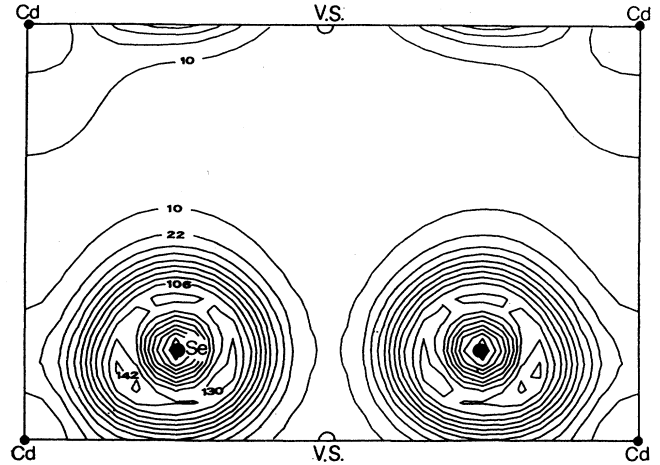


FIG. 6. Total valence charge density on the (110) plane of tetragonal phase of CdIn<sub>2</sub>Se<sub>4</sub>. The units are electrons/cell.

semiempirical results (which are the only ones to show an  $E_g^2$  different from zero). The apparent disagreement in the  $E_g^1$  values given by the first-principles approaches actually reflects the difference in the quantities being computed, since the Bernard-Zunger gap includes the Cd *d* bands which are not taken into account by the Cd pseudopotential used in our work.

Further insight in the properties of CdIn<sub>2</sub>Se<sub>4</sub> can be gained from the analysis of the valence-electron charge-density maps. Figures 6 and 7 give the main features of the charge distribution in the bonding regions for the tetragonal phase and refer to planes (110) and (100), respectively. The plot reported in Fig. 6 shows the charge-

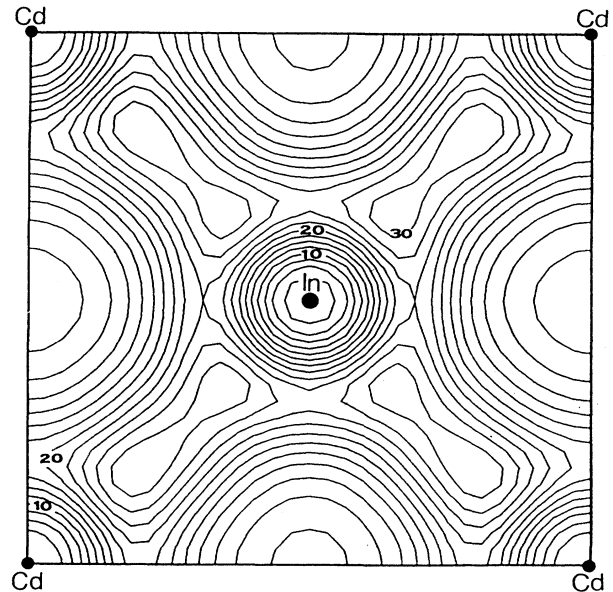


FIG. 7. Total valence charge density on the (001) plane of tetragonal phase of CdIn<sub>2</sub>Se<sub>4</sub>. The units are electrons/cell.

density distortion induced by the presence of a vacant site (VS)  $V$ . One can see a notable charge accumulation along the Se— $V$  direction which is only slightly less (maximum density 130 against 142 electrons/cell) than the one occurring along the Cd—Se bond. This result is clearly consistent with the existence of only slight departures of the anion lattice from a perfect cubic close-packed arrangement. This very picture of a crystal structure essentially held together by the anion lattice is also borne out by the plot of Fig. 7. There one can see that the charge distribution around Cd and In atoms is in practice indistinguishable, as one would expect from an almost completely ionic bond. In addition, it must be noted that the inclusion of the Cd  $4d$  bands should act to reduce the slight Cd-In covalency which might be seen in Fig. 7 and, through a kind of "repelling" In charge, should lead to slightly different charge densities around the two cation sites. The features about the valence-electron density distribution in the spinel structure are given by the plot in Fig. 8, which refers to the (110) plane. The first information one gets from the figure is that the maximum densities along the bond directions are sensibly higher in the spinel than in the tetragonal structure. This fact implies a higher bond strength and, in turn, a substantially higher bulk modulus, in agreement with the numerical results of the preceding section. Additional information is obtained from the comparison of the Cd—Se and the In—Se bonds. Again in spite of the different lengths of the two bonds, we find the same strong similarity we have found in the tetragonal phase. The overall result is confirmation of the highly ionic character of this compound.

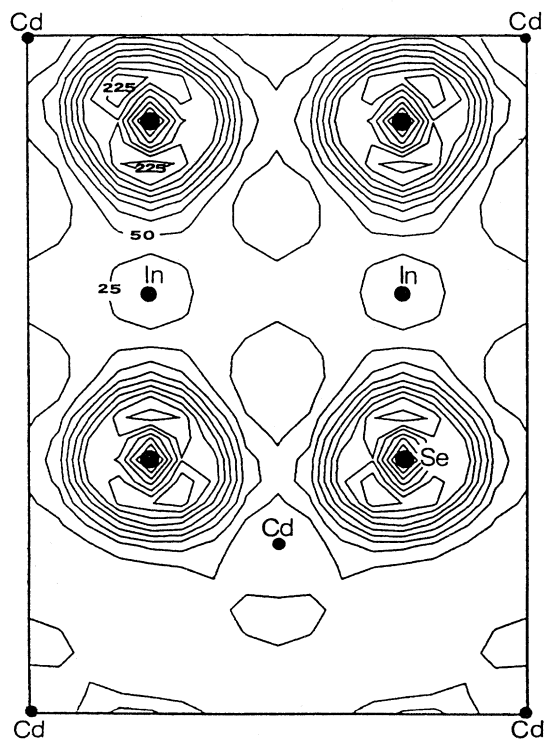


FIG. 8. Total valence charge density on the (110) plane of spinel phase of  $\text{CdIn}_2\text{Se}_4$ . The units are electrons/cell.

Our plane-wave basis set, although adequate for accurately describing valence bands, is not such for the conduction bands. For this reason, besides the well-known problems of density-functional theory for excitation energies, our calculation is not able to make any quantitative prediction of the fundamental gap. As a qualitative result, we find that in both phases  $\text{CdIn}_2\text{Se}_4$  has a direct gap at point  $\Gamma$ . For the tetragonal structure this is in agreement, both with experiments and recent theoretical work.<sup>3</sup>

## VI. CONCLUDING REMARKS

We have performed a set of state-of-the-art first-principles total-energy calculations for several structural modifications of the defect zinc-blende semiconductor  $\text{CdIn}_2\text{Se}_4$ . Besides being in generally good agreement with the experiment, our results help to elucidate some controversial issues. In fact, the existence of an intravalence energy gap which has been put forth in a previous paper<sup>20</sup> has not been confirmed by our calculations, and neither has the anion relaxation perpendicular to the  $c$  axis and the tetragonal compression.<sup>9</sup> Accordingly, we may state that the use of *ab initio* pseudopotentials and self-consistent techniques is indispensable to avoid even qualitative errors in basis properties of ternary compounds.

Actually, our calculations have shown that the tetragonal modification of  $\text{CdIn}_2\text{Se}_4$ , at equilibrium, is characterized by a slight structural distortion corresponding to an anion relaxation parallel to the  $c$  axis. This result clearly shows that the role played by vacant sites in determining the structural properties of this class of compounds is, at least qualitatively, important.

The above behavior is consistent with the picture emerging from our charge-density maps, which show that the bonding in this material is essentially ionic. Even the differences in the charge distributions around tetrahedral and octahedral sites in the spinel phase are rather small and seem to depend more on the different geometrical environments than on the different chemical properties of Cd and In. This overall picture is quite consistent with the extremely small total-energy difference between tetragonal and spinel phases we have found. A final remark concerns the problem of the octahedral versus the tetragonal site preference referred to in the Introduction. The present calculations as well as previous ones on the related  $\text{MgIn}_2\text{S}_4$  compound do not give a definite answer to this issue. It may be that finite temperature and/or kinetic effects, which are beyond the scope of the present work, play an important role.

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