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Ab initio calculations of the pressure-induced structural phase transitions for four II-VI compounds

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We report on pseudopotential calculations of the structural properties and pressure-induced solid-solid phase transitions for four II-VI compounds: ZnSe, ZnTe, CdSe, and CdTe. For each of these compounds, we fix the zinc-blende structure as the ambient pressure phase and consider the rocksalt, cinnabar, and *Cmcm* structures as candidates for the high-pressure phases. We calculate the transition pressures and the changes in specific volume for each compound. The pressure dependences of the structural parameters of the cinnabar and the *Cmcm* phases are determined. The *Cmcm* structure appears to be a common high-pressure phase for the II-VI and III-V semiconductors. [S0163-1829(97)09316-8]

I. INTRODUCTION

The high-pressure properties of II-VI compounds have attracted the interest of researchers for over 30 years. The pressure-induced structural phase transitions for CdS, CdSe, and CdTe were first observed in optical studies by Edwards and Drickamer,[1] and later confirmed in electrical measurements.[2] Subsequent diffraction studies[3–6] reproduced these results, and found the rocksalt phase to be a high-pressure phase for II-VI compounds. After these experiments, the generally accepted transition sequence for II-VI semiconductors was zinc-blende (or wurtzite) → rocksalt → β-tin, with the exception that in the mercury chalcogenides (HgX) the rocksalt phase is preceded by a cinnabar phase which can be intepreted as a distorted rocksalt phase. The cinnabar phase was first identified as the ambient-pressure phase in HgS (Ref. 7) and HgO.[8]

Recent measurements using angle-dispersive x-ray techniques and synchrotron radiation demonstrated that the high-pressure systematics of II-VI compounds are in fact much richer. The cinnabar phase which was thought to exist only in the mercury chalcogenides was found in CdTe and ZnTe.[9,10] In ZnTe the cinnabar phase is found to be stable between 9.3 and 11.0 GPa; in CdTe the cinnabar phase is observed in a very narrow region around 3.5 GPa between the zinc-blende and rocksalt phases. At higher pressure an orthorhombic *Cmcm* structure is found to be stable for both ZnTe and CdTe.[11,12] The rocksalt phase of CdTe transforms into the orthorhombic *Cmcm* phase at a pressure of 10 GPa. The *Cmcm* phase remains stable to at least 28 GPa. ZnTe skips the rocksalt phase; the cinnabar phase transforms directly into the *Cmcm* phase at a pressure of 11.0 GPa.

The observed succession of high-pressure phases for the selenides differs considerably from the tellurides. So far, neither the cinnabar nor the orthorhombic *Cmcm* phases have been found for ZnSe and CdSe. Both of these compounds transform from the zinc-blende into the rocksalt phase under pressure. The rocksalt to a simple hexagonal-type structure transition has been reported[13] for ZnSe in the pressure range between 50 and 60 GPa. To our knowledge no new experimental data were obtained for bulk CdSe in recent years, although a number of interesting experiments on size-dependent structural properties of CdSe nanocrystals were reported in Refs. 14 and 15 (transition from wurtzite to rocksalt).

Experimental findings as well as numerous possibilities for industrial applications initiated a number of theoretical studies of structural[16–21] and electronic[22–26] properties of II-VI compounds. The presence of very localized cation d electrons high in the valence band makes the computations for II-VI semiconductors rather demanding. A number of different techniques have been used to deal with this problem. The pseudopotential method with a high-energy-cutoff plane-wave basis set was employed in Refs. 16, 19, and 21, whereas linear combinations of Gaussian orbitals were used as a basis in Refs. 23 and 24. A full-potential linear-augmented-plane-wave calculation was reported in Ref. 20 and the Hartree-Fock linear-combination-of-atomic-orbitals method was used in Ref. 17. All these structural calculations were generally in good agreement with available experimental data, and with each other. However, they were limited to the ambient-pressure zinc-blende and wurtzite phases and the high-pressure rocksalt phase, with the exception of Ref. 21, where the cinnabar *Cmcm* phases along with other possible high-pressure phases of ZnTe were also considered.

In this paper we present *ab initio* pseudopotential calculations of the structural properties for four II-VI compounds: ZnSe, ZnTe, CdSe, and CdTe. For all these compounds we consider both the cinnabar and *Cmcm* high-pressure phases, and study the succession of phases under pressure. Cation d electrons in II-VI compounds have received considerable attention in the literature.[27–29] It was shown that relaxation of these states is important for both the structural[27] and electronic[19] properties of II-VI semiconductors. In the calculations presented in this paper, we treat the cation d electrons as part of the valence complex.

II. METHOD

The pseudopotential total-energy scheme[30] with a plane-wave basis set is used to find structural parameters and to

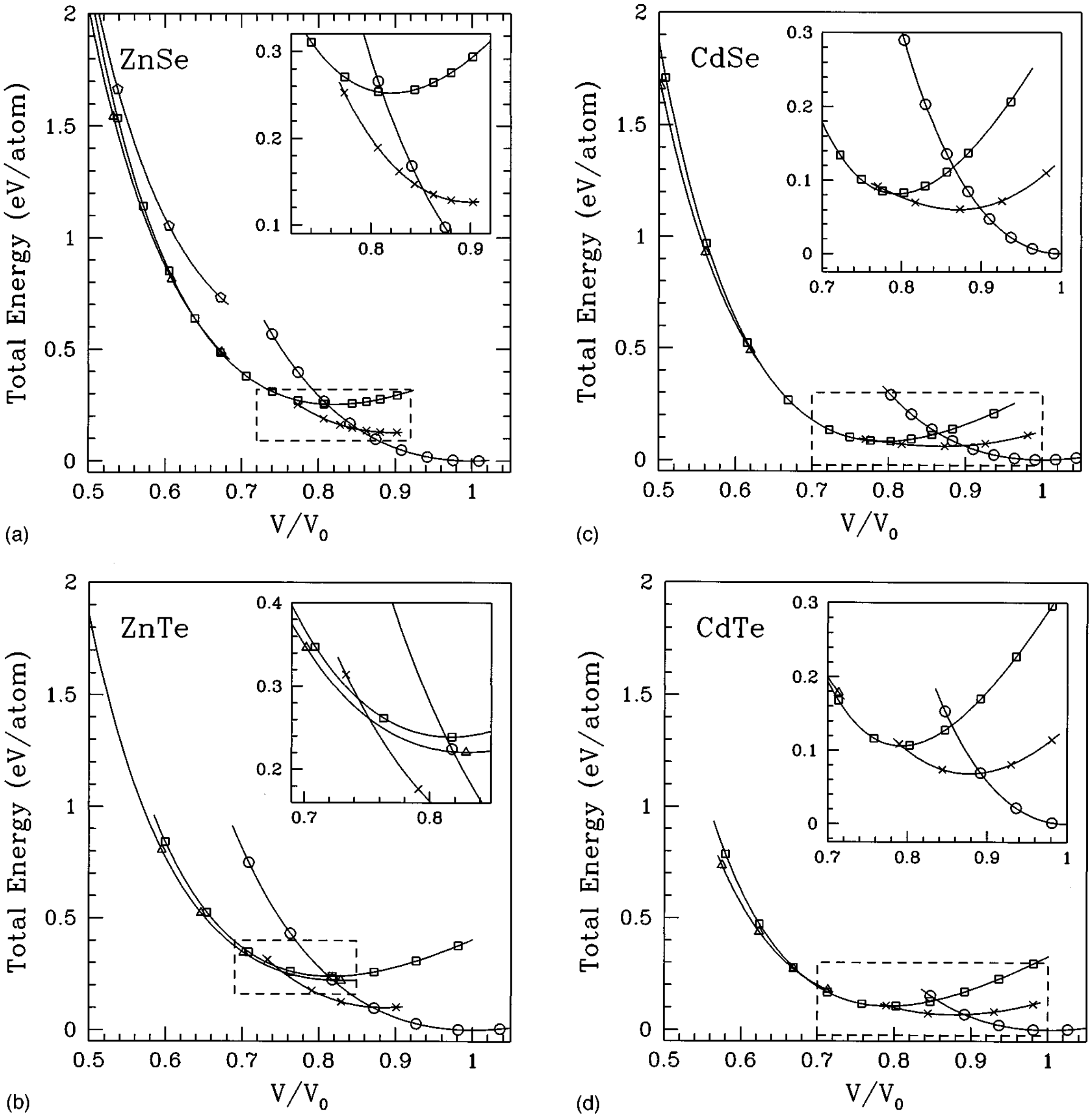

FIG. 1. Calculated total energy vs volume for the zinc-blende (circles), cinnabar (crosses), rocksalt (squares), and orthorhombic (triangles) phases of (a) ZnSe, (b) ZnTe, (c) CdSe, and (d) CdTe. For the ZnSe compound, the simple hexagonal (pentagons) phase is also shown. The curves are constructed using the Birch equation of state (Ref. 38). The blowup of the region indicated by the broken line rectangle is presented in the inset. V_0 is the calculated zero-pressure volume for the zinc-blende phase. The energy of the zinc-blende phase is arbitrary chosen to be zero at zero pressure.

compute total energies of different phases for these compounds. Our calculations are performed with Zn^{+12} and Cd^{+12} pseudopotentials generated using the method of Troullier and Martins.[31] The ionic pseudopotentials for Se and Te are constructed according to the Hamann-Schlüter-Chiang scheme.[32] To describe some of the influence of the Se and Te *d* electrons on the valence complex, partial core corrections for exchange and correlation[33] are included in the

TABLE I. Calculated and experimentally observed pressure ranges (in GPa) for four high-pressure phases of II-VI compounds. The symbol N/R is used to indicate high-pressure phases not found in the calculations, and N/O denotes phases not observed experimentally. The theoretical data for the CdTe compound are reported with the energy of the cinnabar phase shifted down as explained in the text.

	Zinc-blende		Cinnabar		Rocksalt		*Cmcm*	
	Theor.	Expt.	Theor.	Expt.	Theor.	Expt.	Theor.	Expt.
ZnSe	0–10.2	0–11.8 (Ref. 45)	10.2–13.4	N/O	13.4–36.5	11.8–48 (Ref. 45)	>36.5	N/O
ZnTe	0–5.9	0–9 (Ref. 11)	5.9–11.1	9–11 (Ref. 11)	N/R	N/O	>11.1	>11
CdSe	0–2.5	0–3 (Ref. 42)	N/R	N/O	2.5–29.0	>3	>29.0	
CdTe	0–2.5	0–3.5 (Ref. 40)	2.5–2.8	3.5–3.8 (Ref. 40)	2.8-12.0	3.8–10.1 (Ref. 12)	>12.0	>10.1

TABLE II. Calculated and experimentally observed change in specific volume at the transition for four II-VI compounds. The theoretical data for the CdTe compound are reported with the energy of the cinnabar phase shifted down as explained in the text.

ZnSe	theory	ZB → Cin (9.2%)	Cin → RS (7.7%)	RS → Orthor (1.0%)
	experiment	ZB → RS (15.4%) (Ref. 13)		RS → Orthor (N/O)
ZnTe	theory	ZB → Cin (1.1%)	Cin → Orthor (8.4%)	
	experiment	ZB → Cin (—)	Cin → Orthor (5.7%) (Ref. 11)	
CdSe	theory	ZB → RS (19.8%)		RS → Orthor (1.7%)
CdTe	theory	ZB → Cin (13.1%)	Cin → RS (7.5%)	RS → Orthor (1.8%)
	experiment	ZB→Cin (14.3%) (Ref. 40)	Cin→RS (3.7%) (Ref. 40)	RS→Orthor(<1%) (Ref. 12)

Se and Te pseudopotentials. This description of the anion *d* electrons is sufficient, since our structural parameters compare well with those of Ref. 21, where those states have been allowed to relax. All the pseudopotentials are generated with semirelativistic corrections. The Ceperley-Adler interpolation formula[34] for the exchange-correlation energy is used in our total-energy calculations.

We use a cutoff energy of 60 Ry for CdSe and CdTe, and a cutoff energy of 80 Ry for ZnSe and ZnTe. The larger cutoff energy required for the Zn compounds is a result of their generally smaller unit-cell volume. These cutoff energies guarantee convergence of less than 2 mRy (0.027 eV) per atom in the whole range of pressures considered. Our total energies do not include the contribution from the motion of the atoms, whereas the experiments are generally done at room temperature. However, the phonon contribution to the variation in the free energy of the different phases by their zero-point motion and their thermal excitation is estimated to be of the order of our local-density-approximation (LDA) error.

A quasi-Newton method[35] is used to simultaneously relax the internal coordinates and the lattice parameters of the cinnabar and orthorhombic phases under pressure.[36] This method uses the calculated Hellmann-Feynman forces and stresses[37] to minimize the enthalpy of the crystal H-$E+PV$ for a given pressure P. The minimization algorithm preserves the symmetry of the initial configuration. For the given structures, the lattice constant, bulk modulus, and transition pressures are obtained by fitting the energy versus volume curve to the Birch equation of state.[38]

III. RESULTS AND DISCUSSION

The results of our total-energy calculations for four II-VI compounds are presented in Fig. 1 and Table I. The total-energy dependence on volume for different phases is very similar for all four compounds considered. Since different phases are very close in energy in the regions of possible phase transitions (shown in the insets of Fig. 1), very small variations in the total energies may result in changes in the calculated high-pressure phase systematics. This makes reliable theoretical calculations of transition pressures very difficult, since small changes in total energy of the order of typical LDA error (~ 1 mRy/atom) not only change the transition pressures considerably, but also result in either disappearances or appearances of some phases in the calculated succession of high-pressure phases.

TABLE III. Calculated and experimental (Ref. 46) lattice constants and bulk moduli for the zinc-blende phases. The theoretical values are calculated using the Birch equation of state (Ref. 38).

Compound	a_{theor} (Å)	B_{theor} (GPa)	a_{expt}	B_{expt}
ZnSe	5.606	70.5	5.6676	64.7
ZnTe	6.013	54.7	6.089	52.8
CdSe	6.050	57.2	6.052	
CdTe	6.430	46.0	6.482	44.5

Our calculations agree with experimentally observed sequence of high-pressure phases for ZnTe (zinc blende → cinnabar → orthorhombic) and CdSe (zinc blende → rocksalt). For ZnSe the cinnabar phase is found to be stable in the narrow pressure range between 10 and 13 GPa, although, to our knowledge, there are no experimental data confirming the existence of the cinnabar phase for ZnSe. For CdTe our calculations do not reproduce the observed zinc-

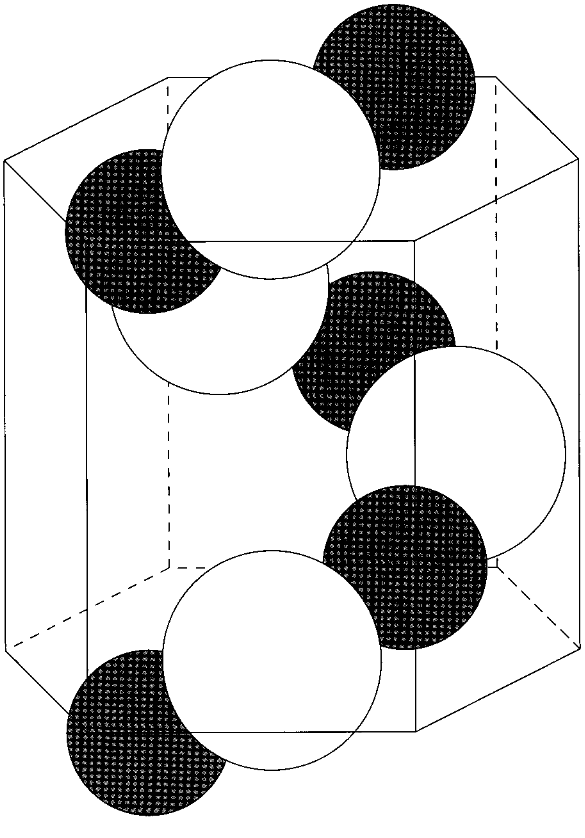

FIG. 2. A hexagonal unit cell of the cinnabar phase.

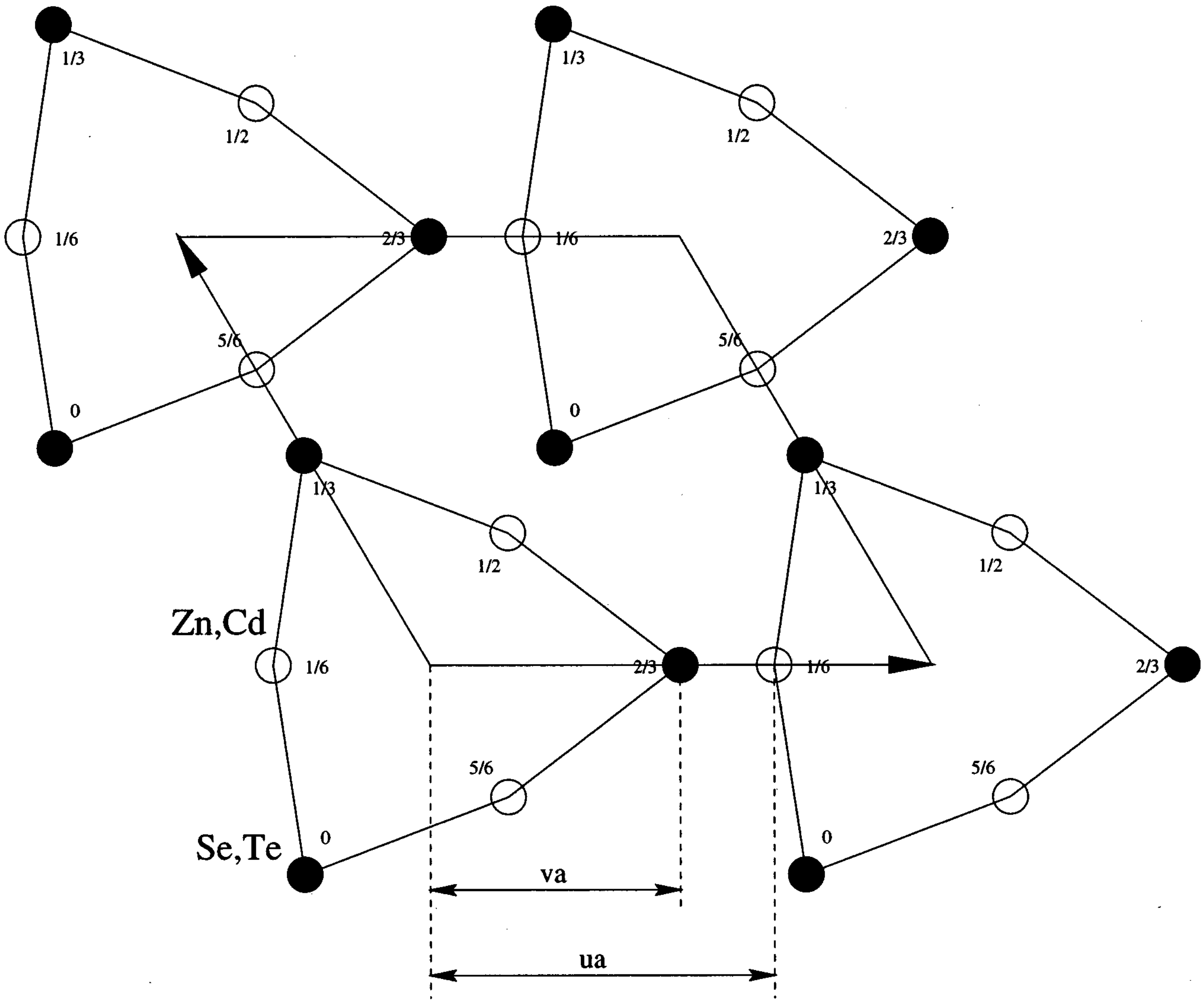

FIG. 3. The cinnabar structure shown in projection onto the *xy* plane. The *z* coordinate is given by each atom. The cations (anions) are represented by open (solid) circles.

blende to cinnabar phase transition, but if the total energy of the cinnabar phase is decreased by an amount smaller than the error of our calculations (0.4 mRy/atom), it becomes stable in a narrow pressure region around 2.6 GPa. Similarly, the cinnabar phase in the ZnSe compound disappears if its total energy is increased slightly.

It is also conceivable that the cinnabar phase in some of the II-VI compounds is metastable, and therefore is most likely to be observed as the pressure is decreased from the rocksalt phase. This in the case for silicon where the $R8$ and $BC8$ structures appear when slowly releasing the pressure on the high-pressure β-tin phase.[39] In the experiments reported in Refs. 40 and 41, we see that the cinnabar phase of CdTe is predominately observed in the downstoke runs. This could explain why we do not find it to be stable in our calculations at any pressure. However, since it is so close in energy, a transition to this phase will still be possible from the rocksalt phase if the transition to the zinc blende is prohibited. It would be interesting if careful experiments on the ZnSe and CdSe compounds could be done where the pressure is slowly decreased from the rocksalt phase to see if the cinnabar phase appears.

We predict the rocksalt to *Cmcm* structural phase transition for ZnSe at around 36 and 29 GPa for CdSe. For the ZnSe compounds, we also calculated the simple hexagonal phase which was reported in Ref. 13. According to our result, the *Cmcm* phase is always energetically preferable to the simple hexagonal structure. Table II shows the calculated and available experimental changes in specific volume at the transition for the four II-VI compounds considered. A general conclusion seems to stem from the calculations, the *Cmcm* phase is predicted to be present as a high-pressure phase for the II-VI compounds. In the following sections we will describe the results of our calculations for the different phases of II-VI compounds in more details.

A. Zinc-blende phase

We treat the zinc-blende phase as the ambient pressure phase for all the compounds considered. Although some of the compounds (e.g., CdSe) can also be found in the wurtzite phase at zero pressure, the total-energy difference between these two phases is extremely small and within the precision

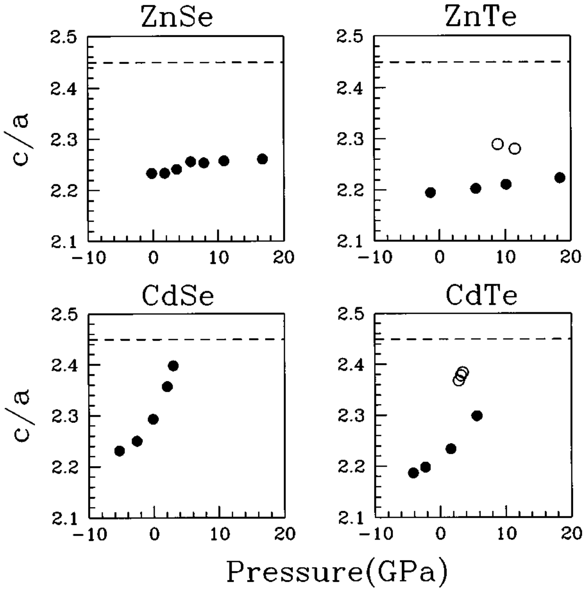

FIG. 4. c/a ratio as a function of pressure for the cinnabar phases of four II-VI compounds. The solid circles represent calculated values. The open circles represent available experimental data (Refs. 11 and 40). The broken line corresponds to the rocksalt phase value of c/a.

of LDA calculations.[19] We choose the zinc-blende phase since it has fewer atoms per unit cell, and is therefore computationally easier to treat.

The results of our calculations for the zinc-blende phase are summarized in Table III. The calculated values of both the lattice constant and the bulk modulus are in good agreement with the experimental data. Typically for LDA calculations, the equilibrium lattice constant is slightly underestimated (~1%), and as a result the bulk modulus is overestimated (~5%).

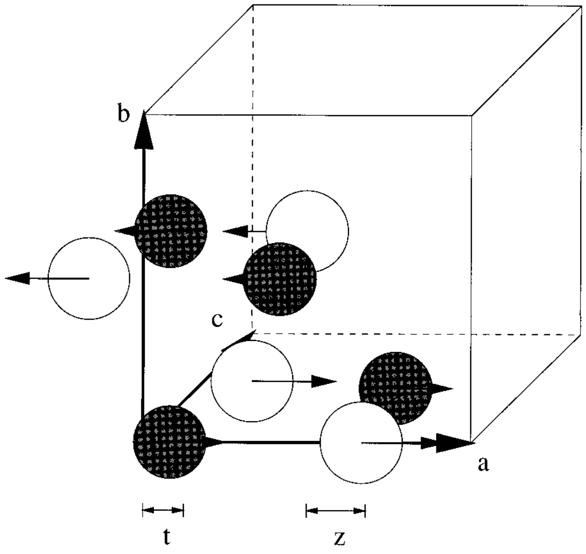

FIG. 6. The *Cmcm* phase as a deformation of the rocksalt structure. The arrows show how the atoms forming the basis of the cubic rocksalt unit cell are shifted in the *Cmcm* structure. The dimensionless parameters z and t give the relative displacements of the cations and anions from their position in the rocksalt structure.

B. Cinnabar phase

The cinnabar phase can be visualized as a hexagonal lattice of two concentric helices of anions and cations (Fig. 2). Lattice parameters a and c define the hexagonal lattice. Two

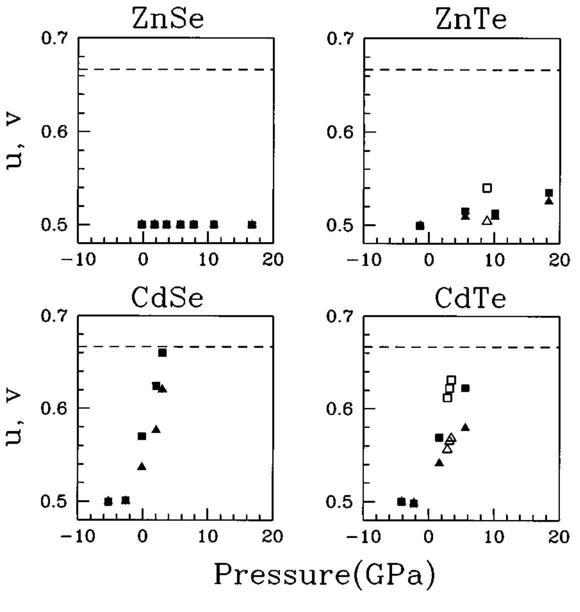

FIG. 5. Calculated dimensionless parameters u (solid squares) and v (solid triangles) as a function of pressure for the cinnabar phases of four II-VI compounds. The open triangles and squares represent available experimental data (Refs. 11 and 40). The broken line corresponds to the rocksalt phase value of u and v.

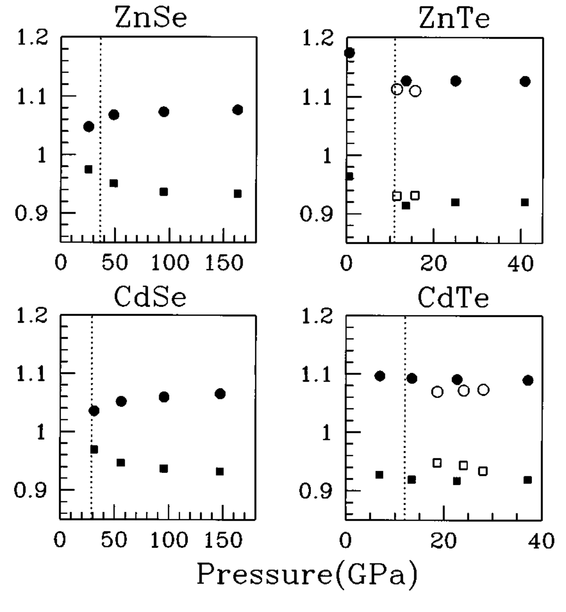

FIG. 7. Calculated b/a (solid circles) and c/a (solid squares) ratios as a function of pressure for the *Cmcm* phases of four II-VI compounds. The open circles and squares represent available experimental data (Refs. 11 and 12). The dotted lines correspond to the calculated transition pressure to the *Cmcm* phase.

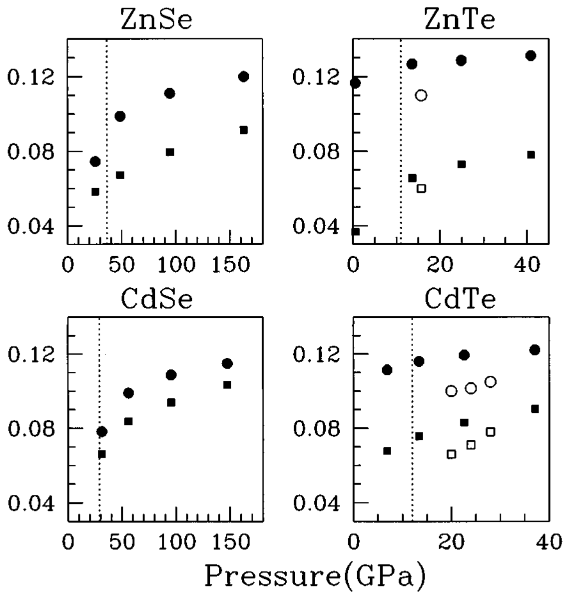

FIG. 8. Calculated dimensionless parameters z (solid squares) and t (solid circles) as a function of pressure for the $Cmcm$ phases of four II-VI compounds. The open squares and circles represent available experimental data (Refs. 11 and 12). The dotted lines correspond to the calculated transition pressure to the $Cmcm$ phase.

internal lattice parameters u and v determine the helix radii for cations and anions, respectively (Fig. 3).

For $u=v=\frac{2}{3}$ and $c/a=\sqrt{6}$, the cinnabar phase coincides with the rocksalt structure. We use this fact to calculate total-energy convergence corrections for the cinnabar phase by adding to the calculated total energy of the cinnabar phase the difference between the rocksalt phase total energy from the fully converged calculation using the conventional unit cell and the total energy of the rocksalt phase calculated using the unit cell for the cinnabar structure.

The values of lattice parameters as a function of pressure calculated using the total-energy minimization procedure and available experimental data are presented in Figs. 4 and 5. Both of these figures show that the pressure dependence of the lattice parameters for compounds with the same cation is very similar. For ZnSe and ZnTe both c/a ratios and the internal parameters u and v change slowly with pressure, whereas for CdSe and CdTe all the parameters quickly approach the rocksalt phase values as pressure increases.

The calculated values of the c/a ratio underestimate the observed values by about 3% for both ZnTe and CdTe. Qualitatively, the calculated pressure dependence is in agreement with the observed increase of c/a in the narrow pressure range around 3 GPa for CdTe. The calculations do not reproduce slight decrease of c/a ratio with pressure observed for ZnTe.

Our results for u and v underestimate the difference between u and v, but otherwise are in generally good agreement with available experimental data. For all the compounds considered the calculated low-pressure values for both u and v are 0.5. For these values of the internal parameters the forces on the atoms are zero by symmetry. Our calculations show that there is always a local minimum of the total energy for $u=v=0.5$. Another local minimum splits off and moves (in parameter space) toward the minimum corresponding to the rocksalt phase as pressure increases, except for ZnSe, where we find u and v equal to 0.5 over the whole range of pressure considered.

C. *Cmcm* phase

The $Cmcm$ phase can be considered as a deformation of the rocksalt structure to an orthorhombic unit cell. The basis atoms of the unit cell are also displaced with respect to their positions in the rocksalt phase. For a given (001) plane of atoms, the cations and anions are shifted along the same (100) direction but by different amounts. The atoms in the adjacent planes are moved in opposite direction. Figure 6 shows a unit cell of the $Cmcm$ structure, with the arrows representing the displacements of atoms from their positions in the rocksalt structure.

The unit cell of the $Cmcm$ structure has five parameters a, b/a, and c/a, and two dimensionless internal parameters z and t describing the displacements of cations and anions, respectively. In our calculations the total-energy is minimized with respect to all these parameters for a given pressure. For $b/a=c/a=1$ and $z=t=0$ the $Cmcm$ phase coincides with the undeformed rocksalt structure.

Calculated values of the lattice parameters for the $Cmcm$ phases using the total-energy minimization procedure together with available experimental data are shown in Figs. 7 and 8 for four II-VI compounds. From these figures, we can conclude that our calculations slightly overestimate the degree of deformation from the rocksalt phase for both b/a and c/a ratios and internal parameters z and t, but reproduce the pressure dependence of the lattice parameters correctly. Interestingly, for the $Cmcm$ phase the pressure dependence of the lattice parameters is closer for the compounds with the same anion (we recall here that for the cinnabar phase the pressure dependence was mostly determined by the cation). The lattice parameters of the selenides exhibit stronger pressure dependence than those of the tellurides. Also, the $Cmcm$ phase for the selenides approaches the rocksalt structure faster as pressure decreases.

IV. CONCLUSION

In this paper we considered high-pressure properties of four II-VI compounds: ZnSe, ZnTe, CdSe, and CdTe. Highly localized cation d electrons treated as valence electrons and necessary minimization of the total energy with respect to lattice parameters for the cinnabar and $Cmcm$ high-pressure phases make this study computationally challenging.

We found that for all compounds considered, three possible high pressure phases—cinnabar, rocksalt, and $Cmcm$—are very close in energy. This makes accurate estimation of the transition pressures difficult since small changes in the total energy of the order of the typical errors of the LDA approximation may result in different calculated successions of high-pressure phases. Our calculations reproduce experimentally observed structural phase transitions for ZnTe and CdSe. According to our calculations the experimentally observed cinnabar phase is not realized as a high-pressure phase of CdTe, although small changes in total energy may result in its appearance in the region close to the experimentally observed pressure range. Our calculations also indicate the possibility of the existence of the cinnabar phase for ZnSe which has not been observed so far. We also predict the existence of the $Cmcm$ high-pressure phase for ZnSe and CdSe. The pressure dependence of the internal parameters in the cinnabar structure is controlled by the cation in the compound, whereas in the $Cmcm$ phase is the anion. We point out that the high-pressure phase $Cmcm$ might not be retricted to II-VI compounds since there is some evidence experimentally that the structure of GaAs-II is $Cmcm$.[43] Theoretical calculations[44] of the $Cmcm$ structure for this compound agree with the available experimental data and seem to be a quite general feature of the high-pressure phases of II-VI and III-V compounds.

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