

Cinnabar and SC16 high-pressure phases of ZnSe: An *ab initio* study

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Total-energy calculations of zinc selenide, done at four different phases under conditions of hydrostatic pressure using the all-electron augmented plane-waves method, reveal the stability interval of two intermediate phases, cinnabar and SC16, between the ambient-pressure zinc-blende and high-pressure rocksalt ones. The results of previous calculations are critically discussed and the importance of the full relaxation of all structure parameters demonstrated. Our simulation sheds light on the fact that the cinnabar phase, apparently of higher enthalpy than the (not yet detected) SC16 one, seems to have been definitely identified in high-pressure experiments in the downstroke only.

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I. INTRODUCTION

The sequence of phase transitions under pressure in semiconductors which are, under ambient conditions, in the zinc-blende (ZB) (B3) structure, has common features over many I-VII, II-VI, and III-V systems, yet the individual variations are rich—see, e.g., Mujica *et al.*¹ for a review. A rather common observation is that, from about 20 GPa on, the rocksalt (B1) structure emerges as the stable one. The transition from B3 to B1 (Refs. 2 and 3) is not straightforward and was subject to several discussions—see Refs. 4 and 5, and references therein. Common candidates for intermediate phases between B3 and B1 are the hexagonal cinnabar (B9 in the *Strukturbericht*) and cubic SC16. The wurtzite phase, whenever detected/discussed, turns out to be almost indistinguishable from the B3, on the energy scale of the other above-mentioned transitions. Whereas a good number of works has been dedicated to further high-pressure transitions from the B1 phase,^{1,6} the B3-B1 intermediary regime is rich in ambiguities, due to difficulties of both experimental characterization and *ab initio* simulations. The reason for difficulties in calculation is that intermediary phases possess relatively low symmetry and large unit-cell size, and need to be carefully relaxed.

In the present work, we discuss only one semiconductor, ZnSe, for which however a bunch of controversial results exists, in what regards its behavior under pressure. We discuss our results in the broad context of information available on a number of related compounds, from both experiment and theory.

For a long time it was thought that the existence of a low-enthalpy cinnabar-type phase at low and moderately high pressures was a characteristic of mercury chalcogenides exclusively—see, e.g., Ref. 7, and references therein. However, the last decade of the last century has seen the discovery of cinnabar-type phases in ZnTe,⁸ CdTe,⁹ and GaAs.¹⁰ Lee *et al.*¹¹ confirmed the stability of the cinnabar phase of ZnTe, using a first-principles pseudopotential plane-wave (PP-PW) technique, whereas that of CdTe has been confirmed by the full-potential linear muffin-tin (MT) orbital calculations of Ahuja *et al.*¹² However, Kelsey *et al.*¹³ and Mujica *et al.*¹⁴ from their respective PP-PW calculations con-

cluded that GaAs and GaP (Ref. 14) might have cinnabar as a metastable phase only.

As concerns the SC16 structure, it has been tried in many early theoretical calculations and found by Crain *et al.*¹⁵ to be a stable high-pressure phase in GaAs, AlSb, and InAs. This was followed by calculations by Mujica *et al.* who showed SC16 to be an instable phase in Al-based^{16–18} and In-based^{18,19} semiconductors and moreover in GaN,¹⁸ but stable in GaAs (Ref. 16) and GaP.¹⁹ Interestingly, it has been argued that the route to BC8, which is the monoatomic analog to SC16, in, say, silicon via the so-called R8 structure²⁰ is such that its “generalization” over binary semiconductors would involve the formation of “wrong” bonds between the like atomic species, and thus is probably forbidden. Nevertheless, the SC16 phase has been observed experimentally in GaAs (Ref. 21) at high pressure. It was obtained by heating the high-pressure *Cmcm* phase to above ~ 400 K at ~ 14 GPa and cooling back to room temperature.²¹ Later on,²² SC16 has been detected as an intermediate phase between zinc-blende and the high-pressure *Cmcm*, on both increase (from about 15 GPa onward) and decrease (from about 18 GPa downward) of pressure in GaAs heated to 400°. Moreover, this structure has been detected in some I-VII compounds, namely, CuCl and CuBr.²³

Côté *et al.*²⁴ have studied the stability of the cinnabar and *Cmcm* phases in ZnSe, ZnTe, CdSe, and CdTe, using a PP-PW method, and predicted a stable cinnabar phase to emerge in ZnSe, before reaching the B1 structure. They reported the pressures “window” for the stability of the cinnabar phase to be 3.2 GPa. Qteish and Muñoz²⁵ carried out another PP-PW calculation for ZnSe, making use of the internal parameters of the cinnabar structure determined by Côté *et al.*,²⁴ which are $u=v=0.5$. Surprisingly, they found the stable phase to be SC16 while the cinnabar being not able to win in any pressure range over the direct B3 to B1 transition. This is in an apparent disagreement with Côté *et al.*²⁴ From the side of experiment, we note that Pellicer-Porres *et al.*²⁶ performed an energy-dispersive x-ray diffraction on ZnSe at room temperature, and were able to obtain a cinnabar phase similar to that observed in GaAs (Ref. 10) and ZnTe.^{27,28} The cinnabar phase was detected within a very small pressure interval 10.4–9.9 GPa while slowly relieving the pressure from the rocksalt phase.

Quite recently, a detection of the cinnabar phase was implied by Ovsyannikov *et al.*²⁹ from their resistivity study of ZnSe (among other semiconductors) under varying pressure. While not accompanied by crystallographic characterization, their identification of an “additional phase” ruled out its possibility to be SC16, on the basis of presumably predicted semimetallicity of the latter.³⁰

In this work we try to clarify the argument about the stability or instability of the cinnabar and SC16 as intermediate phases between the zinc-blende and rocksalt in ZnSe, on the basis of new all-electron total-energy calculations. We apply the full-potential augmented plane-wave (APW) method with local orbitals (FP-APW+lo). We perform full structural optimization in the phases which include internal parameters, discuss the details of phase transformations and, hopefully, shed some light on the apparent controversies between experiment and theory.

II. COMPUTATIONAL DETAILS

The calculations reported in this work are based on the density-functional theory.^{31,32} The total energies (and forces, inasmuch they are needed for optimization of internal parameters) were calculated using the FP-APW+lo method,^{33,34} implemented in the WIEN2K code.³⁵ The method uses the “MT geometry,” separating the space into atom-centered MT spheres and the interstitial. The exchange-correlation (XC) energy of electrons is described both in the local-density approximation (LDA) and in the generalized gradient approximation (GGA) using the functional parametrization of Perdew-Burke-Ernzerhof.³⁶ After necessary tests (to control the stability of energy differences between phases of our interest), we accepted the following values for crucial parameters of calculation: $R_{\text{MT}}K_{\text{max}}=9$, with R_{MT} denoting the smallest MT radius and K_{max} the magnitude of the largest reciprocal-space vector in the plane-wave expansion. The MT radii used in the calculations were 1.3 a.u. for Zn and 1.65 a.u. for Se—i.e., necessarily small to allow the scan, without overlapping the MT spheres, of the range of volumes including those corresponding to quite high compression. The initial step of the radial mesh, a crucial parameter for the accuracy of calculated forces, was set at 5×10^{-5} bohr, acceptedly small enough for medium-weight atoms. The angular expansion of wave functions within the spheres was confined to $l_{\text{max}}=10$. The charge density in the interstitial region was Fourier expanded up to $G_{\text{max}}=20$ Ry^{1/2}. A mesh of 47, 58, 45, and 47 special \mathbf{k} points for ZB, cinnabar, SC16, and RS, respectively, were taken in the irreducible wedge of the Brillouin zone for the total-energy calculation. We emphasize that convergence tests for the plane-wave cutoff and the number of \mathbf{k} points were essential to assure reliable total-energy differences. The variation in c/a parameter (in the cinnabar phase) was done “by hand” for each given volume, whereas the internal coordinates (for each given volume in SC16; for each volume and c/a in cinnabar) were optimized using the MINI script integrated into the WIEN2K package, which takes into account the forces acting on atoms.^{33,37–39} The space group was imposed and kept fixed in WIEN2K throughout the relaxation of each particular system. In this

way, a spontaneous lowering of symmetry from a high-symmetry phase was not possible, but we will see that, other way around, the cinnabar phase at certain conditions finds a way to spontaneously arrange itself in a high-symmetry phase.

III. RESULTS AND DISCUSSION

A. Preliminary considerations and total-energy results

Two of our considered phases, cinnabar and SC16, are characterized by internal coordinates of atoms which may vary under pressure. The hexagonal cinnabar phase (B9), moreover, allows a variation in the c/a ratio. The space group of this phase is either $P3_221$ (Nr 154) or $P3_121$ (Nr 152), the two being enantiomorphic. The Wyckoff positions (3a), say for cation and (3b), say for anion are characterized by u and v internal coordinates, correspondingly. $u=v=\frac{1}{3}$ or $\frac{2}{3}$, with $c/a=\sqrt{6}$, recovers the B1 phase. A continuous transformation exists also between the cinnabar and the B1 phase. The relation between the three has been described by Sowa.^{4,5} What is of importance for us in the present context is that the B3 phase can undergo, at least hypothetically, a transformation into B1 on two different ways, the one passing by B9 and the other not.

The cubic phase SC16 has the space group $Pa3$ (Nr 205), in which both the cations and the anions are in the (8c) positions, each one characterized by a single internal coordinate. While trying the effect of pressure and varying the volume, we performed the relaxation of all the free parameters involved— c/a , $u(\text{Zn})$, and $v(\text{Se})$ for cinnabar, and the cation and anion internal coordinates in the SC16.

The variation in the total energy with volume for all considered structures is presented in Fig. 1. As it is generally known that LDA and GGA do not always arrive at (even qualitatively) consistent conclusions, we compare the results obtained with both these approximations for the XC. The most marked difference is, as could be expected, in smaller equilibrium volume per atom (145.6 bohr³, for zinc blende) in LDA than in GGA (160.8 bohr³), which both values bracket the experimental value (153.8 bohr³), and the resulting overall shift of the whole system of energy-volume curves. The differences in the curves’ shape are noticeable (in favor of generally “softer” GGA prediction) but not excessive: the bulk moduli of rocksalt/cinnabar phases (89/79 GPa in LDA, 68/61 GPa in GGA) stay markedly higher than in zinc blende/SC16 (71/69 GPa in LDA, 55/48 GPa in GGA). With both XC schemes, the SC16 phase is slightly but definitely lower in energy than the cinnabar one, notably in the region of interest between the stability domains of zinc-blende and rocksalt phases. The difference is that, according to the GGA calculation, the two intermediate phases—cinnabar and SC16—protrude more downward between the B1 and B3 than in the LDA case. When transposed into the Gibbs free energy vs pressure diagram (Fig. 2), this yields a small stability region of *both* SC16 and cinnabar phases underway between zinc blende to rocksalt after the GGA calculation, but the presumed stability of SC16 only, and not of cinnabar, according to LDA.

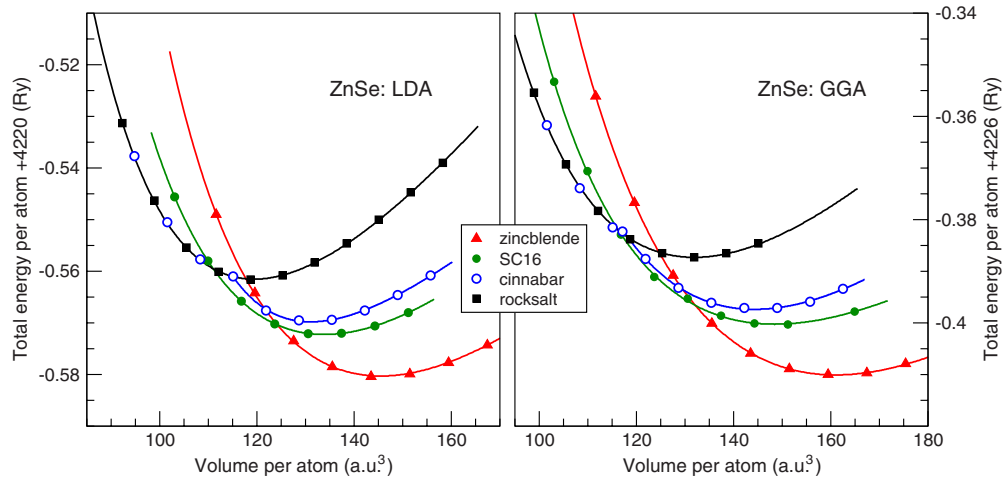


FIG. 1. (Color online) Total energy vs volume for ZnSe in different phases, as calculated within the LDA (left panel) and GGA (right panel). Continuous lines show fit to the Murnaghan equation of state for each phase. In cinnabar and SC16 phases, the internal coordinates have been relaxed in each point.

The spread of LDA/GGA prediction, in view of how they often “bracket” the reality, gives a kind of “tolerance margin” for our and other *ab initio* results. It can be implied, however, on the basis of some experimental evidence addressed below, that the GGA provides somehow more adequate description.

Let us now look at earlier *ab initio* calculations in this context. In what concerns the stability of the SC16 phase, Qteish and Muñoz²⁵ reported that it takes over B3 starting from 9.2 GPa and has a stability range of $\Delta P=7.2$ GPa; in our LDA calculation the pressure range of SC16 is much more narrow, 2.5 GPa, starting from 10.8 GPa. Remarkably, our present GGA prediction of the SC16 stability is not that different—it goes over $\Delta P=4.3$ GPa, setting on at 11.8 GPa. So at least qualitative agreement should be pointed out between different calculation schemes in what concerns the presumed placement of this phase on the pressure-driven phase diagram.

The issue of stability of the cinnabar phase is more subtle. The LDA calculation by Côté *et al.*,²⁴ predicting a stability region for the cinnabar phase between B3 and B1, is at variance with LDA calculations by Qteish and Muñoz²⁵ as well as with our present one (according to which both the cinnabar

remains thermodynamically “hidden” in the zinc-blende to rocksalt transition), and hence seems fortuitous. An emergence of cinnabar as a metastable phase seems to be a qualitatively new result delivered with the GGA. Interestingly, our predicted region of metastability for the cinnabar phase, albeit narrow ($\Delta P=0.55$ GPa, between 13.35 and 13.9 GPa), falls in remarkable agreement with experimental results (0.5 GPa) of Pellicer-Porres *et al.*²⁶ Turning to experiment, we note that the data are not decisive; at least, to best of our knowledge, no experimental study that would combine the effects of high pressure and high temperature, in analogy with the above case of GaAs,¹⁰ has yet been done.

Pellicer-Porres *et al.*²⁶ performed a careful search, under pressure at room temperature, for an intermediate phase of Te-doped ZnSe between the B3 and B1, but none was found in the upstroke. This is at variance with the results of Kobayashi⁴⁰ who claim the existence of a new phase between the zinc blende and rocksalt, observed in the upstroke, however without giving any structural characterization. Moreover, the “additional phase” referred to by Ovsyannikov *et al.*²⁹ as cinnabar, albeit without structural characterization, appears on both upstroke and downstroke, from about 14 GPa onwards and 9 GPa downwards, correspondingly, the existency range in each case being (quite smeared) around 4 GPa.

In the downstroke, Pellicer-Porres *et al.*²⁶ managed to obtain the diffraction pattern of the new high-pressure phase, best pronounced in the spectra of samples with the highest Te content, ZnSe_{0.8}Te_{0.2}. The observed existence²⁶ of this phase is from 10.4 down to 9.9 GPa. The analysis of the diffraction pattern revealed the intermediate phase to be of hexagonal symmetry without further elaborating. By analogy with ZnTe,^{27,28} however, a suggestion has been made about the phase in question being cinnabar. Pellicer-Porres *et al.*²⁶ stressed that, in the composition range of Zn(Se,Te) alloys studied, the cinnabar range of existence diminishes as the Te content is reduced.

Assuming this hypothesis, we are in a need to explain two peculiarities: (i) why the cinnabar phase appears in the downstroke more pronouncedly than in the upstroke, and (ii)

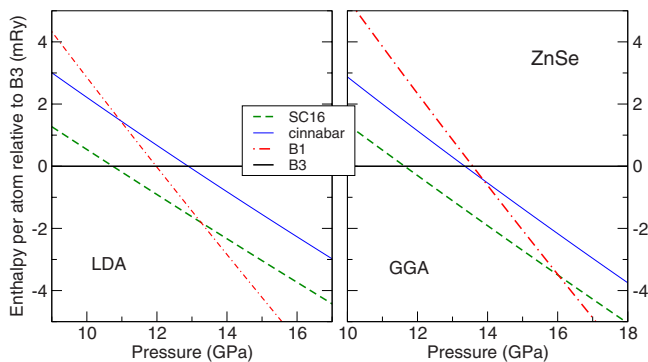


FIG. 2. (Color online) Static enthalpy per atom in different phases of ZnSe, relative to the B3 phase, as calculated with the LDA (left panel) and GGA (right panel).

why does the computationally favorable, according to all calculations, SC16 phase escape experimental detection. Our opinion on the former is that the B3-B1 conversion might not be necessarily reversible. As mentioned above, the B3 structure might be driven to B1, namely, by a nontrivial twist in each xy plane, accompanied by slight opposite z displacements of consecutive atomic planes (see Ref. 4 for details). This scenario roughly maintains the coordination of each atom, until suddenly each one gets six nearest neighbors of the opposite kind, at the place of four. To our knowledge, no experimental evidence of such transformation has yet been reported. Important is that this transformation does *not* pass via the cinnabar structure. At the same time, a *different* structural transformations exist which relate rocksalt structure to cinnabar and then cinnabar to zinc blende. In other words, the three phases B3, B9, and B1 are connected by a “triangular” path (which is moreover almost “equilateral,” judging by average atom displacements in each transformation). Our assumption is that for whatever reason, which might be clarified from modeling the kinetics of the processes, the B3 to B1 transformation (in the upstroke) chooses the direct way, whereas the back transformation (in the downstroke) passes, at least in part of the sample, via the cinnabar.

The second peculiarity, that of experimental absence (at least in room-temperature measurements) of computationally predicted SC16 phase could be so understood that the formation of SC16 is kinetically hindered, presumably due to high-energy barriers.¹⁵ As was suggested in Refs. 15, SC16 may be formed under conditions of high pressure and temperature and could then persist as a metastable state to ambient pressure in analogy to the case of SC16-GaAs,²¹ where SC16 phase appears upon combining the role of high pressure and temperature.

We emphasize that our calculations, as many of those done before, do only probe the zero-temperature energy relations between different phases, whereas molecular dynamics or other calculations involving high temperatures might be useful to shed the light on the mechanisms of how barriers between different phases⁴¹ are overcome.

We turn now to the discussion of how do lattice parameters change with pressure, according to our calculations. Apart from the values of pressure at which the phase transition takes place, the trends are almost the same in LDA and GGA calculations, therefore only the latter ones are covered.

B. Cinnabar structure

We specify for the following that the cinnabar structure is described by the $P3_121$ space group, and remind that we assume Zn in the $(3a)$ positions with internal coordinate u and Se in the $(3b)$ with internal coordinate v . A schematic view of nearest neighborhood to cation and anion sites, for realistic (i.e., between $\frac{1}{3}$ and $\frac{1}{2}$) but exaggeratedly different u and v values, is shown in Fig. 3. The “genuine” internal coordinates, as optimized from total-energy calculations for a range of pressures, are depicted in Fig. 4, and the c , a parameters (along with their ratio) in Fig. 5. At low pressures, c/a increases markedly overlinearly that contests the validity of previous calculations²⁵ which found c/a to change sublin-

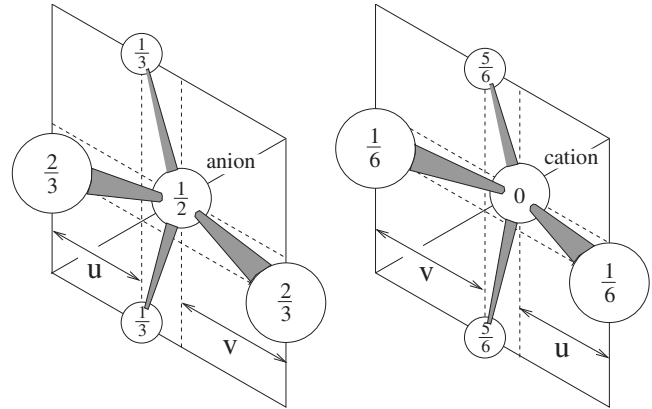


FIG. 3. Scheme of distorted tetrahedral coordinations around anion and cation sites in the cinnabar structure, in the projection onto the (x,y) plane. Numbers in the circles indicate z coordinates of corresponding atoms.

early throughout the cinnabar phase. Eventually at 18 GPa it jumps to $\sqrt{6}$ while u and v set to $\frac{1}{3}$, the values corresponding to the B1 phase. Apparently at this jump the c parameter grows with pressure (see Fig. 5, upper panel). Côté *et al.*²⁴ computed c/a to increase smoothly without exhibiting any discontinuity during the whole range of pressure, apparently due to the fact that they fix u and v to constants throughout the pressure range, thus preventing a transition into the B1 phase.

We note that ZnSe remains semiconducting in the cinnabar phase, until becoming a metal upon a transition into B1. The band gap nearly logarithmically increases with pressure (as was studied over many zinc-blende binary semiconductors by Wei and Zunger⁴²), from 0.5 eV at zero pressure to 1.25 eV at 15 GPa. We remind that our calculation scheme involved a straightforward GGA functional, without special provisions to increase, or otherwise tune, the band gap. The electronic structure of cinnabar ZnSe under pressure is shown in Fig. 6. The LDA calculation, done at the compa-

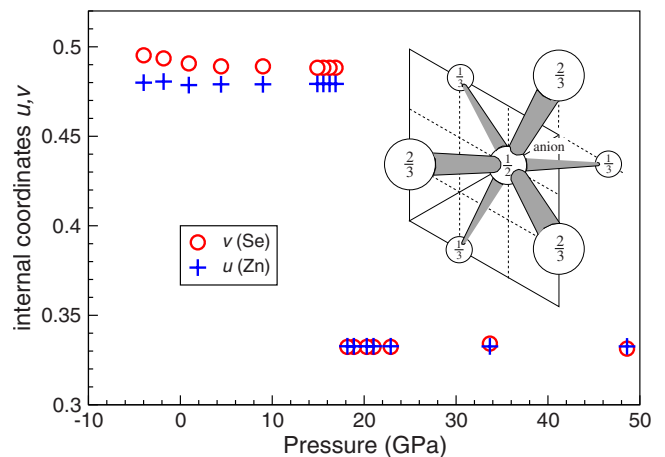


FIG. 4. (Color online) Internal coordinates in the cinnabar phase of ZnSe as function of pressure. Note the collapse into the rocksalt phase at 18 GPa. The crystal structure (around an anion site, as in the left panel of Fig. 3) corresponding to this situation is shown in the inset.

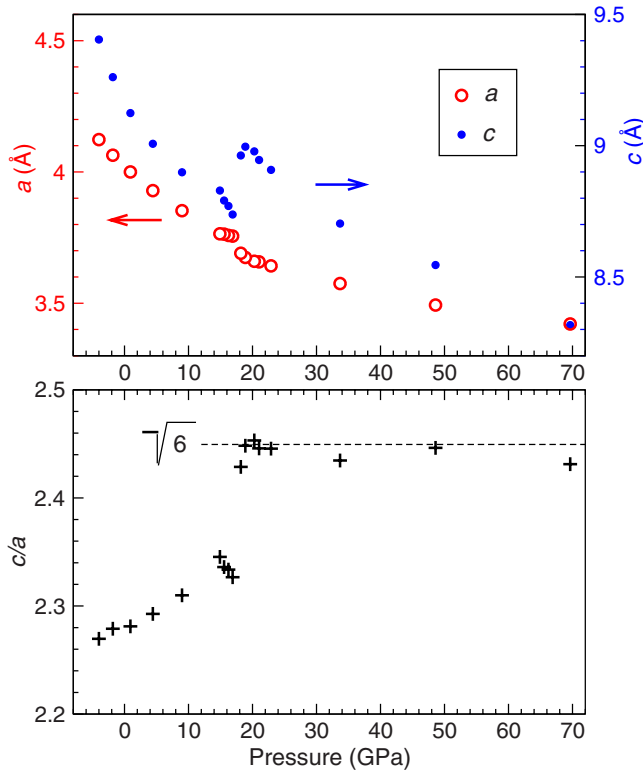


FIG. 5. (Color online) Variation in a , c lattice parameters in the cinnabar phase of ZnSe as function of pressure. The ideal $c/a = \sqrt{6}$ value indicated is for the rocksalt structure represented as hexagonal one.

erable volume, yields a very similar electronic structure: the Se $4s$ and Zn $3d$ bands shift upwards by 0.35 and 0.18 eV, correspondingly, and the band gap squeezes by one third, whereas the band dispersions remain indistinguishable.

It is obvious from Fig. 3 that the four cation-anion bond lengths split into two distinct, for $u \neq v$, pairs. At 13.35 GPa these are two of 2.416 Å and two of 2.384 Å. This can be compared with four bonds lengths of 2.356 Å in ZnSe-zinc blende at the same pressure, indicating a certain relieve of

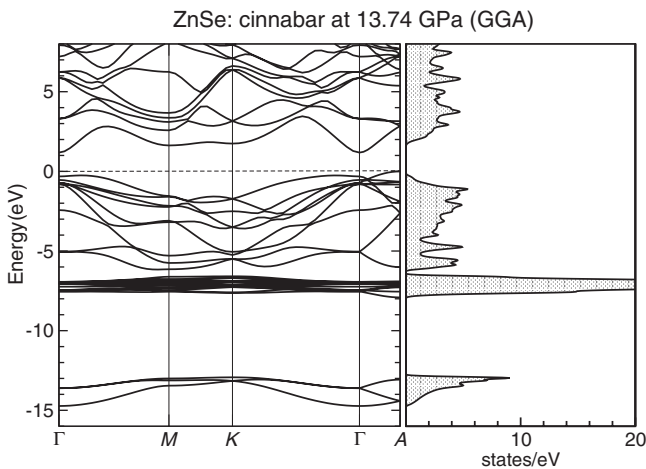


FIG. 6. Band structure and total density of states as calculated in the cinnabar phase of ZnSe within the GGA at the pressure value corresponding to its presumed stability.

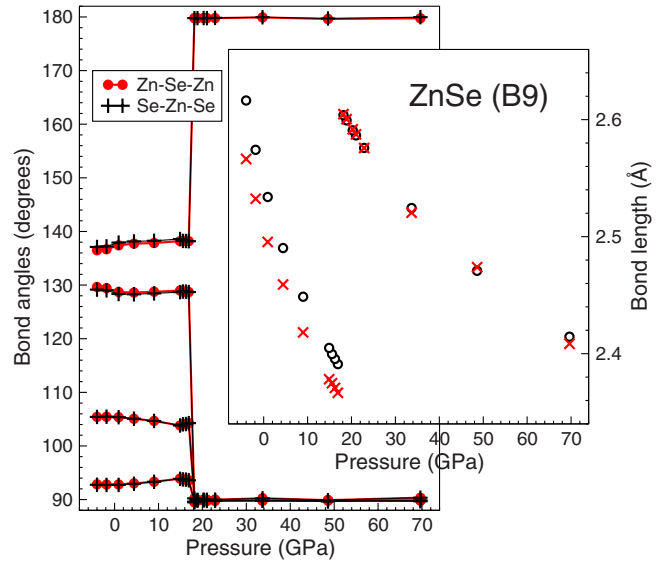


FIG. 7. (Color online) Bond lengths and bond angles as calculated under different pressures in the cinnabar structure of ZnSe. See text for details.

strain on escaping from the zinc-blende geometry. On the other end of our calculated “cinnabar window” (see Fig. 2), at 13.90 GPa, the bond lengths in ZnSe-cinnabar are two at 2.412 Å and two at 2.384 Å, to be compared to six bonds of 2.561 Å in ZnSe-rocksalt at the same pressure—again a relieve of stress at the expense of acquiring a higher coordination.

The six bond angles within a given twisted tetrahedron of the cinnabar structure (Fig. 3) split as 2+2+1+1, whereby Zn-Se-Zn and Se-Zn-Se angles are (slightly⁴³) different. Figure 7 shows variation in bond angles and bond lengths with pressure. Due to a small but noticeable difference between u and v (see Fig. 4), the bond lengths remain split by about 0.04 Å throughout the range of pressures from zero to the collapse of the cinnabar phase (at 18 GPa), experiencing underway a gradual contraction by ~ 0.2 Å. On collapse into the B1 structure, the bond lengths become equal and roughly recover their initial (larger) magnitude at zero pressure, as the structure packing becomes more dense. On further increase in pressure, the bond lengths decrease with pressure at a smaller slope than in the cinnabar phase, preserving the constance of bond angles (90° and 180°).

Each of four inequivalent bond angles undergoes a smooth yet nontrivial variation within about 2° throughout the interval of pressures before the collapse. The doublet angles are the lowest ones, close to 94° and 104° . On the collapse to B1, they drop to 90° , followed by the smallest ($\sim 128^\circ$) of two singlet angles. The largest bond angle ($\sim 138^\circ$), on the collapse, opens to 180° . Simultaneously, two previously more distant atoms (from the adjacent unit cells) approach the atom in the middle of a twisted tetrahedron, completing a neighborhood of a given atom to an octahedron—see inset in Fig. 4.

These variations in bond lengths and angles can be expressed in terms of four independent parameters— a , c , u , and v —and we emphasize that their combined adjustment is essential to allow the structure to gradually accommodate at

high pressure. It is seen from Fig. 4 that, as the variation in u , v under pressure is not large (prior to the collapse into B1), it is, at least, different for Zn and Se. The internal parameters describing both Zn and Se positions remain, at low pressures, close to $\frac{1}{2}$. Even if this value is not set by symmetry, it was used as fixed in some previous calculations, irrespective of pressure.^{24,25} We think that intentionally imposed constraints, or insufficient precision, in some earlier calculations were responsible for inaccurate results.

Coté *et al.*²⁴ reported their u and v to yield the energy minimum at $u=v=0.5$ throughout the whole applied pressure range, which implies that the pseudopotential method underestimated the difference between the anionic and cationic free parameters. Pellicer-Porres *et al.*²⁶ simulated the diffraction pattern corresponding to their observed (presumably cinnabar) structure by accepting $u=v=0.5$, that gave a qualitative agreement with the experimental diffraction intensities. In an alternative try, they²⁶ assumed the evolution of nearest-neighbor distances in ZnSe throughout the phase transitions to be like in HgTe (Ref. 44) and CdTe,⁴⁵ i.e., almost continuously on both B3-B9 and B9-B1 transitions. This demanded the internal parameters to be $u=0.63$ and $v=0.55$ [to compare with $u\sim 0.64$ and $v\sim 0.56$ for CdTe and HgTe (Refs. 44 and 45)]. Setting these values in the diffraction pattern simulation has not provided intensities which would agree with the experimental spectra.

Pellicer-Porres *et al.*²⁶ concluded therefore that their presumably cinnabar structure of ZnSe must be close to that associated with GaAs (Ref. 10) and ZnTe,^{27,28} i.e., having both internal parameters close to 0.5. The difference from the other situation tested is not simply numerical, because the two inspected distinct possibilities to arrange (u, v) give rise either to “2 close+4 distant,” or to “4 close+2 distant” neighbors coordinations.^{45,46} The review by Mujica *et al.*¹ well explains the varieties of cinnabar phases.

The result by Pellicer-Porres *et al.*²⁶ concerning the lattice parameters of their hexagonal phase is $a=3.829$ Å and $c=8.996$ Å, at 10.4 GPa. This compares well to what we have calculated, $a=3.777$ Å and $c=8.840$ Å, at 13.90 GPa—the first theoretical appearance of cinnabar coming from rock-salt. The experimental c/a axial ratio²⁶ falls in the interval 2.31–2.35 in all the studied samples, which is in good agreement with our calculations: we found c/a to vary within 2.335–2.340 in our regime of stability of cinnabar between 13.35–13.90 GPa, whereas the reported c/a ratio from pseudopotential calculations²⁴ is ~ 2.26 , too much off. As in ZnTe and CdTe,²⁴ the pseudopotential method slightly underestimates the c/a ratio. We have computed the volume collapse at the zinc-blende-cinnabar and the cinnabar-rock-salt phase transitions to be 9.03% and 7.57%, respectively, in good qualitative agreement with experimental indications²⁶ (9.8% and 6.3%, respectively).

It should be mentioned that the phase transition from cinnabar to rock-salt phase in HgS has been simulated by Sun and Dong,⁷ who used the same calculation method as we do in the present paper. They traced the variations in all lattice parameters, as we do now. The difference is that the native cinnabar structure of HgS is characterized by very different values of u and v (~ 0.5 for cation, ~ 0.75 for anion—see the above discussion), which converge to $2/3$ on the transition.

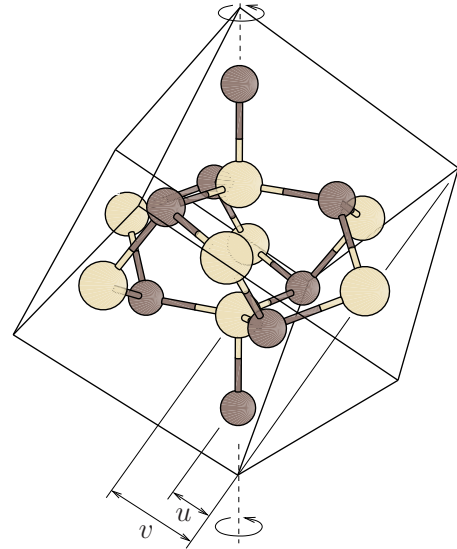


FIG. 8. (Color online) A side view of the cubic primitive cell of the SC16 structure underlying its trigonal symmetry and indicating the definition of internal coordinates u (for cations) and v (for anions).

The variation in c/a with pressure is sublinear in HgS and merges into the $\sqrt{6}$ value without singularity; the bond lengths have no discontinuity. In total, the cited study confirms the experimental indications for the second-order phase transition in HgS, in contrast to presumably first-order character in ZnSe.

C. SC16 structure

The SC16 structure also has one internal parameter to define cation position and one for anions; we retain for them the notations u and v , although their meaning is of course quite different from that in the cinnabar structure. The space group is now $Pa\bar{3}$ (Nr 205), and the sites in question are (8c). Since there is an ambiguity in defining the internal coordinate so as to generate the same set of eight equivalent positions, we specify that the cation at $(u u u)$ and the anion at $(v v v)$ are first neighbors, whose connecting bond length is $a(v-u)\sqrt{3}$ (Fig. 8). Differently from the twist as in the cinnabar phase, the “elementary” tetrahedron undergoes a pyramidal distortion, in which a singular cation-anion bond (from the central atom to the pyramid’s summit, along the spatial diagonal of the cube in Fig. 8) differs from three equal bonds to the ions in the pyramid’s basal plane. Correspondingly, six bond angles in a given tetrahedron split into three involving the singular bond and three others, excluding it. Finally, a pair of cation-anion-cation bond angles is, in general, different from the anion-cation-anion pair.

The lattice parameter and internal coordinates optimized in the SC16 phase of ZnSe as functions of pressure are shown in Fig. 9, and corresponding bond lengths and bond angles—in Fig. 10. Throughout the range of pressures studied, the system remains semiconducting, although the band-gap variation under pressure differs from that in the cinnabar phase. Starting from 0.85 eV at zero pressure, the band gap rises to 1.04 eV at 14 GPa, from where a less steep descent

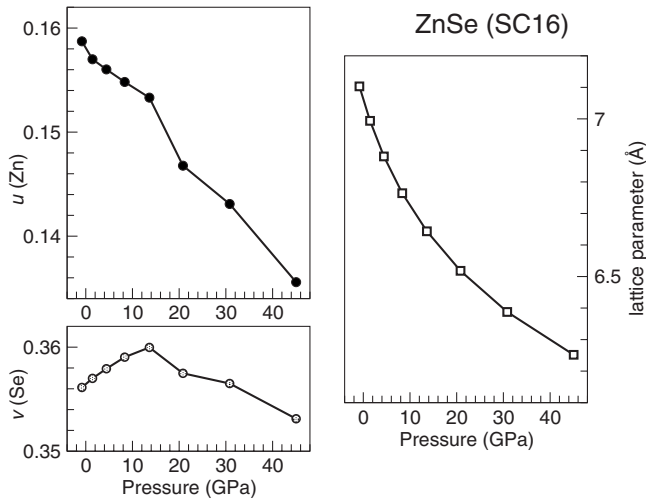


FIG. 9. Internal coordinates u , v (left panels) and lattice parameter (right panel) in the SC16 phase of ZnSe as optimized at different applied pressures.

brings its back to 0.83 eV at 45 GPa. Qualitatively, the variation in the band gap resembles that of the $v(\text{Se})$ parameter in Fig. 9.

We see that the distance from a cation to its second-neighbor (not bonded) counterpart, i.e., between the atoms at $(u\ u\ u)$ and $(\bar{u}\ \bar{u}\ \bar{u})$, is gradually decreasing with pressure, whereas the corresponding anion-anion distance (across the

center of the cubic cell in Fig. 8), although being roughly of the same value, strongly resists compression. Till about 12 GPa, the relative anion-cation separation ($v-u$) in fact grows with pressure, that is however (over)compensated by the volumic compression, so that the both bond species get shortened (at different rate; the triplet bond compresses faster). Near 12 GPa, the change in behavior occurs, as the two bond length values cross:⁴⁷ from here on, the anion-centered tetrahedra become “rigid,” as the bond angles get stabilized at about 97° and 118° . On the contrary, the cation-centered tetrahedra do smoothly “flow” with pressure, the cation being gradually pressed into the basal plane of the pyramide: the Zn-centered bond angles go away toward $\sim 90^\circ$ and $\sim 120^\circ$, the singlet bond contracts only slightly whereas the “planar” triplet bonds get considerably shorter.

We traced the structure modifications in the SC16 phase deep into the region of pressures where the B1 phase must definitely win (according to calculations). At the low-pressure end of the “SC16 window” (Fig. 2), at 11.8 GPa, we interpolate the triplet bonds to be 2.402 Å and the singlet one 2.383 Å. This compares well with four bonds of 2.367 Å in ZnSe-zinc blende at the same pressure. On the opposite end, at 16.1 GPa, we find triplet bonds of 2.367 Å and the singlet one of 2.378 Å, to be compared to six bonds of 2.550 Å in the ZnSe-rocksalt at the same pressure. The calculated volume collapse on zinc-blende-SC16 and SC16-rocksalt phase transitions are 8.7% and 7.56%, respectively. The experimental data to compare with are, as mentioned above, so far not available.

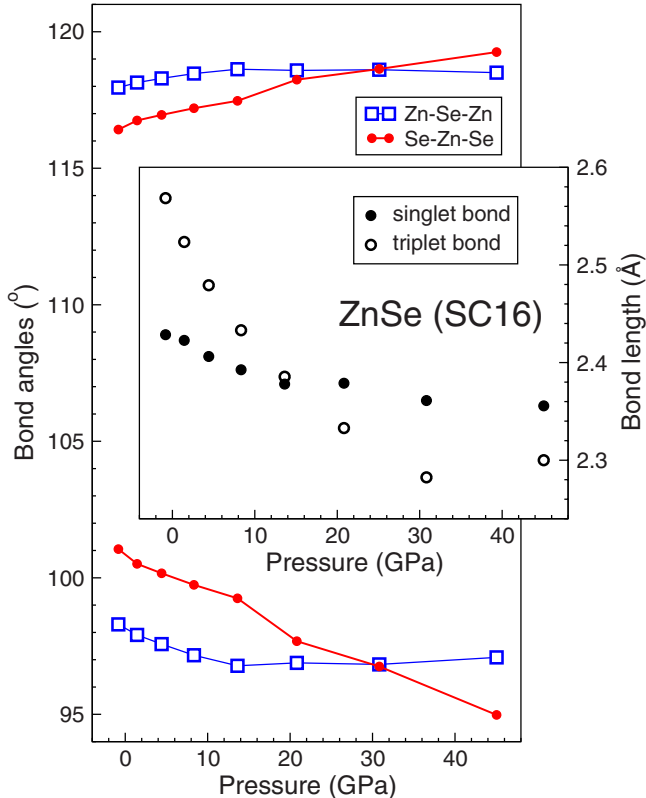


FIG. 10. (Color online) Bond lengths and bond angles in the SC16 phase of ZnSe optimized at different applied pressures. See text for details.

D. General discussion

An important observation from the present study is that when considering the cinnabar phase as intermediate one between the B3 and B1, the optimization of internal coordinates u , v along with the c , a lattice parameters is essential for getting, at the same time, all the following properties right: (i) a preference in energy over both B3 and B1 in a certain window of pressures; (ii) the width of this window; and (iii) the ultimate collapse, at a sufficiently high pressure, of the B9 phase into the B1. An unresolved question remains, why is the SC16 phase, apparently (i.e., consistently over results of many calculations) having lower enthalpy than the B9, not observed experimentally. In order to shed a light on this issue, the study of the energy barrier connecting B3 to SC16, in comparison with that from B3 to B9, has to be done. Such simulation would already be quite helpful when done in a static model, assuming a plausible path for the structure transformation. However, dynamical aspects may also play an important role. So far, the argumentation concerning the absence of the SC16 phase in experiment included that “the formation of SC16 is kinetically hindered, which is extremely likely given the high energy of the intermediate $R16$ structure”.¹³ Moreover, as suggested by Crain *et al.*,¹⁵ SC16 may be formed under conditions of high pressure and temperature and could then persist as a metastable state to ambient pressure. An analogy is known for GaAs, where the SC16 phase was detected to appear under a combined effect of high pressure and temperature.²¹

IV. CONCLUSION

In this paper we have found that the cinnabar phase, a fourfold-coordinated structure formed from twisted tetrahedra, could exist as a high-pressure thermodynamic metastable phase between the semiconducting zinc-blende and the rocksalt metallic phases. The observation of cinnabar phase in the downstroke reveals that a big energy barrier exists between rocksalt and the zinc blende and SC16 phases. We believe that upon pressure increase from the zinc-blende phase, transition to covalently bonded fourfolded coordinates are inhibited by big energy barriers at room temperature. While upon pressure decrease from the rocksalt phase, a transition to SC16 remains hindered, but a transition to the cinnabar phase is possible because there is a low-energy path between rocksalt and cinnabar. There are striking similarities in the calculated high-pressure phase diagrams of ZnSe and GaAs.^{13,14} For both systems, the cinnabar phase occurs as a

low-pressure metastable phase, and were found experimentally, at room temperature, only upon release of pressure from the metallic high-pressure rocksalt [for ZnSe (Ref. 26)] and *Cmcm* [for GaAs (Ref. 10)] phases; also $u \sim v \sim 0.5$ gave an excellent fit to the diffraction pattern in both cases. The striking similarity in behavior between ZnSe and GaAs adds to the developing links between the II-VI and the III-V semiconductors.⁴⁸ It is of high interest to investigate the relationship further by looking for the possibility to arrive at SC16 of ZnSe along a similar path as was discussed for GaAs.^{21,22} We invite experimentalists to explore this possibility.

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