Ab initio study of the phase transformations of ZnSe under high pressure: stability of the cinnabar and SC16 phases

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Abstract. The structural phase transformations of ZnSe under high pressure are studied by using a first-principles pseudopotential method and the local density approximation for the exchange–correlation potential. A new phase, which is simple cubic with a 16-atom basis (SC16), is predicted to be thermodynamically stable between 9.2 and 16.4 GPa, which is below the stability pressure range of the rock-salt structure. The cinnabar structure of ZnSe is found to be unstable, contrary to the findings of a previous theoretical investigation. The structural properties of the zinc-blende, rock-salt, cinnabar and SC16 phases are presented.

1. Introduction

The II–VI compounds have received and still receive considerable interest because of their potential technological applications. The first experimental study of the structural phase transformations of II–VI materials under high pressure was conducted about forty years ago by Edwards and Drickamer [1]. Since then, this subject has attracted a lot of attention. The generally accepted view was that these compounds transform under high pressure from zinc-blende (ZB) or wurtzite to rock-salt (RS) and then to β-Sn phases, except the Hg-based compounds. In the latter compounds, the cinnabar phase (which is the ground-state structure of HgS) appears before the RS phase. However, recent experiments performed by using angle-dispersive x-ray techniques for many II–VI, III–V and group-IV semiconductors have led to significant alterations to the previously widely accepted view of their structural systematics [2]. New low-symmetry phases have been observed, such as: the cinnabar phase in CdTe [3], ZnTe [4] and GaAs [5]; the *Cmcm* form in many II–VI and III–V compounds [2]; SC16 (simple cubic with a 16-atom basis, the binary analogue of the BC8 phase observed in Si and Ge [6]) structure in GaAs [7]. The latter structure has also been observed in some I–VII compounds, namely CuCl and CuBr [8]. The main aim of this study is to investigate the stability of the cinnabar and SC16 phases in ZnSe under high pressure. In addition to these structures, the ZB and RS phases will also be considered.

    The observation of the cinnabar phase in compounds other than the Hg-based ones has prompted several theoretical calculations. Lee *et al* [9] have 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 orbital calculations of Ahuja *et al* [10]. The cinnabar phase in GaAs has been found to be only metastable [11, 12]. Qteish *et al* [13] have investigated the stability of the cinnabar phase in

ZnS by using a PP-PW approach, and they have found it to be unstable, in agreement with a recent experimental investigation [2]. Côté *et al* [14] have studied the stability of the cinnabar and *Cmcm* phases in ZnSe, ZnTe, CdSe and CdTe, using a PP-PW method—the stability of the cinnabar phase of ZnTe has also been demonstrated by these calculations, but this was not the case for that of CdTe. However, they have noted that the instability of the cinnabar structure of CdTe is very critical. Interestingly, they have predicted a stable cinnabar phase in ZnSe, reached before the RS phase. This prediction has not been confirmed experimentally, upon either pressure increase or decrease [2]. Therefore, a theoretical reinvestigation of the stability of the cinnabar phase of ZnSe is in order.

The SC16 phase is also attracting increasing attention. Theoretical calculations have predicted a stable SC16 phase in GaAs and GaP [15–17], while it is found to be unstable in the Al- and In-based semiconductors [17, 18]. It has been argued [15] that the formation of the SC16 phase in semiconductor compounds is kinetically inhibited by the formation of wrong bonds: the binary analogue of the R8 phase (rhombohedral structure with an eight-atom basis, which has been found [15] to be a phase intermediate between β-Sn and BC8 in Si) has five-membered rings. However, SC16-GaAs has been obtained experimentally by heating its high-pressure *Cmcm* phase to about 400 K at a pressure of 14 GPa. Very recently, Qteish and Parrinello [19] have investigated the stability of SC16-ZnS, and they have found it to be a stable high-pressure phase, reached before the RS phase. Moreover, on the basis of the observed trend for the relative stability of the cinnabar and SC16 phases, in III–V compounds, to be strongly cation dependent, and the relative stability of these two structures in ZnS, they have suggested that the SC16 phase would be a stable high-pressure phase in ZnSe and ZnTe. This work will provide a test for the applicability of such a trend to II–VI compounds.

ZnSe is known to transform under high pressure from ZB to RS structure at about 13.5 GPa [20–23]. ZnSe-III has been identified as a *Cmcm* phase [24], with a transition pressure, p_t, for the RS $\rightarrow$ *Cmcm* transition of 30.0 GPa. A third transition takes place to an, as yet, not well specified structure at about 50 GPa, and no further transitions have been observed up to 120 GPa (see reference [2]). The PP-PW calculations of Côté *et al* [14] gave a value for p_t for the RS $\rightarrow$ *Cmcm* transition of 36.5 GPa, which is in good agreement with experiment. For this reason, *Cmcm*-ZnSe has not been considered in this work. However, they have not reported their result for p_t for the ZB $\rightarrow$ RS transition, but it should be above 10.2 GPa (their value for p_t for the ZB $\rightarrow$ cinnabar transition). The reported theoretical values for p_t for the ZB $\rightarrow$ RS transition, obtained from a simple model [25] and first-principles pseudopotential [26] calculations, are 4.4 and 28.2 GPa, respectively. These results are quite far from the above experimental value.

The rest of the paper is organized as follows. In section 2 we describe our method and give the computational details. In section 3 we report and discuss our results for the structural properties and stability of the four forms of ZnSe considered. Finally, in section 4 we summarize our main results and conclusions.

2. Computational details

In the present study we have considered four phases of ZnSe, namely ZB, RS, cinnabar and SC16. The ZB and RS phases can be fully described by just the lattice constant, a. Both the cinnabar and SC16 structures have locally distorted tetrahedral bonding, as can easily be seen from figure 1. In the cinnabar phase there are two pairs of equivalent bonds associated with each atom, whereas in the case of SC16 each atom is connected to its first-nearest neighbours by three equivalent bonds and a fourth of a different type. The cinnabar structure has a hexagonal unit cell of three formula units, and can be fully described by four structural parameters: a, the

(a)   (b)
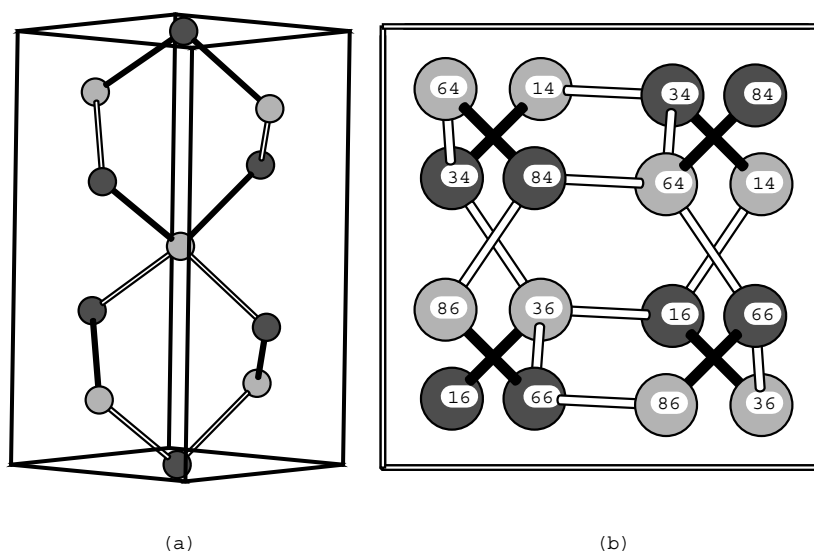
Figure 1. A unit cell of the cinnabar structure (a) and a view down the z-axis of the SC16 unit cell (b). The atomic positions, in the latter phase, along the z-axis are shown on each atom, in units of $0.01a$.

c/a ratio and two internal parameters, x_1 and x_2, for the Zn and Se atoms, respectively. As is evident from figure 1(a), the bond chains in the cinnabar structure consist of two concentric helices of cations and anions. The internal parameters x_1 and x_2 are the helix radii of the cations and anions, respectively. The SC16 form (figure 1(b)) has the space group $Pa3$ [8, 16], with a centre of inversion at $(\frac{1}{4}, \frac{1}{4}, \frac{1}{4})$. For the atomic positions we follow the description of reference [7]: one atomic species is at the 8(c) site (of the $Pa3$ space group) at (u, u, u) with a u of about 0.15 while the other is at another 8(c) position at (v, v, v) with a v of about 0.65. When $v - u \neq 0.5$, the second-nearest-neighbour distances are different for the two atomic species. In this work, the internal parameters u and v will be assigned to the Zn and Se atoms, respectively.

The calculations were performed by using the same Se and optimized Zn pseudopotentials as were used in references [13] and [27] respectively. The semicore 3d electrons of Zn are treated as forming part of the valence states, while those of Se are treated as forming part of the frozen core. The reported results are obtained without including the non-linear exchange–correlation core corrections (NLCC) [28]. The inclusion of such corrections for Se is found to lead to marginal effects on the calculated structural properties, and to a rigid upward shift in the calculated p_t of 0.5 GPa, for the ZB $\rightarrow$ RS and ZB $\rightarrow$ cinnabar transitions.

The other computational details are as follows. As in references [13] and [19], PWs up to a 55 Ryd energy cut-off were used to expand the wavefunctions of the ZnSe structures considered. The Kohn–Sham equations were solved by using the conjugate-gradient methods of references [29] and [30]. For the exchange–correlation potential we have used the local density approximation (LDA) and the Ceperley–Alder [31] data as parametrized by Perdew and Zunger [32]. The integration over the Brillouin zone was done by using a regular $2 \times 2 \times 2$ Monkhorst and Pack [33] mesh (one special point) for the SC16 phase, and a $4 \times 4 \times 4$ mesh is used for the other three structures. The four systems considered are treated as semiconductors. The LDA band structure of RS-ZnSe, at the experimental equilibrium volume (V_0), is shown in figure 2. According to these calculations, RS-ZnSe is a semimetal.
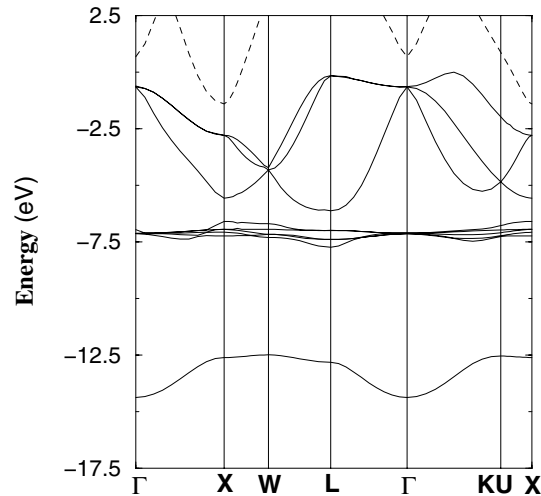
Figure 2. The calculated band structure of the RS phase of ZnSe. Solid curves: valence bands; dotted curve: lowest-energy conduction band. The zero energy is chosen to be at the top of the valence band along the Γ–K direction. No attempt has been made to determine the Fermi energy.

The calculated indirect band gap, E_g, between the conduction band minimum (at the X point) and the valence band maximum (along the Γ–K direction) is of -1.4 eV. On the other hand, the calculated E_g for the corresponding ZB phase is 1.0 eV, which is 1.7 eV smaller than the experimental value. Assuming that the many-body effects on E_g are the same in the two cases, RS-ZnSe is expected to be a semiconductor with an indirect E_g of 0.3 eV. However, resistivity measurements [20, 21] have shown that there is a drastic drop in resistivity at the onset of the ZB $\rightarrow$ RS transition, suggesting a metallic behaviour for RS-ZnSe. Thus, one can conclude that RS-ZnSe is a semimetal with a very small indirect E_g, and, hence, it is appropriate to treat it as a semiconductor (in the LDA calculations). As noted above, both the cinnabar and SC16 phases have locally distorted tetrahedral bonding. Since also the reduction in V_0 caused by going from the ZB structure to these phases is smaller than that for RS structure, both systems are expected to behave as semiconductors. This has been verified by treating them as metals in some test cases. Moreover, the band-structure calculations for the cinnabar phase of ZnS [13] have shown that its E_g is direct (at the Γ point) and it is only 0.16 eV smaller than that of the corresponding ZB system, providing further support for the above choice. The sets of special k-points used have been checked before, and are found to give excellent total-energy convergence [13, 19].

The internal parameters for the SC16 phase and the c/a ratio of the cinnabar form were determined by minimizing the forces on the ions and the stress anisotropy, respectively. The internal parameters of the cinnabar structure have been determined by Côté *et al* [14], and they are found to be V-independent and equal to 0.5, in the volume region of interest. In this work, we have made use of these results.

3. Results and discussion

3.1. Structural properties and relative stability

The calculated (as described above) c/a ratio of the cinnabar form and the internal parameters of the SC16 phase (u and v) as functions of V are shown in figures 3 and 4, respectively.
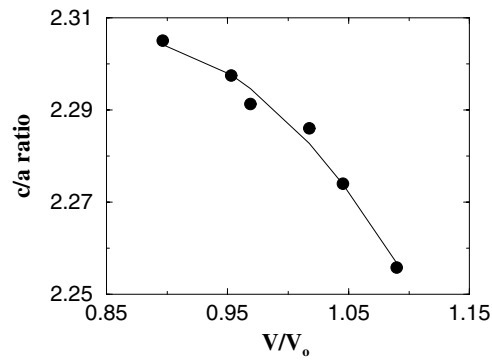
Figure 3. The *c/a* ratio of the cinnabar structure of ZnSe as a function of volume. Solid line: a quadratic fitting to the calculated data.
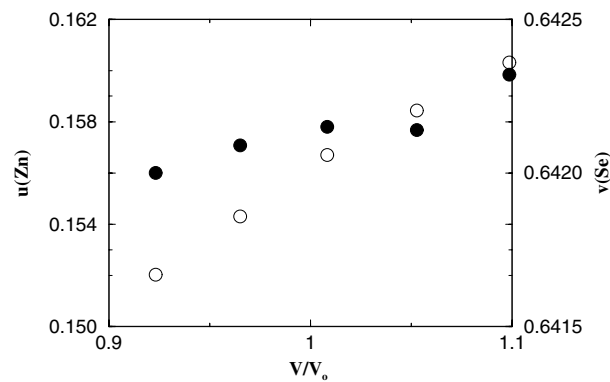
Figure 4. Internal parameters of the SC16 phase of ZnSe as functions of volume. Open circles: *u* (Zn). Solid circles: *v* (Se).

In agreement with reference [14], the *c/a* ratio increases on going to smaller volumes. The *V*-variation of the *c/a* ratio shows a sub-linear behaviour. The variation of *u* is much stronger than that of *v*, and shows an almost linear behaviour. In fact, to a very good approximation, *v* can be assumed to be a constant equal to 0.6421. This behaviour is very similar to that obtained for the SC16 phase of ZnS [19], GaAs and AlAs [16].
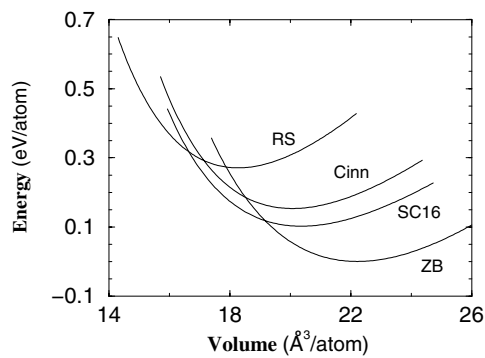
Figure 5. Energy versus volume curves of the ZB, RS, cinnabar and SC16 phases of ZnSe.

Figure 5 shows the E_{tot} versus V curves for the ZB, RS, cinnabar and SC16 phases of ZnSe. These curves are obtained by calculating E_{tot} at several different volumes, and fitting the calculated values to the Murnaghan equation of state. This figure shows that the SC16 phase is more stable than both the cinnabar and RS forms. The ground state E_{tot} of the RS, cinnabar and SC16 structures is higher than that of the ZB structure by 0.271, 0.153 and 0.102 eV/atom, respectively. The difference between the equilibrium E_{tot} of the cinnabar and SC16 phases (0.051 eV/atom) is very close to that obtained for ZnS [19], of 0.042 eV/atom. Therefore, these results suggest that the strong cation dependence of the relative stability of the cinnabar and SC16 phases, observed for III–V compounds, can also be extended to the II–VI ones.

The other calculated structural parameters of the four phases of ZnS considered are listed in table 1, together with the available experimental data. The important features to note are the following:

(i) The calculated structural parameters of the ZB and RS structures are in excellent agreement with experiment. The discrepancy between the calculated and measured values of a_0 is 0.8% and 0.6% for the ZB and RS structures, respectively. In the case of the bulk modulus, B_0, these discrepancies are of 0.5% and 14.9%. It is worth noting that the experimental values of B_0 are determined by using a fixed value for its pressure derivative, B_0'. In view of this, the theoretical and experimental uncertainties and the large difference between the pressure ranges used in the two cases to determine the equation of state, the agreement between the present result for B_0 for RS-ZnSe and experiment is very reasonable.

(ii) B_0 for the SC16 phase has a relatively low value: it is about 5 GPa lower than that of the ZB structure. This result is consistent with those obtained for other compounds [17–19]. However, this behaviour is quite strange, since for the other structures considered, B_0 increases by going to the structures with smaller V_0 (ZB → cinnabar → RS).

(iii) At zero pressure, the value of the c/a ratio of the cinnabar phase is 2.287; those of u and v for the SC16 structure are 0.1563 and 0.6421, respectively.

Table 1. The structural parameters of the four phases of ZnSe considered.

Structural parameter	ZB	RS	Cinnabar	SC16
a_0 (Å)	5.623[a], 5.606[b], 5.667(4)[c]	5.268[a], 5.299(12)[c]	3.932[a]	6.881[a]
B_0 (GPa)	68.9[a], 70.5[b], 69.3(1.1)[c]	88.5[a], 104 (6)[c]	72.6[a]	63.9[a]
B_0'	4.36[a]	4.28[a]	5.5[a]	5.5[a]

[a] Present work (V_0 for the cinnabar phase is 20.070 Å^3/atom, and $(c/a)_0$ is 2.287).
[b] Reference [14].
[c] Experimental data, obtained by using a fixed value of B_0' of 4.0 (reference [34]).

3.2. Phase transformations under high pressure

The values of p_t for the various phase transitions were determined from the constraint of equal static lattice enthalpy, given by

$$H(p) = E_{tot}(V(p)) + pV(p). \tag{1}$$

The calculated $H(p)$ for the RS, cinnabar and SC16 structures of ZnSe relative to that of the ZB phase are shown in figure 6. In table 2, the values of p_t obtained are compared to the available experimental data and other theoretical results. The remarkable features to note from these results are the following:
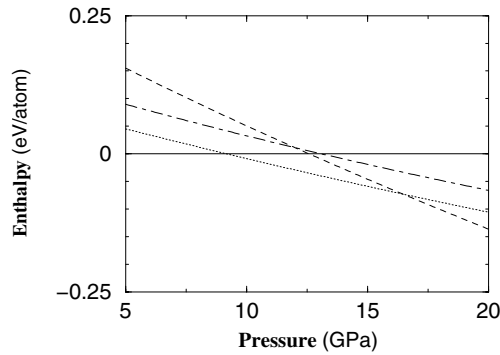
Figure 6. Static lattice enthalpy of the RS (dashed line), cinnabar (dashed–dotted line) and SC16 (dotted line) phases of ZnSe relative to that of the ZB structure.

Table 2. The transition pressures (GPa) of the phase transitions of ZnSe studied here.

Transition	Present work	Other theoretical works	Experiment
ZB → SC16	9.2		
ZB → RS	12.6	4.4[a], 28.2[b]	13[c], 13.5[d,e], 13.7[f]
ZB → cinnabar	13.1	10.2[g]	
SC16 → RS	16.4		

[a] Reference [26]: simple model calculations.
[b] Reference [27]: PP-PW calculations, with empirical PP.
[c] Reference [20].
[d] Reference [21].
[e] Reference [22].
[f] Reference [23].
[g] Reference [14]: PP-PW calculations.

(i) SC16-ZnSe is a thermodynamically stable high-pressure structure. p_t for the ZB → SC16 transition is 9.2 GPa, compared to that for the ZB → RS transition of 12.6 GPa. This finding confirms the suggestion made in reference [19] concerning the stability of SC16-ZnSe, and provides further support for that made for SC16-ZnTe. In the phase diagram of ZnTe, the *Cmcm* phase appears instead of the RS phase (found in ZnS and ZnSe [2]). This makes ZnTe a perfect candidate for a highly desirable experimental attempt to observe the SC16 phase in II–VI compounds, as has been made in the case of GaAs [7].

(ii) The stability range of SC16-ZnSe is quite appreciable (7.2 GPa), since it becomes unstable with respect to the RS phase at about 16.4 GPa. This stability range is more than two times larger than that of SC16-ZnS (3.4 GPa, reference [19]).

(iii) p_t for the ZB → RS transition is 12.6 GPa, which is in very good agreement with the experimental value of about 13.5 GPa. It is worth noting, again, that the inclusion of NLCC for Se increases p_t by 0.5 GPa, bringing it even closer to the experimental data than the above reported value.

(iv) The cinnabar structure of ZnSe is unstable as a high-pressure phase, although it is more stable than the RS structure. p_t for the SC16 → cinnabar transition is very high compared to that for the SC16 → RS transition.

(v) Even in the absence of the SC16 phase, the cinnabar structure is unstable relative to the RS structure. This result is in disagreement with the result obtained by Côté *et al* [14], who predicted a stability range for this system of 3 GPa, below the pressure range of the RS

structure. On the other hand, our result is in agreement with the experimental investigation of Nelmes and McMahon [2] which showed that there is no evidence of a cinnabar phase in ZnSe upon either pressure increase or decrease. However, the stability of the cinnabar phase is a very delicate issue, since a very small change in E_{tot} would lead to a different conclusion.

The volume contractions associated with the ZB $\rightarrow$ SC16, SC16 $\rightarrow$ RS and ZB $\rightarrow$ RS transitions, defined as $\triangle V / V_t$, are respectively of 0.084, 0.081 and 0.159. Here, V_t is the volume—at the onset of the transition—of the phase from which the transition occurs, which is 20.000, 17.354 and 19.424 Å^3/atom for the above three transitions, respectively. $\triangle V / V_0$(ZB) for the ZB $\rightarrow$ RS transition is found to be 0.139, which is in very good agreement with the experimental results (0.133 (reference [34]) and 0.130 (reference [2])).

4. Conclusions

A first-principles pseudopotential method is used to investigate the structural properties and stability of the zinc-blende (ZB), rock-salt (RS), cinnabar and SC16 phases of ZnSe. The semicore 3d electrons of Zn were treated as valence states. Our main results and conclusions can be summarized as follows.

 (i) A thermodynamically stable SC16 phase of ZnSe has been predicted, with an appreciable stability range of 7.2 GPa.
 (ii) The cinnabar phase is found to be unstable, in the presence or absence of the SC16 phase, in agreement with a recent experimental investigation.
(iii) Our calculated transition pressure and volume contraction associated with the ZB $\rightarrow$ RS transition are in very good agreement with experiment.
(iv) The trend of the relative stability of the cinnabar and SC16 phases being strongly cation dependent, observed for III–V compounds, can be extended to the II–VI ones.
 (v) There are strong indications for a stable SC16-ZnTe, which makes this compound a perfect candidate for a highly desirable experimental investigation of the stability of the SC16 phase in II–VI compounds.

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