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Stability and structural properties of the SC16 phase of ZnS under high pressure

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A first-principles pseudopotential method is used to investigate the stability and the structural properties of the SC16 phase of ZnS under high pressure. It has been found that this form is thermodynamically stable in the pressure range from 12.8 to 16.2 GPa, which is below the pressure range in which the rocksalt structure is experimentally observed.

Upon increase of pressure, Si and Ge transform from their ground-state diamond structure to the β-Sn phase at moderate pressures. This process is irreversible, and when pressure is decreased these systems transform to fourfold coordinate structures,[1,2] known as BC8 (body-centered cubic with 8 atoms basis) and ST12 (simple tetragonal with 12 atoms basis). A recent experimental and theoretical investigation by Crain *et al.*[3] has revealed that there is an intermediate phase between the β-Sn and BC8 forms of Si, which is a rhombohedral structure with eight atoms per unit cell (the so-called R8 phase). In addition to their intrinsic interest, these structures have attracted a great deal of attention, because their local distorted tetrahedral bonding is similar to that proposed for the grain boundaries and surface reconstruction in Si.[4] These phases have also been used in modeling the development of the amorphous structures by increasing the short-range disorder in crystalline solids.[5]

The binary analog of the BC8 structure can be obtained by doubling the size of the BC8 unit cell, which leads to a simple cubic structure with 16 atoms per unit cell, known as SC16. This structure has recently received increasing interest.[3,6–11] Theoretical calculations have shown that it is a thermodynamically stable high-pressure phase in GaAs, GaP, AlSb, and InAs.[3,6] However, the subsequent calculations of Mujica *et al.*[7,8] show that the SC16 phase is unstable in the Al- and In-based semiconductors. Such discrepancy can be understood by noting that the instability of the SC16 phase in the latter compounds is quite critical.[7,8] It has been argued[3] that the formation of the SC16 phase of these materials is kinetically inhibited by the formation of wrong bonds at the structural transition: the binary analog of the R8 phase has five-membered rings. However, very recently, SC16-GaAs has been obtained experimentally,[10] by heating its high-pressure $Cmcm$ phase to about 400 K at 14 GPa. Moreover, the same structure has been observed experimentally in some I-VII compounds, namely CuCl and CuBr.[11] To the best of our knowledge, there are no theoretical or experimental investigations of the SC16 phase in the II-VI compounds. In this work, we use a first-principles pseudopotential plane-wave (PP-PW) method to investigate the stability of the SC16 phase in ZnS under high pressure.

ZnS transforms under high pressure from the zinc-blende (ZB) structure to the rocksalt (RS) phase at about 15 GPa. In a preliminary study, Nelmes and McMahon[12] have found that RS-ZnS transforms to a $Cmcm$-like distorted RS structure at 69 GPa. Qteish *et al.*[13] have shown that a very good description of the former phase transformation can be obtained by using the PP-PW and full-potential linear muffin-tin orbital (FP-LMTO) methods. Moreover, they have investigated the stability and electronic structure of the cinnabar phase of ZnS. The cinnabar phase has a local distorted tetrahedral bonding,[13] and has been recently observed in ZnTe and CdTe,[14] and GaAs.[15] They have found that this structure is thermodynamically unstable as a high-pressure phase of ZnS, although it is found to be relatively more stable than the RS structure. It is of interest to study the relative stability of the cinnabar and SC16 phases, since this may lead to some predictions when the stability of only one of them is known.

In Fig. 1 we show a unit cell of the SC16 phase. It is now well established that this structure has the space group $Pa3$,[6,11] with a center of inversion at ($\frac{1}{4},\frac{1}{4},\frac{1}{4}$). For the positions of the Zn and S atoms in the unit cell, we adopt the description of McMahon *et al.*:[10] one atomic species is on the $8(c)$ site (of the $Pa3$ space group) at (u,u,u), with u of about 0.15 while the other is on another $8(c)$ position at

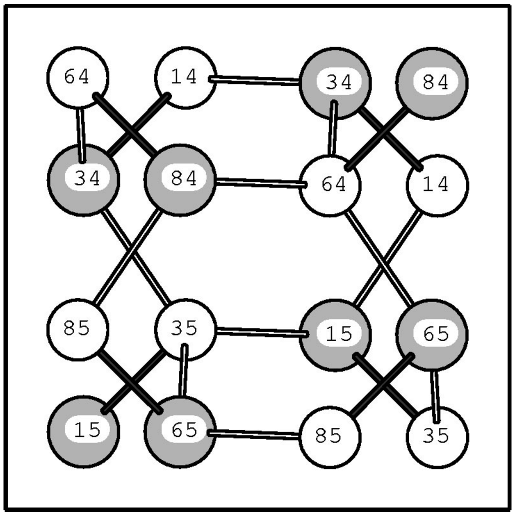

FIG. 1. A view down the z axis of the SC16 unit cell. Solid bonds: type A. Open bonds: type B. The atomic positions along the z axis are shown on each atom, in units of $0.01a$.

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(v,v,v) with v of about 0.65. As is evident from Fig. 1, each atom is connected to its first-nearest neighbors by one bond of type A and three bonds of type B. When $v-u\neq 0.5$, the second nearest neighbors distances are different for the two atomic species. The bond lengths and bond angles are expressed in terms of the internal parameters as

$$R_A=a\sqrt{3}(x_1+x_2), \tag{1}$$

$$R_B=a\sqrt{2(x_1+x_2)^2-(x_1+x_2)+(x_1-x_2)^2+0.25}, \tag{2}$$

$$\Theta_{AB}=\arccos\frac{4(x_1+x_2)-1}{2\sqrt{3[2(x_1+x_2)^2-(x_1+x_2)+(x_1-x_2)^2+0.25]}}, \tag{3}$$

$$\Theta_{BB}=\arccos\frac{2(x_1+x_2)^2-(x_1+x_2)}{2[2(x_1+x_2)^2-(x_1+x_2)+(x_1-x_2)^2+0.25]}, \tag{4}$$

where $x_1=0.25-u$, $x_2=0.75-v$; a is the lattice parameter. In this work, the internal parameters u and v are associated to the Zn and S atoms, respectively.

The calculations were performed by using the same S and optimized Zn pseudopotentials used in Ref. 13. The semicore Zn 3d electrons were treated as valence states. Here, we have also used a 55 Ry energy cutoff, which amounts to an average of 14 000 PW's, to expand the wave functions of SC16-ZnS. The integration over the Brillouin zone was done by using a regular 2×2×2 Monkhorst and Pack[16] mesh (one special point). The total energy, E_{tot}, convergence with respect to the number of special points used is checked by increasing the mesh to 4×4×4 (four special points). We found that this leads to a reduction in the calculated values of E_{tot} of about 1 meV. This level of convergence is similar to that of the ZB structure when the number of special points is increased from 10 (4×4×4 mesh, used in Ref. 13) to 60 (8×8×8 mesh). Thus, our calculations are well converged with respect to both the number of PW's (see Ref. 13) and special points.

For each of the volumes of SC16-ZnS considered, the optimal values of the internal parameters u and v were determined by minimizing the forces on the ions. It has been found that the variation of these parameters with respect to volume, V, can be best fitted to straight lines, given by $u(V/V_0)=0.0983+0.0558V/V_0$ and $v(V/V_0)=0.6412+0.0019V/V_0$, where V_0 is the equilibrium volume. The maximum difference between the calculated and fitted values of both u and v is less than 0.0005, which can be used as a measure of the uncertainty in our calculated values of these parameters. It is important to note that the V dependence of v is much weaker than that of u, which is consistent with the results of Mujica, Needs, and Muñoz[9] for SC16-GaAs and SC16-AlAs. It is also worth noting that the values of u and v at V_0 (0.1541 and 0.6431) are very close to those of SC16-GaAs [experiment (Ref. 10): 0.157(2) and 0.643(2); theoretical calculations (Ref. 9): 0.1583 and 0.6398].

In Fig. 2, we show a contour plot of the calculated E_{tot} as a function of u and v at a certain fixed volume. This figure shows that the variation of E_{tot} along the diagonal on which the difference between v and u is a fixed value is much stronger than that along the other diagonal. This behavior can be easily understood: the sum of v and u along the latter diagonal is a constant, which leads to invariant R_A and to very weak variations of R_B, Θ_{BB}, and Θ_{AB}. These weak variations come from the $(x_1-x_2)^2$ term [see Eqs. (2)–(4)], which is very small compared to the other ones. The other important feature to note from Fig. 2 is the very weak variation of E_{tot} in the considered ranges of v and u. Thus, the estimated errors in the calculated E_{tot} due to the uncertainties in the calculated values of the internal parameters (see above) are less than 1 meV/atom, which have negligible effects on our results and conclusions.

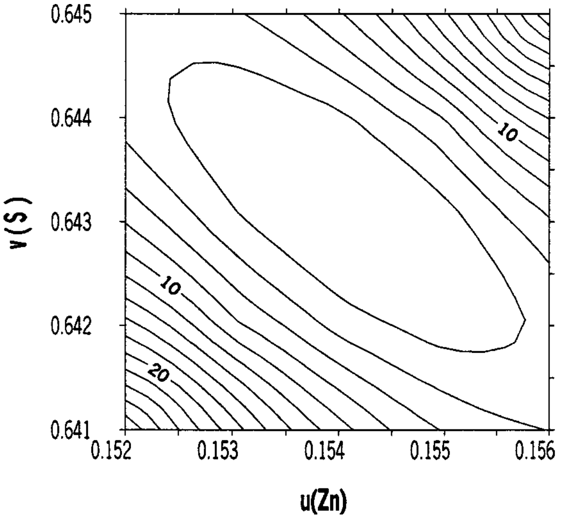

FIG. 2. Contour plot of the total energy (meV/unit cell) as a function of the internal parameters of SC16-ZnS, at the equilibrium volume.

Figure 3 depicts the E_{tot} versus V curves for the ZB, RS, cinnabar, and SC16 phases of ZnS. 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 relatively more stable than both the cinnabar and RS forms. The

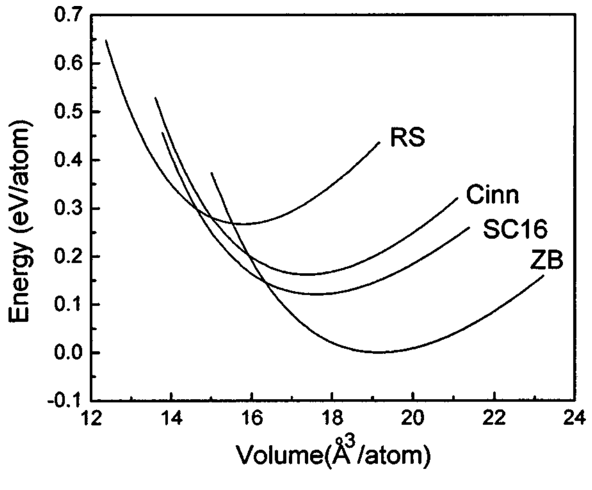

FIG. 3. Total energy versus volume curves for the ZB, RS, cinnabar, and SC16 forms of ZnS.

TABLE I. The calculated lattice parameter, a_0, bulk modulus, B_0, and its pressure derivative, B_0', of ZnS-SC16, compared with those of the other phases considered for ZnS (Ref. 13).

Structural parameter	ZB	RS	cinnabar	SC16
a_0 (Å)	5.352,[a] 5.410[b]	5.017,[a] 5.060[c]	3.765[a]	6.555[a]
B_0 (GPa)	83.1,[a] 76.9[b]	104.4,[a] 103.6[c]	89.3[a]	78.4[a]
B_0'	4.43,[a] 4.9[b]	4.28[a]	4.51[a]	4.73[a]

[a] PP-PW calculations.

[b] Experimental data (Ref. 18).

[c] Experimental data, obtained by using a fixed value of B_0' of 4.0 (Ref. 19).

ground state E_{tot} of the RS, cinnabar, and SC16 structures are higher than that of the ZB structure by 0.267, 0.162, and 0.120 eV/atom, respectively.

The calculated structural parameters of SC16-ZnS are listed in Table I, together with those of the other considered phases of ZnS. The most important feature to note from this table is the relatively low value of the bulk modulus, B_0, of the SC16 phase (about 5 GPa smaller than that of the ZB form). For the other structures considered, B_0 increases by going to the structures with smaller equilibrium volume (ZB → cinnabar → RS). For the III–V compounds, the calculated values of B_0 of the SC16 phase is also found[7,9] to be smaller than expected [either equal to or slightly lower (by 1 GPa) than that of the corresponding ZB phase].

Since the cinnabar phase has been ruled out as a stable high-pressure phase in ZnS,[13] we will focus here on the ZB → RS and the ZB → SC16 phase transitions. The transition pressures, p_t, were determined from the constraint of equal static lattice enthalpy, given by

$$H(p)=E_{tot}(V(p))+pV(p). \tag{5}$$

The calculated $H(p)$ for the RS, cinnabar, and SC16 structures relative to that of the ZB phase are shown in Fig. 4. This figure shows that SC16-ZnS is a thermodynamically stable high-pressure phase. The p_t of the ZB → SC16 transition is of 12.8 GPa, compared with that of the ZB → RS transition of 14.35 GPa. The stability range of the SC16 phase is quite narrow (3.4 GPa), since it becomes unstable with respect to the RS phase at about 16.2 GPa. However, SC16-ZnS has not yet been observed experimentally, which may suggest that the ZB → SC16 (on pressure increase) and RS → SC16 (on pressure decrease) transitions are hindered by high kinetic-energy barriers. The volume contraction associated with the ZB → SC16 transition, defined as $\triangle V/V_t$ (ZB), is of 0.085, which is only about half that of the ZB → RS transition (of about 0.160, see Ref. 13). Here, V_t(ZB) is the volume of the ZB phase at which the ZB → SC16 transition occurs, which is 17.044 Å ^{3}/atom.

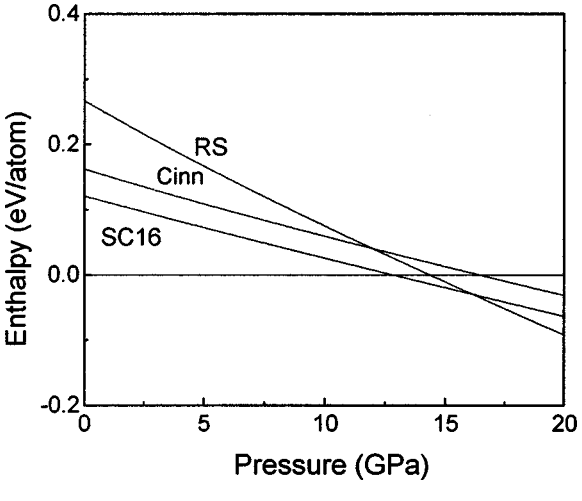

FIG. 4. Static lattice enthalpy of the RS, cinnabar, and SC16 phases of ZnS relative to that of the ZB structure.

The stability of the SC16 and cinnabar phases in III-V compounds has been thoroughly studied in a series of papers by Mujica *et al.*[6–9] They have found that for GaAs and GaP the SC16 phase is a thermodynamically stable high-pressure phase above ZB, while the cinnabar form (which is also a dense distorted tetrahedral structure) is only metastable. The relative stability between these two structures is about 0.05 eV/atom,[6] for both compounds, which is very close to our result for ZnS (0.042 eV/atom). For the Al-based compounds, the two forms have comparable relative stability and both are unstable high-pressure phases.[7] For the In-based compounds, only the SC16 phase is considered and it is found to be unstable.[8] From this work, one can conclude that the relative stability between the SC16 and cinnabar structures depends strongly on the cation, at least in the III-V compounds. Therefore, one may reasonably expect the SC16 phase to be a thermodynamically stable high-pressure phase in ZnTe and ZnSe, where the cinnabar phase has been observed in ZnTe[14] and theoretical calculations have shown that it is stable in both cases.[17]

There are striking similarities in the calculated high-pressure phase diagrams of ZnS and GaAs (Ref. 6). (i) In both cases, the SC16 phase is found to be a thermodynamically stable high-pressure structure, with p_t for the ZB → SC16 transition of about 12.5 GPa. (ii) For both systems, the cinnabar structure is a thermodynamically unstable high-pressure phase. (iii) The ZB → RS (in the case of ZnS) or ZB →*Cmcm* (a distorted RS structure, in the case of GaAs) transitions occur at about 15 GPa. Despite these similarities, the cinnabar phase has been observed in GaAs but not in ZnS. This may be related to the fact that the cinnabar phase in GaAs is obtained by depressurizing the *Cmcm* form, which is not the case for ZnS. Therefore, the possibility of observing SC16-ZnS in a way similar to SC16-GaAs (by heating, in this case, the RS-ZnS at high pressure) is an open question. Experimental and more sophisticated theoretical (using constant pressure molecular dynamics[20]) investigations are invited to explore this possibility.

In summary, we have used a first-principles pseudopotential method to investigate the stability and structural properties of SC16-ZnS. It has been found that this structure is thermodynamically stable in the pressure range from 12.8 to 16.2 GPa, below the rocksalt phase. The internal relaxation parameters and the relative stability of this structure with respect to the ZB form are found to be very similar to those observed in SC16-GaAs. Moreover, the relative stability of the SC16 and cinnabar phases in ZnS are also similar to those of GaAs. From these results and the trends found for the relative stability of the cinnabar and SC16 structures in III-V compounds, we expect the SC16 structure to be a thermodynamically stable high-pressure phase in ZnSe and ZnTe. However, further theoretical and experimental studies are required to confirm these predictions.

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