Brief Reports

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Quantum-mechanical modeling of the high-pressure state equations of ZnO and ZnS

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Equations of state (EOS) for the high-pressure phases of ZnO and ZnS have been determined by carrying out *ab initio* perturbed-ion calculations. The results are used to examine different empirical EOS formalisms proposed for experimental P-V data. The generalized Vinet EOS is shown to be highly sensitive to the uncertainties in experimental data, thus providing a poor extrapolation for the properties at zero pressure. Contrarily, the modified Birch-Murnaghan EOS predicts zero-pressure properties that agree with *ab initio* calculations.

Several empirical equations of state (EOS) have been proposed to fit the experimental P-V measurements on high-pressure phases of polymorphic crystals. Two popular schemes, the modified Birch-Murnaghan finite-strain analysis developed by Jeanloz[1] and the three-parameter universal expression based on Vinet *et al.*[2] EOS led to significant discrepancies when used to extrapolate the recent P-V measurements on the high-pressure rocksalt ($B1$) phase of ZnS.[3]

The aim of this paper is to show that these discrepancies can be resolved by the accurate *ab initio* calculations. These calculations can be performed at conditions not attainable in the laboratory or at which the systems under consideration are not stable. This is true, in particular, for the zero-pressure lattice volume and bulk modulus of high-pressure polymorphs that appear in the empirical EOS. Besides, the *ab initio* calculations provide useful information on the bonding and stability of the crystals.

The *ab initio* perturbed-ion (PI) approach used in this work is based on the theory of electronic separability for weakly overlapping groups. The method describes the total wave function of a pure or defective crystal as an antisymmetrized product of local atomic (or ionic) wave functions, and has been applied to a variety of crystals with remarkable success. For a detailed discussion of the PI approach and its applications, we refer to Luaña and Pueyo[4] and Luaña *et al.*[5] In this paper, we compare our results with experiment and with calculations using CRYSTAL.[6] This program package is a linear combination of atomic orbital implementation of the Hartree-Fock equations in crystalline solids.[7] As an interesting outcome of this work, we report results comparing both approaches on the same systems and properties. It is worthwhile to point out that the sensitive set of properties contained in the EOS are predicted by the two approaches with discrepancies of less than 10%.

ZnO and ZnS belong to the group of IIB-VIA binary semiconductors and have important technological applications. These materials crystallize at normal conditions in the (hexagonal) wurtzite or the (cubic) sphallerite phases and undergo transitions to the rocksalt phase in the region of 10–18 GPa. The low-pressure equation of state of ZnS was measured by means of the ultrasonic pulse superposition technique almost 20 years ago.[8] The high-pressure equation of state has not been unambiguously determined yet, although the P-V data have been reported recently by combining static compression and x-ray-diffraction techniques.[3] For ZnO, Bates, White, and Roy[9] reported the transition from the sphallerite to the rocksalt phase about 10 GPa. This high-pressure phase is found to be metastable at ambient pressure and temperatures below 393 K. However the equation of state in this phase has not been reported either theoretically or experimentally.

Our calculations have been directed to compute the total energy of the $B1$ (rocksalt) phase of ZnS and ZnO in a wide range of lattice parameters ranging from 80 to 110 % of the equilibrium geometries. The energy surface is then used to obtain the volume dependence of pressure and bulk modulus at 0 K. The zero-point vibrational energies, not included in this work, are expected to yield negligible deviations from the results presented here.

Figure 1 shows the P-V_{norm} diagram of ZnS. Here the normalized volume is the ratio of $V(P)$ to V_0, V_0 being the volume at zero pressure of the $B4$ phase. Both the PI (this work) and CRYSTAL (Ref. 6) calculations provide a similar description of the $B1$ phase in excellent agreement with the experimental data. This shows the accuracy and the reliability of the *ab initio* PI approach used here. Also, CRYSTAL calculations provide a very good description of the $B4$ phase as shown in Fig. 1.

Empirical EOS are analytical functions connecting P-V values at a constant temperature. The sensitivity of these functions to the fitting parameters yields different values for extrapolated regions. Two of the empirical EOS formalisms are considered here, namely the modified Birch-Murnaghan finite-strain analysis[1] (JEOS) and the three-parameter Vinet EOS (Ref. 2) (3-VEOS).

The JEOS is a polynomial of an effective strain:

$$G = a + bg + cg^2 + \ldots , \tag{1}$$

where the normalized stress, G, and the effective strain, g, are defined as

$$G = P\{3(1+2g)^{5/2}\}^{-1}; \quad g = \{[V(P)/V_0]^{-2/3} - 1\}/2 . \tag{2}$$

V_0 being again the zero-pressure volume of the low-pressure phase of a given system. This function provides the zero-pressure volume of the high-pressure phase as an extrapolated value.

The universal equation of state of Vinet *et al.* connects isothermal P-V data through the following equation:

$$\ln H = \ln B_0 + 1.5(B_0' - 1)(1 - x) , \tag{3}$$

where H and x are defined as

$$H = Px^2/[3(1-x)]; \quad x = [V(P)/V_0]^{1/3} , \tag{4}$$

and B_0 and B_0' are the bulk modulus and its pressure derivative at zero pressure, respectively. Here V_0 is the zero-pressure volume of the phase under exploration.

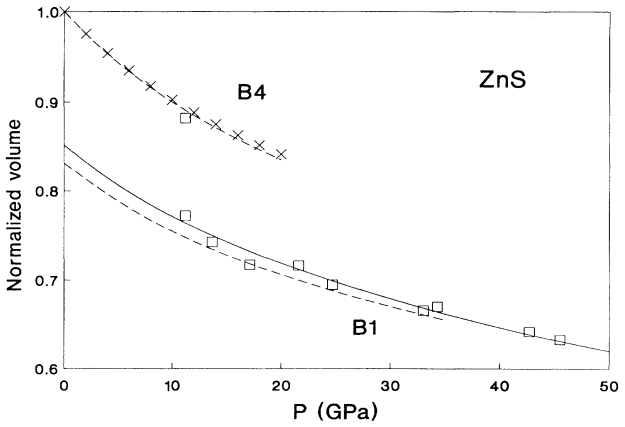

FIG. 1. P-V_{norm} diagram for ZnS according to PI (solid) and CRYSTAL (dashed) calculations (Ref. 6), and experimental data (crosses, Ref. 8), (squares, Ref. 3).

TABLE I. Lattice parameter and elastic constants of the rocksalt phase of ZnS at zero pressure.

	a (Å)	B_0 (GPa)	(dB/dP)
Expt.[a]: JEOS fitting	5.123	85.0	4.0
3-VEOS fitting	5.210	47.5	6.3
PI calculation	5.125	80 (81[b])	4.1
CRYSTAL calculation	5.237	84 (89[b])	4.6

[a]Reference 3.
[b]Obtained from polynomial fitting.

The 3-VEOS is the same as the Vinet EOS, except for the fact that it uses the *unknown* zero-pressure volume (V_0) as a fitting parameter.

Table I lists the zero-pressure structural properties obtained from the calculations, along with the extrapolated values derived from the JEOS and 3-VEOS fittings of the experimental P-V data. Both the PI and CRYSTAL calculations give a very similar description of the structural and elastic behavior of the ZnS($B1$) as expected from Fig. 1. On the other hand, the empirical fitting procedures yield two completely different set of values of (**a**, B_0, B_0'). This discrepancy obviously suggests us to investigate the reliability of the empirical EOS formalisms.

For ZnS($B1$) phase, the JEOS fitting of the computed values (shown in Fig. 2) do not show appreciable deviation from linear behavior. Note that the fittings of the computed and experimental values are almost identical. However, a different scenario emerges in Fig. 3, where we compare the 3-VEOS fitting of the computed and experimental values. The results therefore suggest that the 3-VEOS should be used with caution to extrapolate zero-pressure properties in the present case, in spite of the fact that it provides a satisfactory description of the P-V behavior in the region of $B1$ stability ($P > 11.2$ GPa); see Fig. 1 of Ref. 3.

Table II lists the results of PI calculations for the $B1$

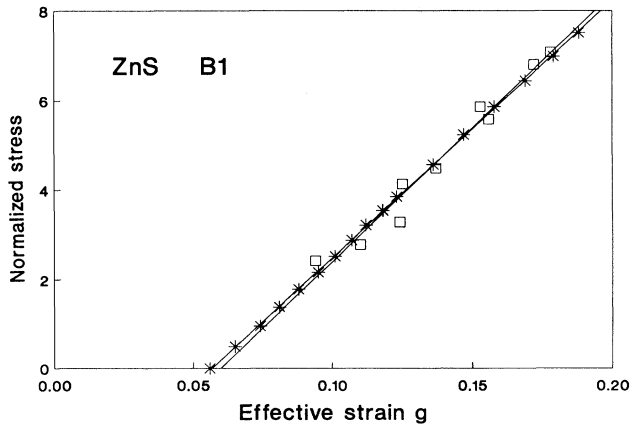

FIG. 2. Finite-strain analysis of the $B1$ phase of ZnS according to PI calculations (stars), and experimental data (squares, Ref. 3). Solid lines are first-order modified Birch-Murnaghan fittings.

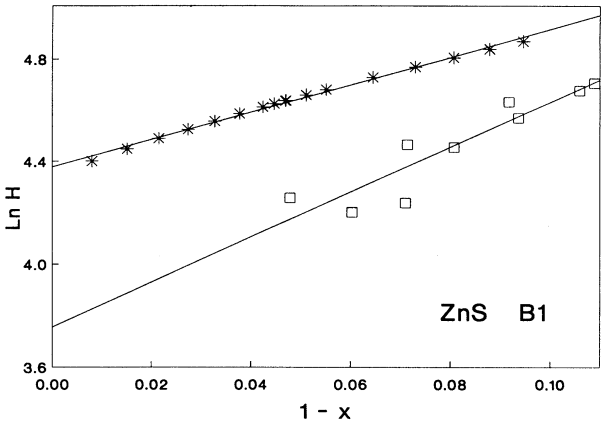

FIG. 3. Plot of $\ln H$ vs $(1-x)$ of the $B1$ phase of ZnS according to PI calculations (stars) and experimental data (squares, Ref. 3). Solid lines are three-parameter Vinet fittings.

phase of ZnO. Contrary to the case of ZnS($B1$), no exploration of empirical EOS has been performed yet for ZnO($B1$). The calculated value of lattice constant at 0 and 10 GPa comes out to be in good agreement with the corresponding experimental values. We now hope that these results on ZnO will stimulate a detailed experimental study of high-pressure phase of ZnO.

In summary, *ab initio* PI calculations have been used to examine the empirical EOS formalisms for fitting the P-V data for high-pressure phase of ZnS. Finally, we would like to emphasize that two different *ab initio* methods, i.e., PI and CRYSTAL (Ref. 6), have been shown to yield similar structural and elastic properties of ZnS($B1$).

TABLE II. Lattice parameter and elastic constants of the rocksalt phase of ZnO.

		a (Å)	B_0 (GPa)	(dB/dP)
0 GPa:	Experiment[a]	4.280		
	PI calculation	4.225	132(134[b])	3.8
10 GPa:	Experiment[a]	4.116		
	PI calculation	4.131	168	

[a]Reference 9.
[b]Obtained from polynomial fitting.

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