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The phase transition, and elastic and thermodynamic properties of CaS derived from first-principles calculations

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Abstract
First-principles calculations of the crystal structures, phase transition, and elastic properties of
B1–B2 phase calcium sulfide (CaS) have been carried out with the plane-wave pseudopotential
density functional theory method. The calculated values (for crystal structures and the phase
transition) are in very good agreement with experimental data as well as with some of the
existing model calculations. The dependence of the elastic constants c_{ij}, the aggregate elastic
modulus, the deviation from the Cauchy relation, and the elastic anisotropy on pressure have
been investigated. The normalized elastic constants c'_{ij} have been introduced to investigate the
elasticity of CaS in detail. Moreover, the variation of the Poisson ratio, Debye temperature, and
longitudinal and transverse elastic wave velocity with pressure P up to 70 GPa at 0 K have been
investigated for the first time.

1. Introduction

The main objective of this work is to investigate systematics of elasticity and thermodynamic properties using *ab initio* results on the phase transition and elastic properties of CaS. This has further implications than the study of the elastic constants of CaS. As an excellent luminescent material, CaS has been considered as an excellent host material for efficient cathode-ray tube phosphors. Therefore, the knowledge of its elastic behavior is very important from a device application point of view. First-principles calculations have been very successful in predicting the phase stability, elastic properties, thermodynamic properties and electronic properties [1–7].

As a wide-band-gap semiconductor material, CaS crystallizes in the rocksalt structure. Wide-band-gap materials

have enormous potential use in devices capable of operating at high power level and high temperature because of the need for optical materials active in the blue–green range. Thus, the study of CaS is of extreme importance. Up to now, some theoretical calculations and experimental measurements [8] have yielded some information on aspects of the structural properties of the B1–B3 structures [9–13] and the electronic properties of the B1 structure [14–16]. Cortonay *et al* [9] have calculated the structural properties using density functional theory within the local density approximation. The structural properties of CaS in the B1–B3 structures have been investigated using nonspherical symmetric effective potentials and a local density functional with non-local pseudopotential calculations by Cortona *et al* [10] and Camp *et al* [11]. Luo *et al* [12] have performed experimental and theoretical investigations of the structural properties of CaS in the B1 and B2 structures. Ekbundit and Chizmeshya [13] have studied

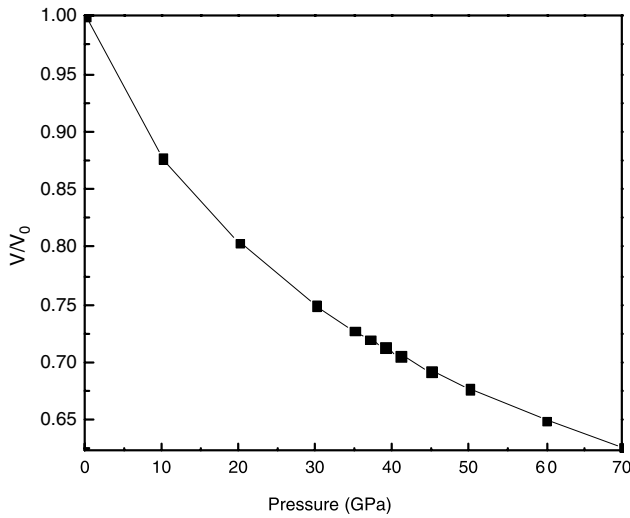[6] Author to whom any correspondence should be addressed.

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Figure 1. Plot of the relative volume V/V_0 of CaS versus pressure, where V_0 is the zero-pressure equilibrium primitive cell volume.

Figure 2. Energy as a function of δ for each strain under 39.8 GPa for the B1 phase CaS.

the structural properties of CaS in the B1 structure using three different electron-gas models and the x-ray diffraction technique. The self-consistent Hartree–Fock method has been applied to compute the electronic structure of CaS in the B1 structure [14]. The band structure of the B1 phase of CaS has been calculated using first-principles local density calculations by Ching *et al* [15]. Chen *et al* [16] have investigated the structural and electronic properties of CaS crystal by using density functional theory.

From the analysis above, we can see that there has been little theoretical and experimental effort focusing on the elastic properties of CaS. Moreover, to the best of our knowledge, systematics of elastic and thermodynamic properties of CaS under high pressure have never been fully investigated. Thus, further theoretical investigations are significantly needed.

2. Theoretical methods

2.1. Elastic properties

Our calculations have been made using the plane-wave pseudopotential density functional theory method, as invoked by the Cambridge serial total energy package (CASTEP) program [17, 18], which allows us to obtain all thermodynamics quantities from the calculated energy–volume points. In the electronic structure calculations, we have applied the non-local ultrasoft pseudopotential introduced by Vanderbilt [19], together with the Perdew–Wang (1991) version (PW91) of the generalized gradient approximation (GGA) exchange–correlation function [20]. Meanwhile, a plane-wave basis set with energy cut-off 500.0 eV has been applied. Pseudo-atomic calculations have been performed for Ca $3s^2 3p^6 4s^2$ and S $3s^2 3p^4$. For the Brillouin-zone sampling, the $10 \times 10 \times 10$ Monkhorst–Pack mesh has been used, in which the self-consistent convergence of the total energy is at 10^{-6} eV/atom. All the total energy electronic structure calculations have been implemented through the CASTEP code.

The total energy E of the B1-type and B2-type CaS has been calculated at different primitive cell volumes, and then
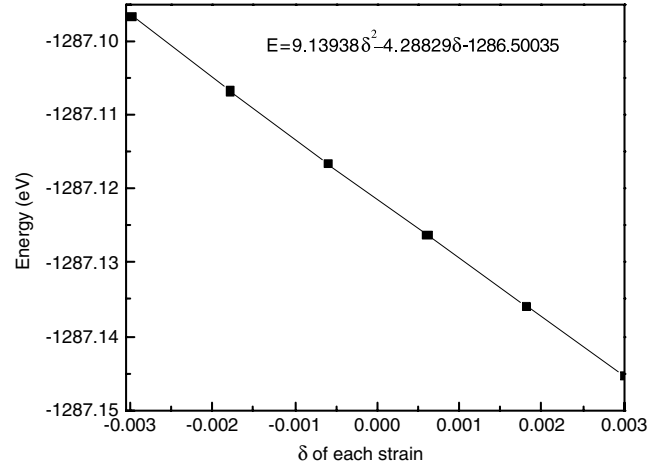
least-squares fits of these energy–volume (E–V) data have been made to the Birch–Murnaghan equation of state (B–M EOS) [21]. At zero temperature and pressure, the equilibrium volume V_0, the bulk modulus B_0, and the pressure derivative B_0' have been estimated by least-squares fitting of calculated V–E curves to the integrated form of the third-order Birch–Murnaghan equation of state. The calculated equation of state of CaS is shown in figure 1.

To calculate the elastic constants under hydrostatic pressure, we have used the strains as non-volume conserving because this method is consistent with our calculated elastic constants using the stress–strain coefficients, which are appropriate for the calculation of the elastic wave velocities. The elastic constants c_{ijkl}, with respect to the finite strain variables are defined as [22–24]

$$c_{ijkl} = \left(\frac{\partial \sigma_{ij}(x)}{\partial e_{kl}} \right)_X, \qquad (1)$$

where σ_{ij} and e_{kl} are the applied stress and Eulerian strain tensors, and X and x are the coordinates before and after the deformation. For the isotropic stress, we have [20–25]

$$c_{ijkl} = C_{ijkl} + \frac{P}{2} \left(2\delta_{ij}\delta_{kl} - \delta_{il}\delta_{jk} - \delta_{ik}\delta_{jl} \right), \qquad (2)$$

$$C_{ijkl} = \left(\frac{1}{V(x)} \frac{\partial^2 E(x)}{\partial e_{ij} \partial e_{kl}} \right)_X, \qquad (3)$$

where C_{ijkl} denotes the second-order derivatives with respect to the infinitesimal strain (Eulerian), and δ is the finite strain variable. The elastic behavior of a completely asymmetric material is specified by 21 independent elastic constants, while for an isotropic material, the number is 2. The necessary number is determined by the symmetry of the materials and it is 3 for cubic crystal. These independent elastic constants are usually referred to as c_{11}, c_{12} and c_{44}. In our calculations, for all strains, $\delta = \pm 0.0006$, ± 0.00018, ± 0.003 have been taken to calculate the total energies E for the strained crystal structure respectively. The calculated E-δ points have been then fitted to second-order polynomials $E(V, \delta)$. In figure 2,

Table 1. The lattice constants (Å), aggregate elastic modulus (GPa), pressure derivatives of bulk modulus and the elastic constants (GPa) for the B1 and B2 phases of CaS at $T = 0$ K and $P = 0$ GPa.

		a_0	B_0	B_0'	c_{11}	c_{12}	c_{44}
B1	Present work	5.6899	58.93	4.72	122.59	21.99	33.13
	Ref [9]	5.598	65.2	4.1, 3.409			
	Ref [10]	5.6	65.0				
	Ref [11]	5.4279	63.8	3.9			
	Ref [13]	5.651 (VIB)	62.3 (VIB)	4.2 (VIB)			
	Ref [13]	5.645 (SCIB)	67.8 (SCIB)	4.06 (SCIB)			
	Ref [13]	5.591 (PIB)	72.7 (PIB)	4.15 (PIB)			
	Ref [16]	5.701	53.79	6.18			
	Exp [12]	5.689	64.0	4.2			
	Exp [13]	5.696	52.6 ± 1.4	4.0			
			56.3 ± 0.6	4.6 ± 0.2			
			52.4 ± 1.0	4.9 ± 0.2			
B2	Present work	3.4753	71.0	4.61	186.50	−1.93	−3.23
	Ref [9]	3.409	71.2	4.2			
	Ref [10]	3.41, 3.44	71.0, 72.0	6.12			
	Ref [11]	3.3234	66.4	3.9			
	Ref [16]	3.482	60.9	5.16			
	Exp [12]	3.46	64.0	4.2			

we have been plotted the E-δ curve of the B1 phase CaS at 39.8 GPa.

Note that under hydrostatic compression, in order to make comparison with experimental results, the elastic constants C_{ij} must be transformed into the observable elastic constants c_{ij} defined with respect to the finite strain variables [24–27]. C_{ij} is transformed into c_{ij} in the case of hydrostatic pressure P as follows:

$$c_{11} = C_{11}, \qquad c_{12} = C_{12} + P, \qquad c_{44} = C_{44} - \frac{P}{2}. \quad (4)$$

In this work, we have estimated the bulk modulus B and the shear modulus G for CaS in terms of the following forms:

$$B = (c_{11} + 2c_{12})/3, \quad (5)$$

$$G = \frac{1}{2}\left[\frac{c_{11} - c_{12} + 3c_{44}}{5} + \frac{5c_{44}(c_{11} - c_{12})}{4c_{44} + 3(c_{11} - c_{12})}\right]. \quad (6)$$

2.2. Thermodynamic properties

The average wave velocity v_m has been approximately calculated from

$$v_m = \left[\frac{1}{3}\left(\frac{2}{v_t^3} + \frac{1}{v_l^3}\right)\right]^{-1/3}, \quad (7)$$

where v_l and v_t are the longitudinal and the transverse elastic wave velocity respectively, which are obtained from Navier's equation in the following forms:

$$v_l = \sqrt{\frac{3B + 4G}{3\rho}}, \quad (8)$$

$$v_t = \sqrt{\frac{G}{\rho}}, \quad (9)$$

where G is the shear modulus, B is the bulk modulus, and ρ is the density.

To investigate the Debye temperature of CaS, we have applied the quasi-harmonic Debye model [28], in which the non-equilibrium Gibbs function $G^*(V; P, T)$ takes the form

$$G^*(V; P, T) = E(V) + PV + A_{\text{Vib}}(\Theta(V); T), \quad (10)$$

where $\Theta(V)$ is the Debye temperature, and the vibrational term A_{Vib} is the Helmholtz free energy for lattice vibrations as given in the quasi-harmonic Debye model

$$A_{\text{Vib}}(\Theta; T) = nKT\left[\frac{9}{8}\frac{\Theta}{T} + 3\ln(1 - e^{-\Theta/T}) - D(\Theta/T)\right], \quad (11)$$

where n is the number of atoms per formula unit, and the Debye integral $D(\Theta/T)$ can be written as

$$D(y) = \frac{3}{y^3}\int_0^y \frac{x^3}{e^x - 1}\,dx. \quad (12)$$

For an isotropic solid, Θ is expressed as

$$\Theta = \frac{\hbar}{k}[6\pi^2 V^{1/2}n]^{1/3} f(\sigma)\sqrt{\frac{B_S}{M}}, \quad (13)$$

where M is the molecular mass per formula unit, B_S is the adiabatic bulk modulus, which can be approximated by the static compressibility [28]

$$B_S \approx B(V) = V\left(\frac{d^2 E(V)}{dV^2}\right). \quad (14)$$

The Poisson ratio σ and $f(\sigma)$ [29, 30] can be given in the following forms:

$$\sigma = \frac{3B - 2G}{6B + 2G}, \quad (15)$$

$$[f(\sigma)]^3 = 3\left[2\left(\frac{2}{3}\frac{1+\sigma}{1-2\sigma}\right)^{3/2} + \left(\frac{1}{3}\frac{1+\sigma}{1-\sigma}\right)^{3/2}\right]^{-1}. \quad (16)$$
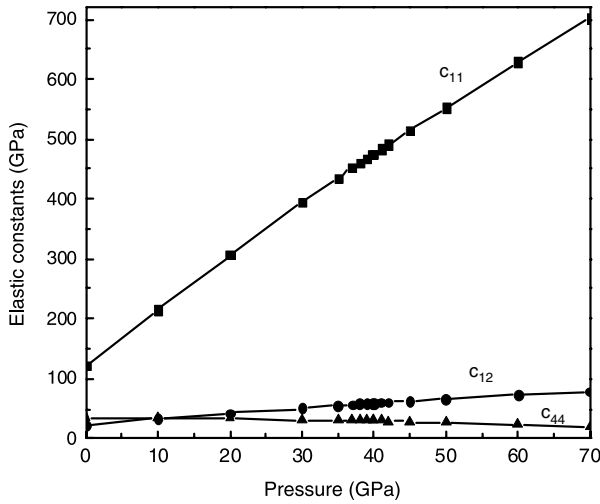
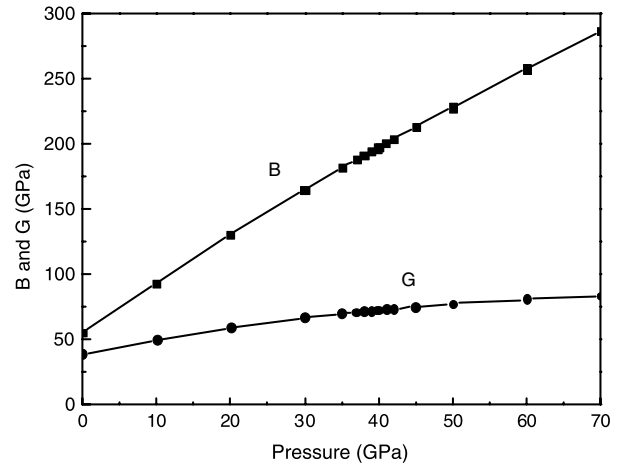**Figure 3.** Static elastic constants of CaS as a function of pressure.

Figure 4. Bulk and shear modulus of CaS as a function of pressure.

3. Results and discussion

In table 1, we have presented the calculated lattice constant (a_0) of the equilibrium volume, the bulk modulus B_0 and its pressure derivative B_0' for the B1- and B2-type CaS at zero temperature and pressure, which are consistent with the experimental and theoretical results [8–13, 16]. The calculated elastic constants of the B1- and B2-type CaS have also been listed in table 1. Although there are no values available to compare with the elastic constants, our data will be beneficial to future investigation. Noticeably, the elastic constant c_{12} equals -1.39 GPa and c_{44} equals -3.23 GPa for the B2-type CaS. For cubic crystals, their elastic constants satisfy the generalized elastic stability criteria under hydrostatic pressure

$$c_{11} + 2c_{12} > 0, \qquad c_{44} > 0, \qquad c_{11} - c_{12} > 0. \quad (17)$$

So we can confirm that the mechanical properties of the B2-type CaS are not stable. That is to say, the B2-type CaS is unstable at zero temperature and pressure.

In table 2, we have presented the pressure dependence of the elastic constants c_{ij} and the aggregate elastic modulus (B, G) of the B1 phase CaS at zero temperature and different pressures. It has been found that c_{11} varies substantially under pressure when compared with the variations in c_{12} and c_{44}. The elastic constant c_{11} represents elasticity in length. A longitudinal strain produces a change in c_{11}. The elastic constants c_{12} and c_{44} are related to the elasticity in shape, which is a shear constant. A transverse strain causes a change in shape without a change in volume. Therefore, c_{12} and c_{44} are less sensitive to pressure as compared with c_{11}. As pressure increases, c_{11}, c_{12} and B for the B1 phase CaS at zero temperature increase monotonically, but c_{44} decreases monotonically. The relation of pressure to elastic constants has been plotted in figure 3. The dependence of the bulk modulus and the shear modulus for CaS under pressure are shown in figure 4. In figure 4, we can see that the bulk modulus and the shear modulus of CaS increase linearly with pressure.

Experiment indicated that the phase transition of CaS from the B1 phase to the B2 phase occurs at 40 GPa or 37.1 ±

Table 2. The aggregate elastic modulus (GPa), and the elastic constants (GPa) for the B1 phase of CaS at $T = 0$ K and $P = 0$ GPa.

P	c_{11}	c_{12}	c_{44}	B	G
0	122.59	21.99	33.13	55.52	40.78
10	214.43	33.23	33.02	93.63	52.33
20	306.91	42.29	32.92	130.49	62.34
30	394.18	50.50	31.62	165.06	69.90
35	435.56	55.12	30.74	181.93	72.96
37	452.39	57.44	30.33	189.09	74.09
38	459.90	57.74	30.12	191.79	74.63
39	467.85	58.48	29.90	194.93	75.17
39.8	474.27	59.05	29.70	197.45	75.57
40	475.55	59.01	29.66	197.85	75.67
41	484.16	60.44	29.42	201.68	76.17
42	491.33	60.45	29.17	204.07	76.66
45	514.66	62.49	28.41	213.21	78.08
50	553.28	66.00	26.98	228.42	80.17
60	629.34	73.03	23.48	258.46	83.37
70	702.85	79.15	19.89	287.05	86.13

2.9 GPa [12]. Compared with other results [9–11, 13, 16], our result (39.8 GPa, which is obtained in figure 5) is in better agreement with experimental values [12]. In order to investigate the systematics of elasticity and thermodynamic properties clearly and in detail, in this work, we have set the calculated pressure ranges to be wider than the pressure ranges where the B1 phase is stable. Calculations of the pressure dependence of the elastic properties for the B2 phase will be reported in another publication. The approach is seen to be permitted when we refer to other work [31–33].

We might study theoretically the elasticity of CaS by means of models which assume that the interatomic forces have a certain shape and directionality. One common approach is to assume that the atoms are connected with springs and that the resulting forces are only in the direction of the nearest neighbors (central force mode). The deviation from the Cauchy relation $\delta = c_{12} - c_{44} - 2P$ is a measure of the contribution from the noncentral many-body force since the Cauchy relation $c_{12} = c_{44} + 2P$ should be satisfied when interatomic potentials are purely central. Figure 6 shows the pressure dependence of δ. The deviation δ becomes larger as
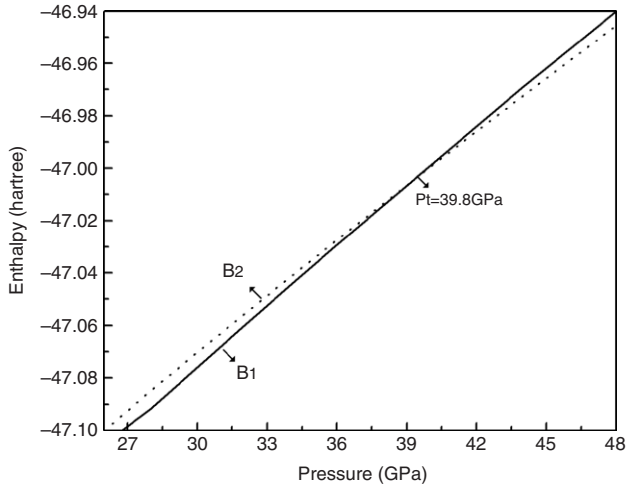
Figure 5. Enthalpy as a function of pressure for the B1 and B2 phases of CaS.
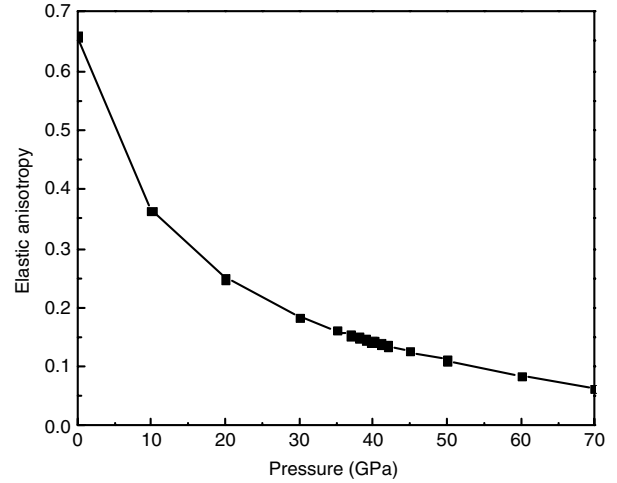

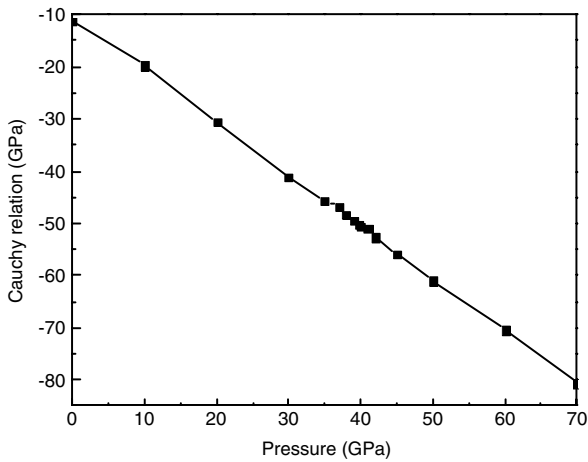**Figure 7.** The pressure dependence of the elastic anisotropy of CaS.

Figure 6. The pressure dependence of the Cauchy relation of CaS.
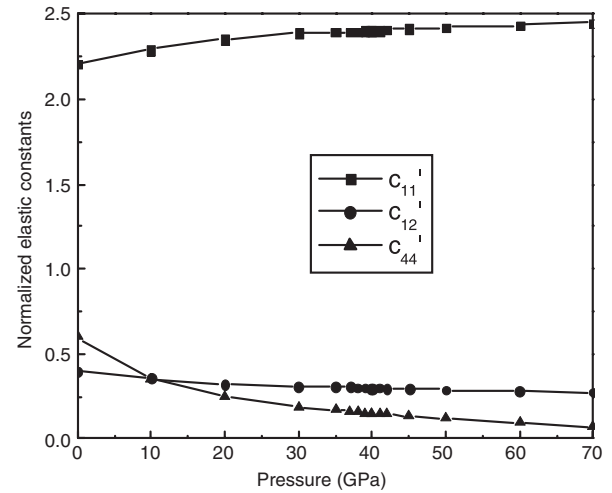

Figure 8. The pressure dependence of the normalized elastic constants of CaS.

the pressure increases, which proves that the noncentral many-body force becomes more and more important at high pressure. Thus, it is necessary to consider the third-order and the fourth-order elastic constants when the anharmonic properties of CaS are discussed by means of elastic constants at high pressure.

Figure 7 shows the pressure dependence of the elastic anisotropic parameter A at the pressure up to 70 GPa, which is the ratio of two shear moduli c_{44} and $(c_{11} - c_{12})/2$, and which becomes unity for isotropic elasticity. It is known that even the cubic crystal, which is isotropic in structure, has elastic anisotropy as a result of a fourth-rank tensor property of elasticity. From figure 7, we can see that the B1 phase CaS exhibits low elastic anisotropy at zero pressure and the degree of the anisotropy increases with pressure. The anisotropy increases when pressure increases, which indicates that the anisotropy is more obvious under pressure. In order to investigate elasticity of CaS in detail, we have used normalized elastic constants c'_{ij} [30]. The value of c'_{ij} is obtained by dividing a specific elastic constant by the bulk modulus

$$c'_{ij} = c_{ij}/B = 3c_{ij}/(c_{11} + 2c_{12}). \quad (18)$$

Divided by the bulk modulus, the interatomic forces are normalized with an average restoring force of the system. At zero pressure, if a cubic crystal is elastically ideal, namely an isotropic Cauchy solid, 1.8, 0.6, and 0.6 for c'_{11}, c'_{12}, and c'_{44} can be found respectively. We have extended the concept of the normalized elastic constant to the high pressure condition. c'_{ij} for CaS as a function of pressure has been plotted in figure 8. The figure shows that all normalized elastic constants c'_{ij}, c'_{44} and c'_{12} decrease slowly with increasing pressure. The values of c'_{12} decrease slowly and the figure shows that the pressure dependence of c'_{12} is almost linear. Comparing with c'_{12} and c'_{44} under pressure, c'_{11} alone increases.

The pressure dependence of the sound velocity, Poisson ratio, and Debye temperature are shown in figures 9 and 10 respectively. The figures show that the sound velocity, Poisson ratio, and Debye temperature increase with pressure. To illustrate the dependence of the longitudinal, transverse velocity (v_l, v_t), the Debye temperature (Θ), and the Poisson ratio on the applied pressure in detail, we have made a nonlinear fourth-order polynomial fitting up to 70 GPa. The
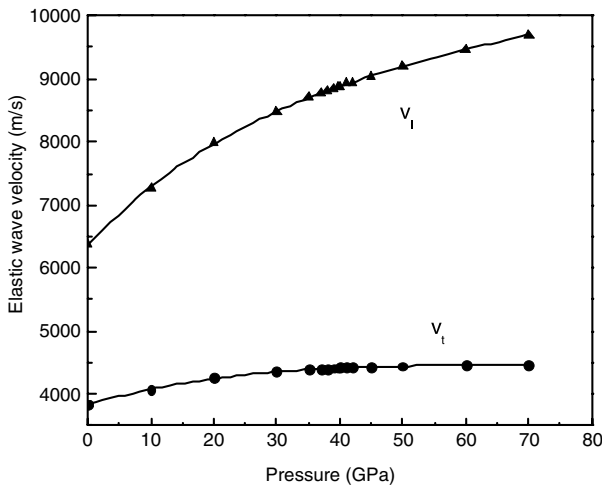
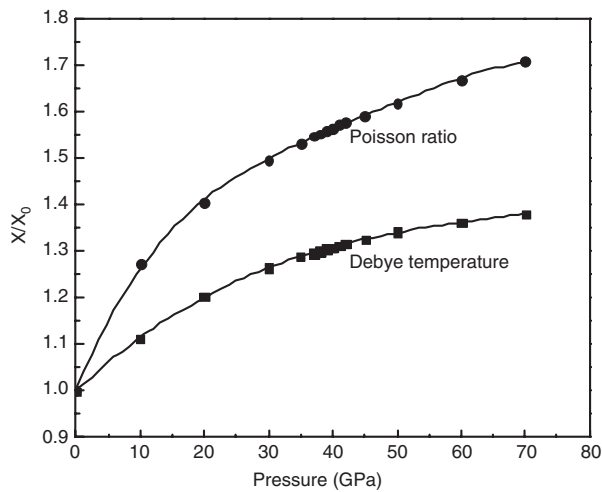**Figure 9.** The pressure dependence of the elastic wave velocity of CaS.

Figure 10. Variations of thermodynamic parameters X (X: Poisson ratio, Debye temperature) with pressure P. These are normalized by X/X_0, where X and X_0 are the Poisson ratio, Debye temperature under any pressure P and zero temperature.

polynomials obtained are

$$v_t (\text{m s}^{-1}) = 3837.55 + 27.63P - 0.391P^2 + 1.36 \times 10^{-3} P^3$$
$$+ 5.456 \times 10^{-6} P^4, \tag{19}$$

$$v_l (\text{m s}^{-1}) = 6366.65 + 105.13P - 1.483P^2$$
$$+ 1.227 \times 10^{-2} P^3 - 4.03 \times 10^{-5} P^4, \tag{20}$$

$$\frac{\sigma}{\sigma_0} = 1.00262 + 0.03376P - 8.88 \times 10^{-4} P^2$$
$$+ 1.26115 \times 10^{-5} P^3 - 6.78325 \times 10^{-8} P^4, \tag{21}$$

$$\frac{\Theta}{\Theta_0} = 0.99961 + 0.01334P - 1.81 \times 10^{-4} P^2$$
$$+ 1.25 \times 10^{-6} P^3 - 1.9665 \times 10^{-9} P^4. \tag{22}$$

The experimental values of the sound velocity, Poisson ratio, and Debye temperature under high pressure are not yet available for comparison, but when we consider the

case of [31–33] (which investigated thermodynamic properties using high pressure elastic constants agreeing very well with experimental data), our predicted results should be credible. It should be pointed out that the significance of this work is not only in calculating the high pressure elastic constants for the first time but also in predicting the sound velocity, Poisson ratio, and Debye temperature for CaS.

Acknowledgment

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