Cohesive properties and behaviour under pressure of CaS, CaSe, and CaTe: results of *ab initio* calculations

Cohesive properties and behaviour under pressure of CaS, CaSe, and CaTe: results of *ab initio* calculations

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Abstract. We have performed *ab initio* calculations of CaS, CaSe and CaTe in the B1 (NaCl) and B2 (CsCl) phase. For each compound, we report results for the standard cohesive properties (equilibrium lattice parameters, bulk moduli, cohesive energies), for the equation of state and for the phase transition (transition pressure, compression ratio at the phase transition, percentage change of volume in the phase transition). A detailed comparison with recent experimental results is also performed.

1. Introduction

In a recent article [1], Luo *et al* performed an extensive experimental study of the behaviour of CaS, CaSe and CaTe under pressure. They showed that the first two compounds have a phase transition from the B1 (NaCl) to the B2 (CsCl) phase at a pressure of a few tenths of a GPa, and that CaTe first transforms to an intermediate state which is a mixture of the NaCl and MnP phases and then, at a pressure slightly greater than 30 Gpa, to the B2 phase. Their work, together with previous studies of CaO [2–4] and of CaTe [5] performed by other authors, provides a complete experimental description of the calcium chalcogenides under pressures up to almost 60 GPa.

In a preceding article [6], Cortona *et al* reported the results of *ab initio* calculations for all the alkali-earth sulphides. As their article was written practically at the same time as [1], a comparison of the theoretical results for CaS with the experimental data of Luo *et al* could not be included. The calculated equation of state was compared with the old data of Perez-Albuerne and Drickamer [7] (which only concern the B1 phase) and the transition pressure with the value estimated by Zimmer *et al* [5] on the basis of the observed trend of the transition pressures of various compounds.

In the present paper, the results of *ab initio* calculations for all the compounds considered by Luo *et al* [1] are reported, and an extensive comparison is made with their experimental data.

2. The method

As the method used for our calculations has been extensively described elsewhere [8, 9], only a brief summary of it is reported here. The framework is that of density-functional

theory [10], and the method is based on a partition of a system in atomic-like subsystems. The electron density of each subsystem (to be determined) is written in terms of one-electron wavefunctions as follows:

$$\rho_j(\mathbf{r}) = \sum_i 2n_{ij}|\psi_{ij}(\mathbf{r})|^2 \tag{1}$$

where j specifies the subsystem, i stands for the quantum numbers characterizing the wavefunctions of the subsystem, n_{ij} are fermionic occupation numbers and the factor of 2 comes from the sum on the spin coordinate. The total electron density ρ of the overall system is then constructed by superposing the subsystem densities.

Considering the total energy of the system, all the contributions can be explicitly written in terms of the total electron density (at least if the local approximation is used for the exchange and correlation energy) with the exception of the kinetic energy. The latter is then split into two terms,

$$T[\rho] = \sum_j T[n_{ij}, \psi_{ij}] + \left(T[\rho] - \sum_j T[n_{ij}, \psi_{ij}] \right) \tag{2}$$

where the first is the sum of the internal kinetic energies of the subsystems defined by the usual expression

$$T[n_{ij}, \psi_{ij}] = \sum_i 2n_{ij}\langle\psi_{ij}| -\tfrac{1}{2}\nabla^2|\psi_{ij}\rangle \tag{3}$$

while the second gives the contribution to the kinetic energy coming from the interactions among the subsystems. For this second term an approximation is introduced: if $T^{approx}[\rho]$ is any approximate expression of the kinetic energy functional, the parenthesis in equation (2) is replaced by $T^{approx}[\rho] - \sum_j T^{approx}[\rho_j]$. This gives rise to a total energy functional which can be written as follows:

$$E_v^{approx}[n_{ij}, \psi_{ij}] = \sum_j T[n_{ij}, \psi_{ij}] + \left(T^{approx}[\rho] - \sum_j T^{approx}[\rho_j] \right) + J[\rho] + E_{xc}^{approx}[\rho]$$
$$+ \int V_{ext}(\mathbf{r})\rho(\mathbf{r})\,\mathrm{d}^3r \tag{4}$$

where $V_{ext}(\mathbf{r})$ is the potential generated by the nuclear charges, J is the electrostatic interaction energy of the electrons and E_{xc}^{approx} is any approximate expression of the exchange-correlation energy functional. Minimizing $E_v^{approx}[n_{ij}, \psi_{ij}]$ with respect to the wavefunctions ψ_{ij} and the occupation numbers n_{ij}, the following equation is obtained:

$$\left(-\frac{1}{2}\nabla^2 + V_{ext}(\mathbf{r}) + \frac{\delta J}{\delta\rho} + \frac{\delta E_{xc}^{approx}}{\delta\rho} + \frac{\delta T^{approx}}{\delta\rho} + \frac{\delta T^{approx}}{\delta\rho_j} \right)\psi_{ij}(\mathbf{r}) = \varepsilon_{ij}\psi_{ij}(\mathbf{r}) \tag{5}$$

which must be solved self-consistently, with the occupation numbers chosen according to Fermi statistics [8]. Using the solutions of equation (5), one can construct the electron density of the system and calculate its total energy.

3. Technical remarks

The calculations were performed using the local-density approximation for the inter-subsystem kinetic energy, for the exchange and for the correlation energy. The latter was taken into account by means of the Perdew and Zunger expression [11].

The effective potential in equation (5) was spherically-averaged around each atomic site. However, the total energy of the system was calculated by performing tri-dimensional

integrations within the primitive cell: thus, the nonspherical contributions are included at the level of accuracy of first-order perturbation theory. Further details on this subject can be found in [12].

For each compound, we have performed 21 self-consistent calculations corresponding to lattice parameters spaced at 0.05 Å for the B1 structure and 0.03 Å for the B2 structure. These lattice parameters were chosen to be approximately symmetrically distributed around the calculated equilibrium lattice constant. A very high level of self-consistency was required [13]. The calculated total energies were fitted by polynomials of the lattice parameter a and of $V^{-2/3}$, V being the volume of the primitive cell of the crystal. Polynomials of degrees varying from two up to six were used in both cases. The fits were repeated, reducing progressively the number of total energy values in a symmetric way around the minimum in order to evaluate the uncertainties in the calculated values. An example of this kind of analysis is given in tables 1 and 2, where we report part of the results we have found for the bulk modulus of CaSe in the B1 phase (table 1), and for its derivative with respect to the pressure (table 2). On the basis of this analysis, we have reported in tables 3–5 results which are affected by numerical errors smaller than one unity on the last digit shown.

Table 1. Calculated bulk modulus values of CaSe in the B1 phase.

Polynomial variables	No total energy values used in fit	Degrees of polynomials used for best fit				
		2	3	4	5	6
a	21	52.865	58.508	56.458	56.233	56.242
	15	60.480	57.673	56.196	56.241	56.249
	9	59.428	56.653	56.247	56.254	56.442
$V^{-2/3}$	21	56.022	56.204	56.246	56.244	56.242
	15	56.382	56.232	56.246	56.241	56.243
	9	56.366	56.222	56.239	56.249	56.412

Table 2. Values of the bulk modulus derivative with respect to the pressure at $p = 0$ for CaSe in the B1 phase.

Polynomial variables	No total energy values used in fit	Degrees of polynomials used for best fit			
		3	4	5	6
a	21	3.827	4.216	4.141	4.138
	15	4.254	4.183	4.143	4.162
	9	4.292	4.197	4.208	4.227
$V^{-2/3}$	21	4.132	4.133	4.136	4.137
	15	4.126	4.134	4.142	4.170
	9	4.174	4.184	4.204	4.256

For the compounds considered in the present paper, an extensive comparison of our results with those of other *ab initio* density-functional calculations is impossible. In fact, we have found only one calculation of the cohesive properties for one of these cristals: this was carried out by Yamashita and Asano for CaS by the KKR method [14]. The lattice parameter, the cohesive energy and the bulk modulus obtained by these authors were

5.708 Å, 10.09 eV and 61 GPa, respectively. Furthermore, they found that the equilibrium phase at $p = 0$ should be the B2 one, in contradiction with the experiment. In contrast, some oxides (MgO and CaO, in particular) have been extensively studied in the past by a variety of *ab initio* methods. A detailed comparison with our results can be found in [15] (see also [12] for a comparison of the B1 → B2 transition pressures). We just recall here that the main conclusions were the following: (i) for these compounds our method is as accurate as the full-potential linearized-augmented-plane-waves (FLAPW) method, and more accurate than the methods using pseudopotentials or the atomic-sphere approximation; (ii) the differences between our results and those obtained by a given approach (for example, FLAPW) are not greater than the differences between results obtained by different band structure calculations (for example, FLAPW and the pseudopotential method, or KKR and LMTO).

Finally, a comparison is also possible in the case of MgS. For this compound, our results [6] agree very well with those obtained by Froyen *et al* [16], who used an *ab initio* pseudopotential approach.

4. Results and discussion

The results of our calculations for the cohesive properties of CaS, CaSe and CaTe are reported in tables 3 and 4 for the B1 and B2 phases, respectively. In the same tables we also report the corresponding experimental values [1, 17]. We recall that B and B', the bulk modulus and the derivative of the bulk modulus with respect to the pressure at $p = 0$, have been obtained in [1] by fitting the results of static compression measurements by a Birch–Murnagham equation of state:

$$p = \frac{3}{2}B\left[\left(\frac{V}{V_0}\right)^{-7/3} - \left(\frac{V}{V_0}\right)^{-5/3}\right]\left\{1 + \frac{3}{4}(B' - 4)\left[\left(\frac{V}{V_0}\right)^{-2/3} - 1\right]\right\}. \quad (6)$$

It is important to notice that V_0, the equilibrium volume at $p = 0$, is a measured quantity for the B1 phase, while it is a free fitting parameter for the B2 phase.

Table 3. Calculated cohesive properties of CaS, CaSe and CaTe in the B1 (NaCl) phase. The experimental values of the lattice parameter a, of the bulk modulus B and of the derivative of the bulk modulus at $p = 0$, B', have been taken from [1]; the experimental cohesive energies (referred to free atoms) have been deduced from the data reported in [17].

		a (Å)	E (eV)	B (GPa)	B'
CaS	Exp.	5.689	9.7	64	4.2
	Theor.	5.598	9.95	65.2	4.1
CaSe	Exp.	5.916	8.0	51	4.2
	Theor.	5.829	8.94	56.2	4.1
CaTe	Exp.	6.348	—	41.8	4.3
	Theor.	6.231	7.61	45.4	4.2

Comparing the theoretical and the experimental results, it appears that they are in close agreement. For the B1 phase, the discrepancies are smaller than 2% and 10% for the lattice parameters and the bulk moduli, respectively. Furthermore, the thermal effects are not included in the theoretical calculations. If they are taken into account, the lattice parameters will slightly increase and the bulk moduli will decrease by a few GPa, thus the agreement between theory and experiment will be enhanced. For the B2 phase, the discrepancies for

Table 4. Calculated cohesive properties of CaS, CaSe and CaTe in the B2 (CsCl) phase. The experimental values of $V_0(B2)/V_0(B1)$, B and B' have been taken from [1].

		$V_0(B2)/V_0(B1)$	B (GPa)	B'
CaS	Exp.	0.90	64	4.2
	Theor.	0.904	71.2	4.2
CaSe	Exp.	0.91	51	4.2
	Theor.	0.911	61.0	4.2
CaTe	Exp.	0.95	41.8	4.3
	Theor.	0.907	50.2	4.2
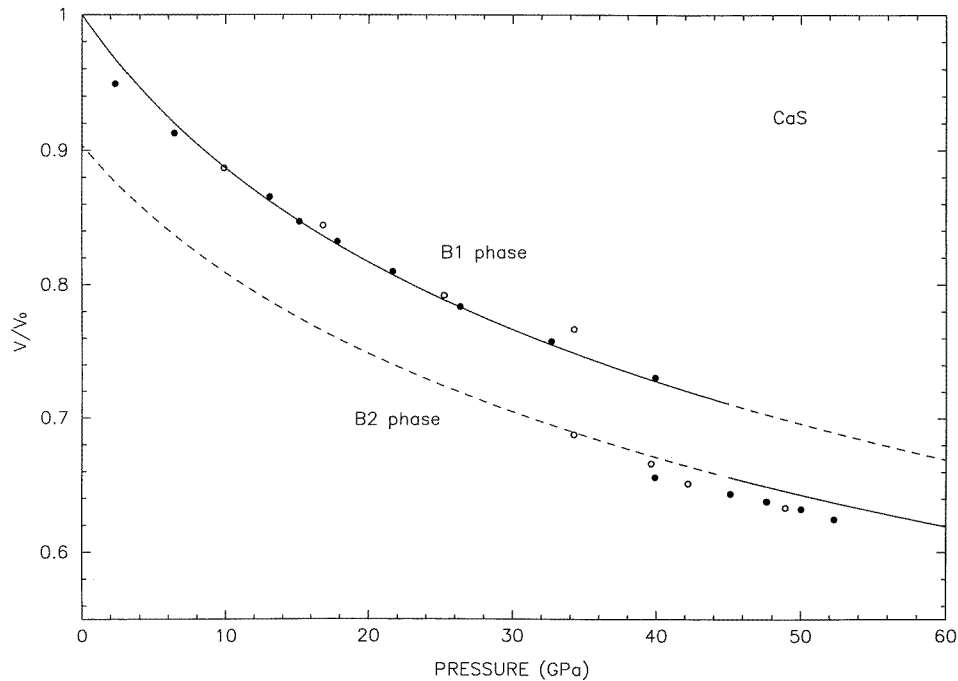
Figure 1. Equation of state of CaS. The full curve corresponds to the (calculated) equilibrium phase. Full and open circles correspond to experimental data obtained by increasing and decreasing the pressure, respectively.

the bulk moduli are greater, while the calculated and the experimental values of the ratio $V_0(B2)/V_0(B1)$ agree very well. However, these remarks should be considered with some caution. For the B2 phase of each compound, there are only few experimental data points in a small range of values of p: consequently, the uncertainties on the fitted parameters should be quite large. Furthermore, it can be noticed that Luo *et al* reported identical values of B and B' for the B1 and B2 phases. This may indicate that the available experimental data were not sufficient for a three-parameter fit and that these authors have limited themselves to optimize the value of $V_0(B2)/V_0(B1)$.

In figures 1–3, we have reported the experimental compression ratios as a function of the applied pressure, using the same conventions as in [1]: full and open circles correspond
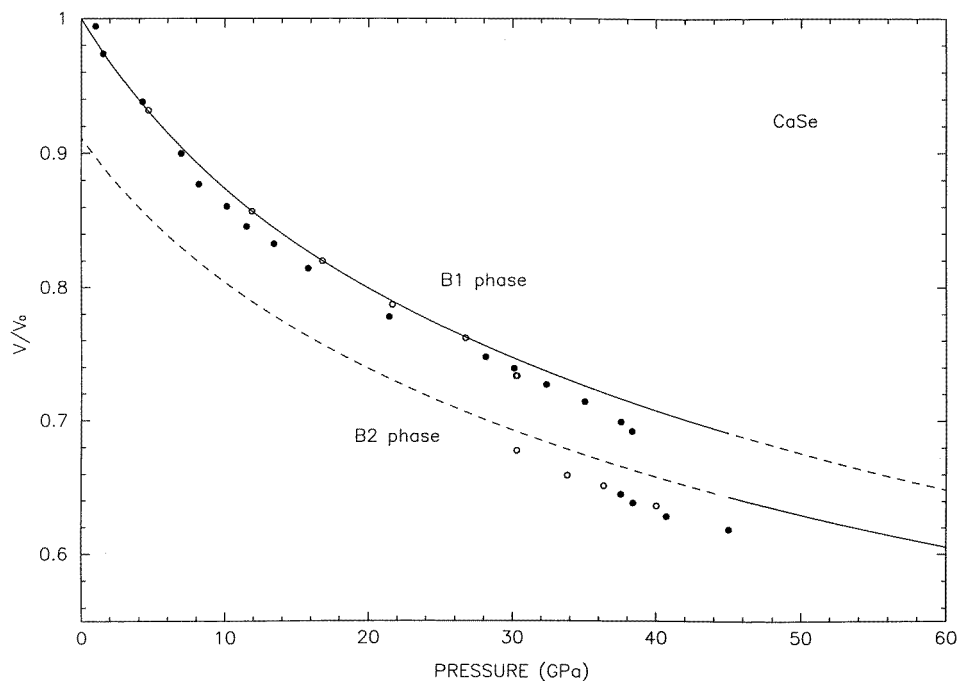
Figure 2. Equation of state of CaSe. The full curve corresponds to the (calculated) equilibrium phase. Full and open circles correspond to experimental data obtained by increasing and decreasing the pressure, respectively.

to measurements performed by increasing and decreasing the pressure, respectively. In the case of CaTe, Luo *et al* have only reported results for increasing pressures. The reason for this is probably that the hysteresis of the compression–decompression process for this compound is particularly strong: decreasing the pressure, the transformation to the B1 phase is completed only at 1 GPa. Furthermore, CaTe, before transforming to the B2 structure, transforms to a state which is a mixture of the NaCl and the MnP phases (the compression ratios of the latter are represented by full squares in figure 3). Increasing the pressure, this state is observed for pressures between about 25 GPa and 33 GPa.

The curves reported in the figures correspond to the calculated equations of state. It appears that theory and experiment agree very well for the B1 phase. In the B2 case, our calculations slightly overestimate the compression ratios of CaS and CaSe. In order to understand the real meaning of this discrepancy, it is important to emphasize the role of $V_0(B2)/V_0(B1)$, the ratio of the equilibrium volumes at $p = 0$ of the B2 and B1 phases. In fact, what is shown in the figures is not the equation of state of the B2 phase for the various compounds, but its product with $V_0(B2)/V_0(B1)$. Thus, the discrepancies can be due to the imprecision either of the values of the parameters entering the equation of state or of the ratio $V_0(B2)/V_0(B1)$. For example, considering CaS, the calculated value of $V_0(B2)/V_0(B1)$ is 0.904. If, instead of this value, $V_0(B2)/V_0(B1)$ is assumed to be equal to 0.89, using the calculated values of B and B' reported in table 4, one finds an *excellent* agreement with the experimental data. As the calculated value of B is quite different from the experimental one, this means that large changes of B can be compensated by slight modifications of $V_0(B2)/V_0(B1)$, the agreement with the experimental data remaining
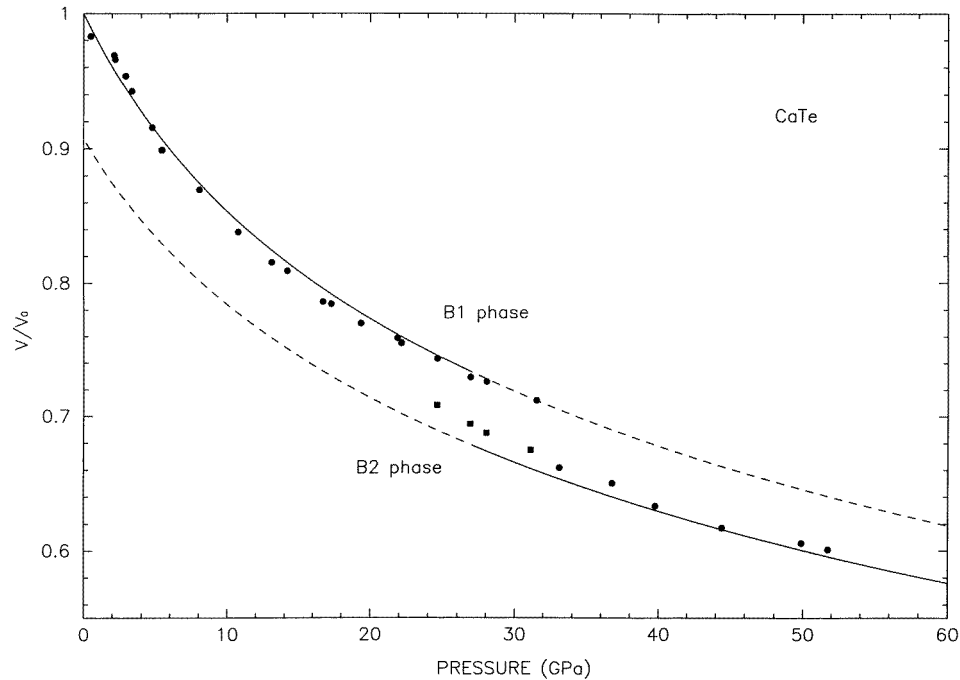
Figure 3. Equation of state of CaTe. The full curve corresponds to the (calculated) equilibrium phase. The circles correspond to experimental data for the B1 and B2 phases; the squares correspond to data for the intermediate phase which is a mixture of the NaCl and MnP ones. Only experimental results obtained for increasing pressures are reported.

Table 5. Transition from the B1 (NaCl) to the B2 (CsCl) phase: p_t = transition pressure; V_t/V_0 = compression ratio of the B1 phase at the transition pressure; $-\Delta V/V$ = percentage change of volume. Experimental values from [1].

		p_t (GPa)	V_t/V_0	$-\Delta V/V$ (%)
CaS	Exp.	40	0.73	10.2
	Theor.	45	0.71	7.7
CaSe	Exp.	38	0.70	7.7
	Theor.	45	0.69	7.1
CaTe	Exp.	33	0.74	—
	Theor.	27	0.73	6.1

practically the same. In other words, the discrepancies between our calculated equations of state and the experimental data can be interpreted as a relatively large error on the bulk modulus or a relatively small error on $V_0(\text{B2})/V_0(\text{B1})$, both interpretations being compatible with the available experimental data.

Finally, in table 5 are reported the calculated and the experimental transition pressures and some related quantities: the compression ratio of the B1 phase at the transition pressure and the percentage change of volume in the phase transition. It appears that our calculations slightly overestimate the transition pressures of CaS and CaSe, while, in the case of CaTe, the

calculated value is within the range of pressures where this compound is in the intermediate state. The compression ratios of the B1 phase at the transition pressures are in good agreement with the experiment: this is a consequence of the good quality of the theoretical equations of state and of the fact that the calculated transition pressures are not far from the experimental ones. In contrast, the discrepancies are relatively large for the percentage changes of volume: these discrepancies are almost entirely due to the overestimation of the compression ratio of the B2 phase of CaS and CaSe.

5. Conclusions

Our method gives a good description of CaS, CaSe and CaTe in the B1 phase. The calculated cohesive properties are in good agreement with the experiment, and the same is true for the equations of state in the overall range of pressure where the B1 phase is the equilibrium one.

For the B2 phase, there are some discrepancies between theory and experiment. The interpretation of these discrepancies is not easy: this is mainly due to the fact that large changes of B can be compensated by small changes of $V_0(B2)/V_0(B1)$ without affecting in a significant way the agreement with the experiment. This conclusion is true not only for the compounds considered in this paper, for which only a small set of experimental data is available, but also for CaO, whose B2 phase has been investigated in a larger range of pressures [4].

The calculated transition pressures are in reasonable agreement with the experiment. The differences between our theoretical values and those experimentally found are almost equal (but of opposite sign) to the differences between the transition pressures observed for increasing and decreasing pressures.

It would be interesting (and useful in experimental works) to know if our method gives a good prediction of the difference between the bulk modulus of the B1 and B2 phase of a given compound at $p = 0$. Unfortunately, the analysis performed in the present paper does not answer this question: further investigations of this point are necessary.

Finally, we would like to recall that the method used in the present paper has some interesting features: it makes practically no use of the translational symmetry of the crystals, the computing time increases approximately in a linear way with the size of the system and the effects due to an external perturbation can be easily taken into account. These properties can be usefully exploited for studying partially disordered solids, large systems or for calculating dielectric properties.

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