

## High-pressure phases of magnesium selenide and magnesium telluride

P. E. Van Camp and V. E. Van Doren

*Department of Physics, University of Antwerpen, Groenenborgerlaan 171, B-2020 Antwerpen, Belgium*

J. L. Martins

*Instituto de Engenharia de Sistemase Computadores, Rua Alves Redol 9, P-1000 Lisbon, Portugal*

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The electronic structure, the charge density, and the total energy of MgSe and MgTe in the rocksalt ( $B1$ ), cesium chloride ( $B2$ ), zinc blende ( $B3$ ), wurtzite ( $B4$ ), nickel arsenide ( $B8_1$ ), and iron silicide ( $B28$ ) structures are studied using first-principles self-consistent local-density calculations in a large plane-wave basis employing soft nonlocal pseudopotentials. Experimentally for MgSe a transition was observed from the rocksalt to the iron silicide structure at 107 GPa. We find this transition between the same structures at 160 GPa. For MgTe the experimental ground state is the wurtzite structure, while the nickel arsenide structure obtained at 1–3.5 GPa persists after unloading to normal pressure. Up to 60 GPa no other transition was observed. Theoretically we find a nickel arsenide ground state and a transition to the cesium chloride structure at 69.6 GPa. The wurtzite and nickel arsenide structures are energetically very close. The difference at the minimal energy in these two structures is only 20.3 meV per atom. [S0163-1829(97)01102-8]

### I. INTRODUCTION

The magnesium chalcogenides MgO, MgS, MgSe, and MgTe are wide band-gap semiconductors and are of technological and scientific interest. The first three have the rocksalt structure and transform under pressure to the cesium chloride structure.<sup>1–4</sup> The last, MgTe, was first determined to have the wurtzite structure,<sup>5–8</sup> but recently it has been found that the wurtzite structure undergoes a phase transformation at 1–3.5 GPa to the nickel arsenide structure and that this structure persists after unloading and annealing.<sup>9</sup> The two *ab initio* calculations on MgTe reported in the literature<sup>10,11</sup> also find a nickel arsenide ground state (at  $T=0$ ). For MgSe one calculation of three structures was reported.<sup>12</sup> This paper presents theoretical results of total-energy calculations of the two compounds in six different structures: rocksalt ( $B1$ ), cesium chloride ( $B2$ ), zinc blende ( $B3$ ), wurtzite ( $B4$ ), nickel arsenide ( $B8_1$ ) and iron silicide ( $B28$ ).

### II. CALCULATIONAL DETAILS

The calculations are performed in the framework of local-density (LDA) functional theory together with nonlocal norm-conserving pseudopotentials. The first step is the generation of soft *ab initio* pseudopotentials. Here we employ the method of Troullier and Martins,<sup>13,14</sup> which puts the pseudowave function identical to the all-electron wave function outside the core radius and replaces the pseudowave function by a parametrized analytical expression inside the core radius.

The parameters are determined by imposing the norm conservation of the wave functions, the continuity of the wave functions and its first four derivatives at the core radius and that the screened pseudopotential be finite, analytic and have zero curvature at the origin. These nonlocal potentials are then transformed into separable form by means of the Kleinman-Bylander procedure.<sup>15</sup> As a consequence of this

last step substantial savings in computer time and storage are achieved, since it does not require the calculation of the full Hamiltonian matrix but rather of the product of the matrix and an eigenvector. The diagonalization of the large Hamiltonian matrix is performed using the dual-space formalism.<sup>16</sup> This method combines the iterative procedure of the direct inversion of the iterative subspace algorithm<sup>28</sup> with the calculation of the product of the Hamiltonian matrix by a wave vector through the use of a fast-Fourier transform algorithm. In order to ensure convergence a kinetic energy cutoff of 60 Ry is used. This corresponds to about 7225 plane waves for the  $B28$  phase of MgSe. It should be noted that some of the high-pressure phases are metallic (e.g., the  $B2$  phase). Hence a large number of integration points over the Brillouin zone is necessary. We use the Monkhorst-Pack scheme<sup>17</sup> with a (12,12,12) division for the cesium chloride and iron silicide, a (8,8,8) division for the zinc-blende and rocksalt structures, a (12,12,8) division for the nickel arsenide structure and a (10,10,6) division for the wurtzite structure. This corresponds to, respectively, 56, 76, 60, 60, 76, and 60 points in the irreducible part of the zone. These division numbers lead to approximately equivalent special point sets. This means that the integration schemes integrate exactly approximately the same set of symmetrical plane waves, so that the accuracy obtained for different structures is comparable.

For the correlation part we use the Ceperley-Alder<sup>18</sup> expression as parametrized by Perdew and Zunger.<sup>19</sup> This correlation functional is the only one consistent with the local-density approximation as it is a fit to the Monte Carlo solution of the uniform electron gas. It is well known that use of the Wigner interpolation formula leads to lattice constants closer to experiment.

To fit the total energy and to determine the equilibrium lattice constant, the bulk modulus, etc., we use the third-order Birch equation of state<sup>20</sup> or the Vinet equation of state.<sup>21</sup> The Birch equation of state is derived from the expansion of the total elastic energy to third order in the dis-

TABLE I. Calculated and experimental ground-state properties of MgSe: lattice constant  $a$  and  $c$  (in Å), bulk modulus  $B_0$  (in GPa), pressure derivative of the bulk modulus  $B'_0$ , and cohesive energy  $E_c$  (in eV/atom).

	Calculation	Other calculations	Experiment
<b>B1</b>			
$a$	5.5036	5.434 (Ref. 12)	5.463 (Ref. 22)
$B_0$	65.4	68 (Ref. 12)	
$B'_0$	4.14	4.04 (Ref. 12)	
$E_c$	-4.083		
<b>B2</b>			
$a$	3.4359		
$B_0$	62.5		
$B'_0$	4.10		
$E_c$	-3.561		
<b>B3</b>			
$a$	5.9764	6.072 (Ref. 12)	5.89 (Ref. 23)
$B_0$	47.8	58 (Ref. 12)	
$B'_0$	4.04	2.89 (Ref. 12)	
$E_c$	-4.041		
<b>B4</b>			
$a$	4.2374	4.319 (Ref. 12)	4.145 (Ref. 24)
$c$	6.8369	6.919 (Ref. 12)	6.723 (Ref. 24)
$c/a$	1.6135	1.602 (Ref. 12)	1.622 (Ref. 24)
$u$	0.3785	0.38 (Ref. 12)	
$B_0$	50.0	56 (Ref. 12)	
$B'_0$	3.94	3.07 (Ref. 12)	
$E_c$	-4.046		
<b>B8<sub>1</sub></b>			
$a$	3.8659		
$c$	6.4716		
$c/a$	1.6741		
$B_0$	65.1		55.2±1.6 (Ref. 4)
$B'_0$	4.11		4.5±0.1 (Ref. 4)
$E_c$	-4.067		
<b>B28</b>			
$a$	5.4492		
$B_0$	64.1		
$B'_0$	4.14		
$E_c$	-3.627		

placements. Typically the fits are performed using total energies at 10 different volumes ranging from 0.5 to  $1.2V_0$ . The pressure is then determined through analytical differentiation of the equation of state (Birch or Vinet), i.e., we use the relation  $p = -dE/dV$ . It should be noted that for the wurtzite and nickel arsenide structures the internal parameters are fully optimized. On the other hand, for the iron-silicide structure we use the internal parameters as given in the literature.<sup>26</sup> This structure is included here because there is recent experimental evidence that it is a high-pressure phase of MgSe.<sup>4</sup>

### III. RESULTS

Tables I and II show the calculated and experimental results for the six structures considered in this paper. The usual

trends of LDA are apparent from the tables: an overbinding and an overestimation of the bulk modulus. It should be noted that the main difference between the calculations of Refs. 10 and 11 and the present one is the use of the present work. The calculation of Ref. 12 is not LDA but uses Hartree-Fock (HF) theory. Usually LDA and HF results compare favorably but HF calculations seem to depend somewhat upon the quality of the basis used.

The only exception is the lattice constant of the B3 phase of MgSe. In that case both the result of Ref. 12 and the present work give a lattice constant larger than the experimental value. It should be remarked that the experimental value quoted is actually an extrapolation from the ZnMgSe alloy. We tend to believe that this extrapolation is rather inaccurate. The situation is less clear for the pressure deriva-

TABLE II. Calculated and experimental ground-state properties of MgTe: lattice constant  $a$  and  $c$  (in Å), bulk modulus  $B_0$  (in GPa), pressure derivatives of the bulk modulus  $B'_0$ , and the cohesive energy  $E_c$  (in eV/atom).

	Calculation	Other calculations	Experiment
<b>B1</b>			
$a$	5.9242	5.8548 (Ref. 11); 5.846 (Ref. 10)	
$B_0$	54.5	48.6 (Ref. 11)	
$B'_0$	4.04	3.88 (Ref. 11)	
$E_c$	-3.496		
<b>B2</b>			
$a$	3.6826		
$B_0$	49.5		
$B'_0$	4.20		
$E_c$	-3.057		
<b>B3</b>			
$a$	6.4454	6.3423 (Ref. 11); 6.364 (Ref. 10)	
$B_0$	38.0	36.2 (Ref. 11)	
$B'_0$	3.96	3.89 (Ref. 11)	
$E_c$	-3.502		
<b>B4</b>			
$a$	4.5303	4.7040 (Ref. 11); 4.505 (Ref. 10)	4.550 (Ref. 9); 4.54 (Ref. 6)
$c$	7.4056	7.2497 (Ref. 11); 7.358 (Ref. 10)	7.394 (Ref. 9); 7.39 (Ref. 6)
$c/a$	1.6347	1.6217 (Ref. 11); 1.633 (Ref. 10)	1.625 (Ref. 9); 1.628 (Ref. 6)
$u$	0.3751	0.3772 (Ref. 11); 0.376 (Ref. 10)	
$B_0$	42.8	37.3 (Ref. 11)	
$B'_0$	3.82	3.93 (Ref. 11)	
$E_c$	-3.490		
<b>B8<sub>1</sub></b>			
$a$	4.1830	4.1009 (Ref. 11); 4.142 (Ref. 10)	4.178 (Ref. 9)
$c$	6.8410	6.700 (Ref. 11); 6.724 (Ref. 10)	6.823 (Ref. 9)
$c/a$	1.6355	1.6338 (Ref. 11); 1.624 (Ref. 10)	1.633 (Ref. 9)
$B_0$	58.3	51.4 (Ref. 11)	60.6±5.4 (Ref. 9)
$B'_0$	3.89	3.89 (Ref. 11)	4.1±0.3 (Ref. 9)
$E_c$	-3.510		
<b>B28</b>			
$a$	5.8598		
$B_0$	51.4		
$B'_0$	4.19		
$E_c$	-3.144		

tive  $B'_0$ . From previous experience on several other materials we know that the Wigner interpolation formula for the correlation energy gives lattice constant in better agreement with the experimental values. However, the Ceperley-Alder expression is the only one consistent with the LDA.

The results given in the tables are obtained from the Birch equation. Using the Vinet equation leads to slightly different values: virtually the same values for  $a$ , the bulk moduli are smaller by up to 11% and the pressure derivatives of the bulk moduli are bigger by up to 20%. It should be noted that for the equation-of-state fits typically energies are used corresponding to the range 0.5 to  $1.2V_0$ . Experimentally this range is much narrower usually from 0.8 to  $V_0$ .

To determine the most stable structure at finite pressure

and temperature, the free energy  $G = E + pV - TS$  should be used. For the experimental data considered here the contribution of the last term is small and is therefore neglected in the rest of the calculation. We thus work with the enthalpy  $H = E + pV$ . Furthermore, we only employ six structures. This means that we cannot exclude the possible existence of other structures that are more stable.

Figures 1 and 2 show the total energy versus the atomic volume for the structures considered. For MgSe it is clear that the rocksalt structure is stable and that the nickel arsenide, wurtzite, zinc-blende, and cesium chloride structures are always unstable. The remaining iron-silicide structure is metastable.

The common tangent between the rocksalt and the iron

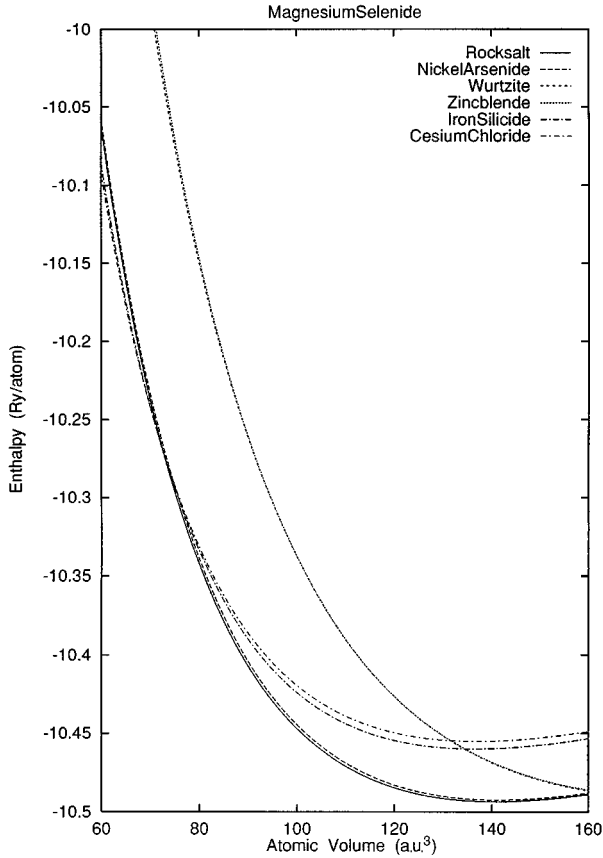


FIG. 1. Enthalpy (in Ry per atom) versus the atomic volume (in a.u.) for the six structures of MgSe.

silicide curves determines the transition path between both structures. The slope of this line is given in Table III where it is compared with the experimental value. In Ref. 12 a pressure of 60 GPa is reported for the transition of wurtzite to rocksalt. It also should be noted that in the present calculation all internal parameters were optimized except those of the  $B28$  structure. In that case the literature values are used.<sup>26</sup> The transition pressure really means that it is the pressure where the enthalpies of both structures are equal.

For MgTe the nickel arsenide structure is stable, while the zinc blende, wurtzite, iron silicide, and cesium chloride are unstable. The remaining rocksalt structure is metastable, and

TABLE III. Calculated and experimental values of the transition pressure, the transition volumes, the volume change at the transition pressure  $\Delta V_t$  (in %) and the energy difference  $\Delta E_t$  (in eV) for MgSe.

	Calculation	Experiment
$p_t$	160.3	$107 \pm 8$ (Ref. 4)
$V_t(B1)$	0.528	
$V_0$		
$V_t(B28)$	0.510	
$V_0$		
$\Delta V_t$	3.50	0.9 (Ref. 4)
$\Delta E_t$	0.374	

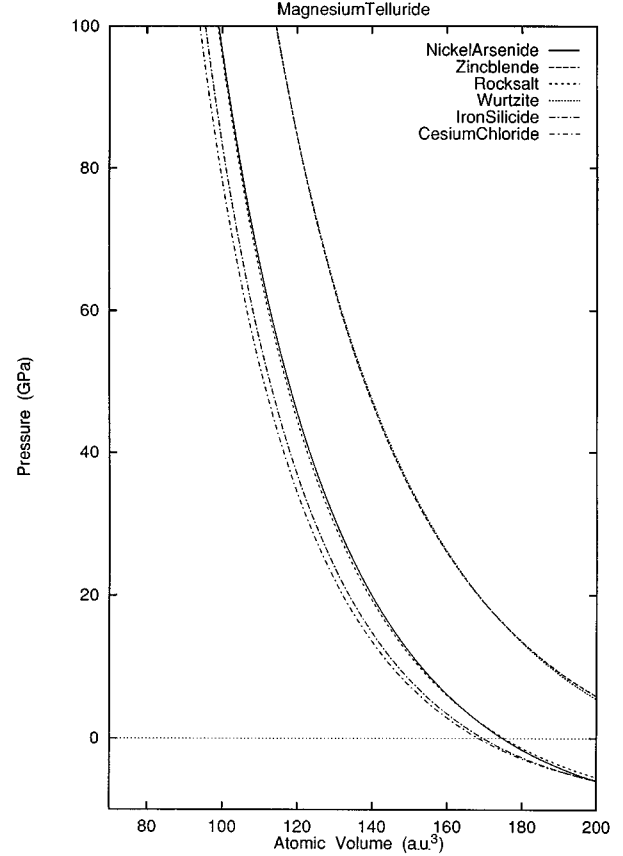


FIG. 2. Pressure (in GPa) versus the atomic volume (in a.u.) for the six structures of MgTe.

the transition pressure is given in Table IV. The Mg compounds can be compared with the Mn compounds because the supplementary  $3d$  electrons in the latter can be considered as chemically inactive. The Mn compounds crystallize in the rocksalt structure (MnO, MnS, and MnSe) or in the nickel arsenide structure (MnTe). The fact that the ground state of MgTe is nickel arsenide is therefore not surprising. Our earlier calculation<sup>11</sup> is based on different pseudopotentials (taken from Ref. 25), using a smaller cutoff (18 Ry) and less integration points over the Brillouin zone, but gives the same ground state.

Tables V and VI show the main direct and indirect band

TABLE IV. Calculated and experimental values of the transition pressure, the transition volumes, the volume change at the transition pressure  $\Delta V_t$  (in %), and the energy difference  $\Delta E_t$  (in eV) for MgTe.

	Calculation	Experiment
$p_t$	69.6	$>60$ (Ref. 9)
$V_t(B8_1)$	0.622	
$V_0$		
$V_t(B2)$	0.588	
$V_0$		
$\Delta V_t$	5.52	
$\Delta E_t$	0.380	

TABLE V. Calculated values of the main band gaps (in eV, with respect to the top of the valence band at  $\Gamma$ ) and their pressure derivatives (in meV/GPa) for MgSe.

	$E_0$	$\frac{dE_0}{dp}$
$\Gamma$ gap	2.206	91.5
$X$ gap	1.605	19.0
$L$ gap	3.650	17.9
$W$ gap	5.284	57.7

gaps and their pressure coefficients. In both cases we find that the top of the valence band is at  $\gamma$ . For MgSe the bottom of the conduction band is at  $X$  (1/2,0,1/2) with a band gap of 1.57 eV. For MgTe the bottom of the conduction band is at  $K$  (-1/3,2/3,0) with a band gap of 0.80 eV. It should be realized that LDA calculations usually give band gaps too small by a factor of 2. On the other hand the calculated pressure coefficients, in LDA, compare favorably with the experimental values as shown, e.g., in Ref. 27.

#### IV. SUMMARY

In this paper results are reported of *ab initio* calculations of the total energies of MgSe and MgTe in the rocksalt, cesium chloride, zinc-blende, wurtzite, nickel arsenide, and

TABLE VI. Calculated values of the main band gaps (in eV, with respect to the top of the valence band at  $\Gamma$ ) and their pressure derivatives (in meV/GPa) for MgTe.

	$E_0$	$\frac{dE_0}{dp}$
$\Gamma$ gap	2.354	101.1
$M$ gap	2.408	9.0
$A$ gap	2.952	55.9
$L$ gap	2.054	18.4
$K$ gap	0.809	1.04
$H$ gap	3.391	-1.24

iron silicide structures. The calculated lattice constants, bulk moduli, and their pressure derivatives agree well with the experimental values. Also determined are the transition pressures for the structural phase transition for MgSe from the rocksalt to the iron silicide structure, and for MgTe from the nickel arsenide to the cesium chloride structure.

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