

Ground-state properties and structural phase transformation of beryllium oxide

This article has been downloaded from IOPscience. Please scroll down to see the full text article.

1996 J. Phys.: Condens. Matter 8 3385

(<http://iopscience.iop.org/0953-8984/8/19/013>)

View [the table of contents for this issue](#), or go to the [journal homepage](#) for more

Download details:

IP Address: 171.66.16.208

The article was downloaded on 13/05/2010 at 16:38

Please note that [terms and conditions apply](#).

Ground-state properties and structural phase transformation of beryllium oxide

P E Van Camp and V E Van Doren

Department of Physics, University of Antwerpen (RUCA), Groenenborgerlaan 171, B-2020 Antwerpen, Belgium

Received 11 December 1995, in final form 15 February 1996

Abstract. The electronic structure, the charge density and the total energy of BeO in the rocksalt (B1), caesium chloride (B2), zincblende (B3), wurtzite (B4), nickel arsenide (B8₁) and iron silicide (B28) structures are studied using first-principles self-consistent local-density calculations in a large plane wave basis employing soft non-local pseudopotentials. Experimentally no transition was observed up to a pressure of 55 GPa. The wurtzite structure is the calculated ground state with $a = 2.639 \text{ \AA}$, $c = 4.299 \text{ \AA}$, $c/a = 1.629$ and an internal parameter $u = 0.377$. The experimental values are respectively 2.699 \AA , 4.373 \AA , 1.62 and 0.378 . The zincblende structure is energetically very close to the wurtzite structure. The difference at the minimal energy between these two structures is only 5.6 meV. At a pressure of 137 GPa we observe a transition to the sixfold-coordinated rocksalt structure. From that structure on, no other transition is found to any of the calculated structures.

1. Introduction

The alkaline-earth oxide BeO is a very interesting material as it has special properties which are quite different from those of the other compounds (BeS, BeSe, BeTe) in the series. It has a hexagonal ground state (B4), while the others are cubic (B3). It has a high thermal conductivity, a low electrical conductivity and a high melting point and hardness. It is therefore an interesting ceramic.

Under pressure most wurtzite compounds undergo a first-order structural phase transformation to the rocksalt structure.

Only a few experimental [1, 2] and theoretical [3–7] investigations have been performed, some of the results of which are contradictory. Experimentally no phase transformation was observed up to a pressure of 55 GPa [2]. Theoretical calculations gave a transition pressure of 21.7 [4], 40 [2] and 95 GPa [7]. This paper presents theoretical results of total energy calculations of BeO in the six structures, B1, B2, B3, B4, B8₁ and B28, and of the transition pressure from B4 to B1.

2. Computational details

The calculations are performed in the framework of local density functional theory together with non-local norm-conserving pseudopotentials. The first step is the generation of soft *ab initio* pseudopotentials. Here we employ the method of Troullier and Martins [8, 9], which puts the pseudo-wavefunction identical to the all-electron wavefunction outside the core radius and replaces the pseudo-wavefunction by a parametrized analytical expression

inside the core radius. The parameters are determined by imposing the norm conservation of the wavefunctions, the continuity of the wavefunctions and their first four derivatives at the core radius and that the screened pseudopotentials be finite, analytic and have zero curvature at the origin. These non-local potentials are then transformed into separable form by means of the Kleinman–Bylander procedure [10]. 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 that of the product of the matrix and an eigenvector. The diagonalization of the large Hamiltonian matrix is performed using the dual-space formalism [11]. This method combines the iterative procedure of the direct inversion of the iterative subspace algorithm [23] with the calculation of the product of the Hamiltonian matrix by a eigenvector through the use of a fast Fourier transform algorithm. In order to ensure convergence a kinetic energy cut-off of 100 Ryd is used. This corresponds to about 3400 plane waves for the B4 phase. A large number of integration points over the Brillouin zone is necessary. We use the Monkhorst–Pack scheme [12] with a (12, 12, 12) division for the caesium chloride and iron silicide, an (8, 8, 8) division for the zincblende 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 approximately the same symmetrized plane wave is not integrated exactly by the different point sets.

For the correlation part we use the Ceperley–Alder [13] expression as parametrized by Perdew and Zunger [14]. This correlation functional is the only one consistent with the local density approximation (LDA) 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 [15] or the Vinet equation of state [16]. The Birch equation of state is derived from the expansion of the total elastic energy to third order in the displacements. Typically the fits are performed using total energies at 10 different volumes ranging from 0.6 to 1.3 V_0 . 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 [20]. This structure is included here because there is recent experimental evidence that it is a novel high-pressure phase of MgSe [21].

3. Results

Tables 1 and 2 show the calculated and experimental results for the six structures considered in this paper. The usual trends of LDA are apparent from table 1: a slight overbinding and an overestimation of the bulk modulus.

From previous experience on several other materials we know that the Wigner interpolation formula [17] for the exchange correlation energy gives a 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 1.8% and the pressure derivatives of the bulk moduli are bigger by up to 7.9%. The same trend was also observed in other materials [22]. It should be noted that the root mean square error of the Vinet fit is always bigger than that of the Birch fit (for

Table 1. Calculated and experimental ground state properties of BeO in the zincblende (B3) and wurtzite (B4) structures: lattice constants a and c (Å) and bulk modulus B_0 (GPa).

	Present work	Other calculations	Experiment
B3			
a	3.7264	3.766 [4]; 3.678 [7]; 3.800 [5]	3.797 [6]
B_0	228.1	229 [7]; 297 [4]; 251 [5]; 242 [6]	—
B'_0	3.96	—	—
B4			
a	2.6390	2.688 [7]; 2.644 [4]; 2.680 [5]; 2.697 [6]; 2.7750 [2]	2.6995 [1]
c	4.2999	4.324 [4]; 4.336 [5]; 4.356 [7]; 4.361 [6]; 4.3845 [2]	4.3732 [1]
u	0.3769	0.3798 [5]; 0.3791 [6]; 0.385 [2]	0.378 [1]
c/a	1.6294	1.623 [4]; 1.6179 [5]; 1.6170 [6]; 1.58 [2]	1.62 [1]
B_0	227.6	239 [7]; 283 [4]; 253 [5]; 244 [6]; 186 [2]	210 [1]; 249 [18]; 224 [19]
B'_0	3.96	—	5.1 [1]

Table 2. Calculated ground state properties of BeO in the rocksalt (B1), caesium chloride (B2), nickel arsenide (B8₁) and iron silicide (B28) structures: lattice constants a and c (Å) and bulk modulus B_0 (GPa).

	B1		B2	B8 ₁	B23
	Present work	Other calculation			
a	3.5709	3.590 [7]	2.3269	2.5072	3.6812
c		—		4.2051	
c/a		—		1.6772	
B_0	266.1	372 [7]	225.9	259.8	222.8
B'_0	3.80	—	3.84	3.89	3.83

wurtzite by a factor of 2.4). Also here the empirical rule that a compound is stable in the wurtzite structure if its c/a value is smaller than the ideal value (1.6330) is obeyed.

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.

Figure 1 shows the total energy versus the atomic volume for the structures considered. It is clear that the wurtzite structure is the most stable. The zincblende structure is energetically very close, the difference between the minimal energies only being 5.6 meV. This result is not surprising because of the high similarity between the two structures. The local environment of any atom in either zincblende or wurtzite is exactly the same as far as the second neighbours. The nickel arsenide, caesium chloride and iron silicide structures are always unstable. The remaining rocksalt structure is meta-stable. The common tangent between the wurtzite and the rocksalt curves determine the transition path between both structures. The slope of this line is given in table 3 where it is compared with other theoretical values. The transition pressure is really the pressure where the enthalpies of both structures are equal. Experimentally [2] no transition has been observed up to a pressure of 55 GPa.

There is a large difference between the transition pressures calculated in the present

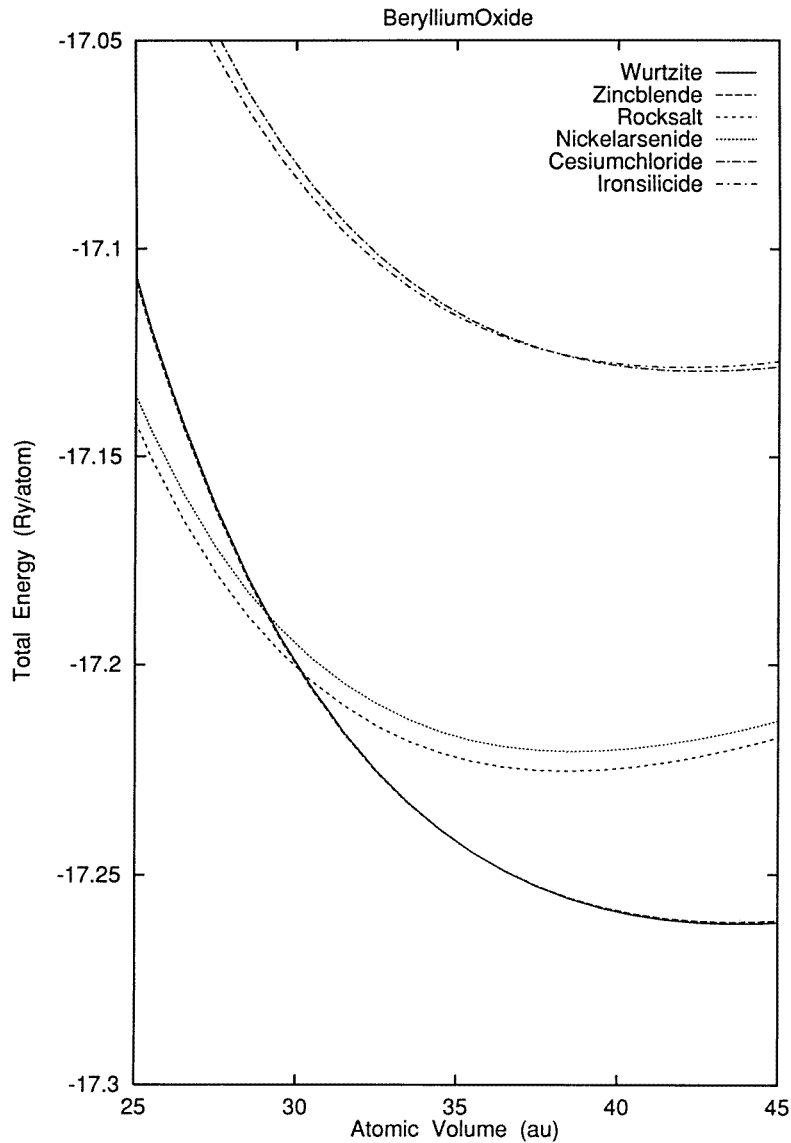


Figure 1. Total energy (Ry/atom) versus the atomic volume (au) for the six structures of BeO.

work and the older theoretical work. The calculation of [4] is similar to the present one, the main difference being that here a larger cut-off, more Brillouin zone integration points, a different exchange–correlation functional and softer pseudopotentials are used. The main consequence of all this is a vertical shift of the total energy curves, leading to a very different transition pressure. The total energy difference between the minima of the wurtzite and rocksalt phases is 185 meV/atom in [4], while we find 495 meV/atom. The calculation of [2] is based on the potential-induced breathing model using a local Thomas–Fermi functional for the kinetic energy. Although this model gives reasonable ground state properties for the wurtzite phase it probably places the rocksalt structure too low, giving rise to a smaller

Table 3. Calculated values of the transition pressure, the transition volumes and the volume change at the transition pressure ΔV_t (%) for BeO.

	Present work	Other calculations
p_t	137.3	21.7 [4]; 40 [2]; 95 [7]
$V_t(B4)/V_0$	0.7306	0.934 [4]
$V_t(B1)/V_0$	0.6573	0.745 [4]
ΔV_t	11.2	11.0 [2]

transition pressure.

There is a very good agreement between a recent calculation [7] and the present work. In [7] results of both an LMTO and an LGTO calculation are reported. The values quoted in tables 1 and 2 are the LMTO results because the exchange–correlation functional used in that calculation is the same as that used here. The lattice constants and bulk moduli agree very well, although in [7] no optimization of the c/a ratio and of the u -value was performed. This is probably the origin of the discrepancy between the calculated transition pressures. It should be noted that a small shift of the wurtzite curve can lead to a sizeable change in the transition pressure.

4. Summary

In this paper results are reported of *ab initio* calculations of the total energies of BeO in the wurtzite, zincblende, rocksalt, nickel arsenide, caesium chloride and iron silicide structures. The calculated lattice constants, bulk moduli and their pressure derivatives agree very well with the experimental values. Also determined is the transition pressure for the structural phase transition from the wurtzite to the rocksalt structure.

Acknowledgments

This work was supported by the Belgian NSF (NFWO) under grant No 9.0053.93. and partly by the HCM network *Ab initio Calculations of Complex Processes in Materials*.

References

- [1] Hazen R M and Finger L W 1986 *J. Appl. Phys.* **59** 3728
- [2] Jephcoat A P, Hemley R J, Mao H K, Cohen R E and Mehl M J 1988 *Phys. Rev. B* **37** 4727
- [3] Chang K J, Froyen S and Cohen M L 1983 *J. Phys. C: Solid State Phys.* **16** 3475
- [4] Chang K J and Cohen M L 1984 *Solid State Commun.* **50** 487
- [5] Lichanot A, Caillet M, Larrieu C, Dovesi R and Pisani C 1992 *Chem. Phys.* **164** 383
- [6] Lichanot A and Rerat M 1993 *Chem. Phys. Lett.* **211** 249
- [7] Boettger J C and Wills J M to be published
- [8] Troullier N and Martins J L 1990 *Solid State Commun.* **74** 613
- [9] Troullier N and Martins J L 1991 *Phys. Rev. B* **43** 1993
- [10] Kleinman L and Bylander D M 1982 *Phys. Rev. Lett.* **48** 1425
- [11] Martins J L and Cohen M L 1988 *Phys. Rev. B* **37** 6134
- [12] Monkhorst H J and Pack J D 1976 *Phys. Rev. B* **13** 5188
- [13] Ceperley D and Alder B 1980 *Phys. Rev. Lett.* **45** 566
- [14] Perdew J P and Zunger A 1981 *Phys. Rev. B* **23** 5048
- [15] Birch F 1978 *J. Geophys. Res.* **83** 1257
- [16] Vinet P, Ferrante J, Smith J R and Rose J H 1987 *J. Phys. C: Solid State Phys.* **19** L467

- [17] Wigner E P 1934 *Phys. Rev.* **46** 1002
- [18] Cline C F, Dunegan H L and Henderson G W 1967 *J. Appl. Phys.* **38** 1944
- [19] Bentele G G 1966 *J. Am. Ceram. Soc.* **49** 125
- [20] Pauling L and Soldate A M 1948 *Acta Crystallogr.* **1** 212
- [21] Li T, Greene R G, Luo H, Ruoff A, Trail S S and DiSalvo F J 1995 to be published
- [22] Van Camp P E, Van Doren V E and Martins J L 1995 *Phys. Status Solidi b* **190** 183
- [23] Wood D M and Zunger A *J. Phys. A: Math. Gen.* **18** 1343