

Theoretical study of the structural phase transformation of BeO under pressure

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We study the pressure induced phase transformation of BeO using a first-principles pseudopotential method within the local-density-functional approximation, and find a transition sequence from wurtzite to zinc blende, and then to rocksalt. With the generalized-gradient approximation for the exchange-correlation potential, we find the transition pressures to be increased significantly, without altering the transition sequence. The wurtzite structure transforms into the zinc-blende structure at 91 GPa, while the zinc-blende-to-rocksalt transition occurs at 147 GPa. This unusual transition sequence is attributed to the large charge asymmetry and the small bond length of BeO. [S0163-1829(99)09721-0]

From the Phillips' ionicity (f_i) argument, it is known that tetrahedrally coordinated compounds with ionicities larger than a critical value of $f_i=0.375$ tend to transform into a sixfold rocksalt structure under pressure, while they prefer a metallic phase for $f_i<0.375$.¹ Since the Phillips' ionicity of BeO is 0.602, it is not unreasonable to expect a phase transition from wurtzite (WZ) to rocksalt (RS) at high pressures. Earlier first-principles pseudopotential calculations predicted the WZ-RS transition at 22 GPa and the same transition at 40 GPa was also found by using the potential-induced-breathing method.^{2,3} In other similar calculations using soft nonlocal pseudopotentials,⁴ although a much higher transition pressure of 137 GPa for the WZ-RS transition was predicted, the wurtzite phase was shown to first transform into the zinc-blende structure at 74 GPa. A similar series of phase transitions was also predicted by two all-electron and full-potential electronic-structure calculations; the transition pressures for the WZ-ZB and ZB-RS transitions are 63–76 and 95 GPa, respectively.⁵ Because of the structural similarity between the wurtzite and zinc-blende phases, the energy difference between the two structures is extremely small, thus the transition pressure is very sensitive to the binding energies. Since previous first-principles calculations rely on the local-density-functional approximation (LDA), which usually overestimates the cohesive energy, it is desirable to go beyond the LDA calculations. In fact, for Si and Ge, the transition pressures for the diamond-to- β -Sn transition were found to be increased by including gradient corrections to the exchange-correlation energy, resulting in better agreement with experiments than the LDA results.⁶ Experimentally, Raman spectra³ showed no evidence for a phase transition up to 55 GPa in BeO and Hugoniot data⁷ did not reveal any volume change for stresses up to 100 GPa.

In this paper, we examine the phase transformation of BeO under hydrostatic pressure through first-principles pseudopotential calculations based on the generalized-gradient approximation (GGA) for the exchange-correlation potential. We fully optimize the c/a ratio and the internal parameter u in the wurtzite structure by employing a conjugate gradient technique, which eliminate the ambiguity of calculations due to the small energy difference between the WZ and ZB structures. We find that with increasing pressure BeO undergoes a series of structural transformations from

wurtzite to zinc-blende and then to rocksalt, which is the same as that predicted by the LDA. However, the GGA calculations give much higher transition pressures. To explain the unusual transition sequence of BeO, we analyze individual contributions to the total energies of the wurtzite and zinc-blende phases, and compare with those for GaN, which undergoes a wurtzite-rocksalt transition. We also investigate the charge asymmetry coefficient and the bonding characteristics under compression.

Our calculations are based on the first-principles pseudopotential method within the LDA.⁸ Soft nonlocal pseudopotentials are generated by the scheme of Troullier and Martins⁹ and transformed into a separable form of Kleinman and Bylander.¹⁰ For the LDA exchange-correlation potential, we use the Ceperley-Alder expression as parametrized by Perdew and Zunger.¹¹ In the GGA calculations, we employ the functional form (PW91) proposed by Perdew and co-workers¹² for the exchange-correlation energy, and find that the cohesive energy of BeO is improved and the transition pressures are increased by 20–30 GPa. In this case, nonlinear core corrections to the exchange-correlation part are included to generate appropriate GGA pseudopotentials.¹³ The wave functions are expanded in a plane-wave basis set with a kinetic energy cutoff of 110 Ry throughout this work. Testing a higher energy cutoff of 196 Ry, we find that the change of the cohesive energy of the ZB phase with respect to the WZ phase is less than 0.2 mRy per molecule. A similar error is also found between the ZB and RS structures, resulting in similar transition pressures. To perform the summation of the charge density over the Brillouin zone, we use equivalent sets of \mathbf{k} points to minimize the calculational error for the WZ and ZB structures. For the ZB structure, we use a hexagonal supercell containing six atoms, whose atomic layers are stacked along the cubic [111] direction, and compare its energy with that of the WZ structure. The equivalent sets of 12 and 10 special \mathbf{k} points are chosen in the irreducible sectors of the WZ and ZB Brillouin zones, respectively, while for the RS structure a set of 10 special \mathbf{k} points is used. When testing 90, 110, and 85 \mathbf{k} points for the WZ, ZB, and RS structures, respectively, the errors in the total-energy difference are less than 0.2 mRy per molecule. In this case, the change of the total-energy difference between the ZB and WZ structures is less than 0.01 mRy per molecule, indicating that our equivalent sets of

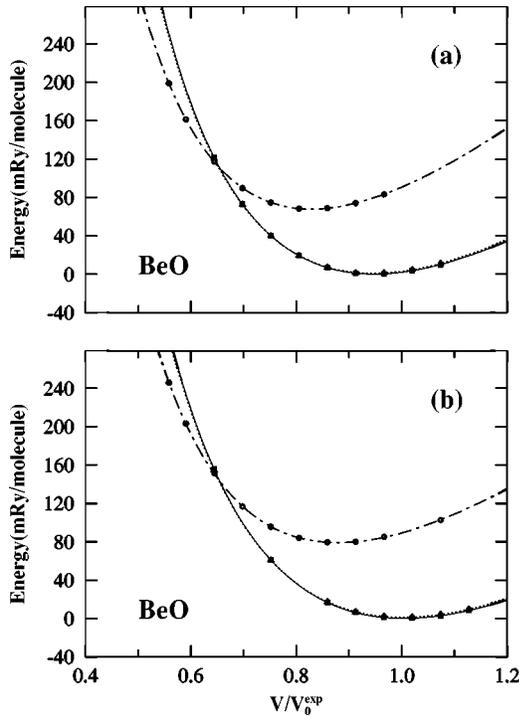


FIG. 1. The (a) LDA and (b) GGA total energies for the wurtzite (solid line), zinc-blende (dotted line), and rocksalt (dot-dashed line) phases of BeO are plotted as a function of volume, which is normalized by the experimentally measured equilibrium volume ($V_0^{\text{exp}} = 93.06$ a.u. per molecule) of the wurtzite structure.

\mathbf{k} points are very accurate, although the axial ratio of the WZ phase is not ideal. The energy functional is fully minimized by the modified-Jacobi relaxation method.¹⁴ The structural parameters such as the equilibrium lattice constant (a_0), the bulk modulus (B_0), and its pressure derivative are obtained by fitting the calculated total energies to the Murnaghan's equation of state,¹⁵ choosing about ten different volumes between 0.6 and 1.2 V_0 , where V_0 is the equilibrium volume. The c/a ratio in the WZ structure is optimized for each volume by fitting the energies to a quadratic polynomial, with the internal parameter u obtained by averaging the two optimized values for the near equilibrium and transition volumes.

The calculated total energies for the WZ, ZB, and RS phases of BeO are plotted in Fig. 1 and the results for the ground-state properties are given in Table I. For the wurtzite phase, the GGA equilibrium lattice constant and bulk modulus are 2.703 Å and 203 GPa, in better agreement with the measured values of 2.698 Å and 212 GPa,¹⁶ compared with the LDA results. The GGA cohesive energy (E_c) is calculated to be 0.952 Ry/molecule, close to the experimental value of 0.9 Ry/molecule,² while the LDA cohesive energy is overestimated by about 0.16 Ry/molecule. In both the LDA and GGA calculations, we find similar results for the c/a ratio and the internal parameter u , in good agreement with experiments. Our LDA results for the ground-state properties of wurtzite BeO generally agree well with previous similar calculations,⁴ which used the same soft nonlocal pseudopotentials of Troullier and Martins.

In both the LDA and GGA calculations, the wurtzite lattice of BeO transforms into the zinc-blende structure and

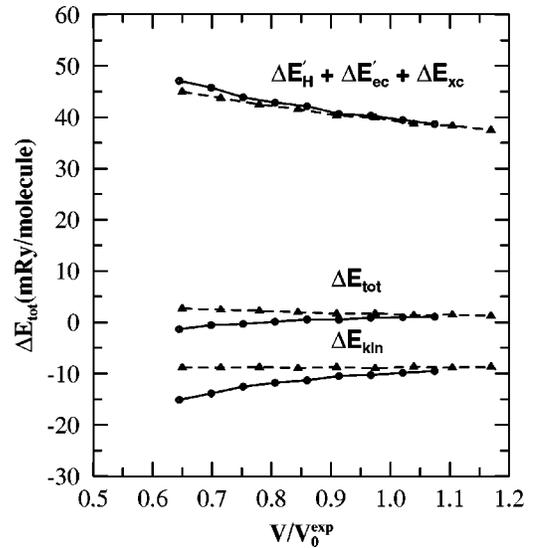


FIG. 2. The kinetic energy (ΔE_{kin}) and other ($\Delta E'_H + \Delta E'_{ec} + \Delta E_{xc}$) contributions to the electronic energy difference (ΔE_e) and the total-energy difference (ΔE_{tot}) are plotted as a function of normalized volume for BeO (solid circles) and GaN (solid triangles). Here ΔE_{tot} is defined as the subtraction of the wurtzite total energy from that for the zinc-blende structure.

then into the rocksalt structure with increasing pressure. The results for the transition pressure and transition volume are given in Table II. From the equal-free-energy condition for the WZ and ZB phases, the transition pressure by the LDA calculations is estimated to be 62 GPa, slightly lower than other calculated values of 74–76 GPa.^{4,5} Including the gradient correction for the exchange-correlation energy, we obtain a much higher value of 91 GPa for the transition pressure. At this transition, the volume change is found to be extremely small, less than a half percent of the equilibrium volume, and this feature results from the fact that the packing fraction is almost invariant under transformation. We find the LDA transition pressure for the ZB-RS transition to be 127 GPa, similar to the previous LDA result of 139 GPa.⁴ In the GGA calculations, the total energies for the rocksalt phase are shifted to the higher energy, relative to the wurtzite phase, so that a higher transition pressure of 147 GPa is estimated. We point out that for both the WZ-ZB and ZB-RS phase transitions, the GGA calculations give higher transition pressures than the present LDA and previous all electron calculations.⁵ In this case, the energy difference between the WZ and RS structures is increased, while that between the WZ and ZB structures is little changed.¹⁷ This is because the gradient corrections are more significant for the wurtzite and zinc-blende structures than for the more close-packed rocksalt lattice. Experimentally, Raman spectroscopy³ and shock-wave experiments⁷ showed no evidence for a phase transition in BeO up to 55 GPa.

In recent studies, Cohen and Garcia suggested the asymmetry coefficient (g) of the charge density to be a measure of the ionic character of a bond.¹⁸ Although there is a correspondence between the coefficient g and the Phillips' ionicity f_i for many compound materials, several compounds such as BN and SiC, which contain first-row elements, were shown to have larger g values than their ionicities; the asymmetry coefficients for BN and SiC are in the intermediate

TABLE I. Calculated and experimental structural parameters for the wurtzite, zinc-blende, and rocksalt phases of BeO: lattice constants a_0 (Å), bulk moduli B_0 (GPa), and cohesive energies E_c (Ry/mol). GGA and LDA denote the results of the present work. Note that the c/a ratio is optimized in both Ref. 3 and this work.

Structure	Method	a_0	c/a	u	B_0	E_c
Wurtzite	GGA	2.703	1.620	0.377	203	0.952
	LDA	2.650	1.624	0.378	224	1.058
	other calc. ^a	2.668	1.633		239	1.034
	other calc. ^b	2.639	1.629	0.3769	228	
	other calc. ^c	2.775	1.58		186	
	expt. ^d	2.698	1.622	0.378	212	
	expt. ^e					0.9
Zinc-blende	GGA	3.810			201	0.951
	LDA	3.737			224	1.057
	other calc. ^a	3.768			229	1.033
	other calc. ^b	3.726			228	
Rocksalt	GGA	3.648			231	0.873
	LDA	3.577			264	0.990
	other calc. ^a	3.590			272	0.972
	other calc. ^b	3.571			266	

^aReference 5.

^bReference 4.

^cReference 3.

^dReference 16.

^eReference 2.

range around 0.5 separating the zinc-blende and wurtzite structures.¹⁹ Thus it was suggested that the WZ structure is preferred over the ZB structure, if g is roughly above 0.5. For wurtzite BeO, since the value of g is 0.842, the wurtzite structure is stabilized against the zinc-blende structure like AlN and GaN with the asymmetry coefficients close to 0.8. However, as pressure increases, both AlN and GaN undergo a different structural transition from wurtzite to rocksalt.

To analyze the WZ-ZB transition in BeO, we examine various contributions to the total energies for the wurtzite and zinc-blende structures. It was shown that the phase stability of a solid depends on a detailed balance between the

TABLE II. Calculated pressure for each transition (P_t), initial transition volumes (V_t), and fractional volume changes ($\Delta V/V_t$) for the wurtzite-to-zinc-blende and zinc-blende-to-rocksalt transitions are listed and compared with other theoretical calculations.

Transition	Method	P_t (GPa)	V_t (a.u./mol)	$\Delta V/V_t$
WZ \rightarrow ZB	GGA	91.2	70.55	-0.003
	LDA	61.8	72.48	-0.002
	other calc. ^a	76.2	72.64	-0.002
	other calc. ^b	74	70.70	-0.002
ZB \rightarrow RS	GGA	147.1	63.77	-0.092
	LDA	126.5	63.87	-0.096
	other calc. ^a	94.1	70.04	-0.113
	other calc. ^b	139	63.31	-0.099

^aReference 5.

^bReference 4.

electronic (E_e) and Ewald (E'_{cc}) contributions to the total energy, where E_e is defined as the sum of the electronic kinetic energy (E_{kin}), the electron-ion interaction energy (E'_{ec}), the electron-electron Coulomb energy (E'_H), and the exchange-correlation energy (E_{xc}); in Si and Ge, the Ewald contribution was found to be dominant in determining the diamond-to- β -tin transition.²⁰ The electronic (ΔE_e) and Ewald ($\Delta E'_{cc}$) contributions to the total-energy difference (ΔE_{tot}) between the zinc-blende and wurtzite structures are analyzed for BeO and GaN. We find that the variation of ΔE_e with decreasing volume is much weaker for BeO than for GaN, while $\Delta E'_{cc}$ varies similarly. Among the contributions to ΔE_e , the partial sum of ΔE_{xc} , $\Delta E'_H$, and $\Delta E'_{ec}$ varies similarly with pressure for BeO and GaN, as shown in Fig. 2. We find this partial sum to stabilize the wurtzite structure against the zinc-blende structure, which is attributed to the fact that the wurtzite structure has more attractive interactions between the cation and anion atoms than for the zinc-blende structure, because of the shorter third-nearest-neighbor distances. The remaining kinetic energy contribution (ΔE_{kin}) to ΔE_e in BeO is found to decrease more rapidly with increasing pressure than for GaN, favoring the zinc-blende structure. This different feature of the kinetic energy term can be explained by the character of the valence charge distribution under compression. We note that the charge asymmetry coefficient for the wurtzite structure is slightly higher than that for the zinc-blende structure, causing a larger variation of the wave function around the anion atom and thereby a higher kinetic energy. Since the bond length of BeO is much smaller than that for GaN, two neighboring sidewise bonds, which face each other along the hex-

agonal axis of the wurtzite structure, are closely aligned, influencing strongly their charge distributions. In addition, BeO maintains more directional bonds near the transition pressure due to the strong O potential, while in GaN the charge distributions around the anion atoms become more spherical. Thus the kinetic energy of wurtzite BeO increases more rapidly than for the zinc-blende structure, and it plays an important role in the phase transition into the zinc-blende structure. As compared to other metals or insulators, which undergo structural phase transitions via metallization and/or increase of coordination number, the WZ-ZB transition of BeO is unusual, because the packing fraction is invariant. Since the wurtzite and zinc-blende structures belong to fairly open structures and the charge asymmetry coefficient is still very high, it is not unreasonable to expect the rocksalt phase rather than metallic phases such as β -Sn, as pressure increases further.

In conclusion, we have investigated the structural phase transitions of BeO under pressure through the first-principles pseudopotential calculations. Both the LDA and GGA calculations show that the wurtzite lattice of BeO first transforms into the zinc-blende structure and then into the rocksalt phase, while in other tetrahedrally coordinated compounds such as AlN and GaN, the rocksalt structure appears as a high-pressure phase. In our GGA calculations, we estimate the transition pressure of 91 GPa for the wurtzite-to-zinc-blende transition and 147 GPa for the zinc-blende-to-rocksalt transition, which are higher by about 20–30 GPa than the LDA results. We find that BeO has the larger charge asymmetry coefficient and maintains more directional bonds under compression, as compared to GaN, resulting in the unusual wurtzite-to-zinc-blende transition.

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