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Theoretical investigation of graphitic BeO

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The possibility of whether BeO, a wide-band-gap semiconductor (7.8–10.7 eV), may exist in the layered graphitic phase—as do the other members of the family of first-row compounds C and BN—is investigated employing a first-principles total-energy local-density-approximation study of the electronic structure of this series of compounds in the layered and the dense wurtzitelike phases. We obtain the minimum-energy path between these phases in BeO and compare with those of C and BN. The chemical trends responsible for the relative metastability along the series are revealed after a detailed analysis of the differences of the energy components of the compounds in the two phases. We also offer a process for the synthesis of BeO which is based on recent progress in the synthesis of new graphitic materials by chemical vapor deposition.

I. INTRODUCTION

Density-functional theory (DFT) (Ref. 1) coupled to realistic electronic structure calculations using the local-density approximation (LDA) (Ref. 1) has provided us with a reliable technique to assess quite detailed aspects of electronic systems. In particular, a class of problems that have become possible to investigate is the determination of microscopic mechanisms that aid or hinder compound formation. This genre of chemical trend would be impossible to study in detail otherwise.

This approach well suits the study of the intriguing series of compounds formed by first-row elements, C, BN, and BeO. Similar to the other members of the family of octet semiconductors, these compounds exist in dense phases like diamond and zinc blende, or hexagonal diamond (lonsdaleite) and wurtzite;[2] however, whereas C and BN also exist in low-density graphitic phases,[2] BeO does not.

Until now it has not been understood if the absence of BeO in this latter series is caused by simple technical difficulties in preparing the compound or by an intrinsic structural instability of the graphitic phase with respect to the dense wurtzite phase. Apparently, due to difficulties connected with toxic hazard problems inherent to Be compounds, few papers have been published about the synthesis and properties of this material in any phase and therefore the direct investigation of the possible metastability of its layered phase has not been an issue of primary concern. There is however some interest in layered BeO because of its expected exotic intercalation chemistry.

In view of recent progress in the syntheses of new materials by chemical vapor deposition (CVD) this question has taken on practical as well as scientific importance. The CVD technique has produced thin films of some of the materials in this series, like graphite,[3] layered BN,[4] and diamond,[5] and has recently been able to produce new layered (graphitelike) materials formed by combinations of first-row elements, such as BC_3,[6,7] BC_2N,[8,9] and C_5N.[6] Behind the *design* of these syntheses, the underlining idea is the induction of reactions between vapors of especially shaped molecular species. For instance, the synthesis of graphite is readily achieved by CVD of benzene,[3] which is a planar species, while the synthesis of diamond is more easily reached by CVD of methane,[4] which is a tetrahedrically coordinated species.

In the recent syntheses of BC_3 and BC_2N, it was realized that an especially favorable condition for synthesis is obtained if the reaction involves the liberation of HCl(gas) (Refs. 6 and 8), which has a large enthalpy of formation. This is the same principle that is the basis of the formation of layered BN (Ref. 4) from NH_3 and BCl_3. In this case, the importance of the shape of the initial molecules is quite apparent, since only the layered phase of BN is formed by simple CVD,[10] in which the atoms maintain the threefold and planar nature of the original molecular species regardless of the fact that the layered phase is metastable with respect to the dense phase.[11] The recognition of this fact made possible the synthesis of BC_2N at much lower temperatures than the previously achieved synthesis of pseudobinaries $B_xC_{1-x}N_x$.[12]

This knowledge suggests that thin films of BeO, perhaps in any of the forms mentioned above, could also be obtained by CVD, especially if the process involves the liberation of HCl as in

$$\mathrm{BeCl_2(linear)+H_2O(angular)} \\ \rightarrow 2\ \mathrm{HCl(gas)+BeO(solid)}\ .$$

In this case the linear and angular nature of the molecular species involved may permit a more flexible arrangement of the atoms during the formation of the solid phase. Besides this, the possibility of such a reaction to occur is strongly supported by a comparison of the free energy of formation at 298 K (ΔG_f^0) of the compounds involved,[13] which indicates that if this reaction occurred at room temperature it would be exothermic and liberate -10.24 kcal/mol (≈ 0.44 eV/pair).[13] Of course, for kinetic reasons this reaction is expected to occur at much higher temperatures and unfortunately the absence of more detailed thermodynamic data for wurtzite-structure BeO at high temperatures prevents us from determining the feasibility of this reaction in such a regime. It is of interest therefore to know in advance about the relative stability of the layered and dense phases in order to learn if such a reaction could promote the syntheses of layered BeO.

The first-principles assessment of the stability of layered BeO should be made by comparing the internal energy of this structure, as well as of those corresponding to neighboring atomic configurations, to that of the wurtzite structure. Of particular interest are those configurations which lead, through simple deformations of the layered structure, to the dense wurtzite phase, i.e., a possible minimum energy path between the two phases. This path, which maintains D_{6h}^4 ($P6_3/mmc$) symmetry along the transformation, is well known and is shown in Fig. 1. Energy barriers for this transition have already been computed for BN (Ref. 12) as well as for the hypothetical homopolar analog, graphite to diamond transition in C.[14] There is also a similar path, which maintains rhombohedral symmetry, between the layered solid with the $ABCABC\cdots$ stacking sequence and leads directly to the dense zinc-blende or diamond phase.[11,15] Since the wurtzite phase is known to be the most stable zero-pressure dense phase of BeO, and the $AaAa\cdots$ stacking of layers is the usual sequence in the relative heteropolar compound BN, it seems that the path shown in Fig. 1 is the most appropriate for investigation.

It is the purpose of this paper to obtain the energy barrier for such a transition in BeO from a realistic first-principles total-energy calculation and to compare the energetics of this transition with those of the other members of the isoelectronic series, BN and C. The next section contains the results of our calculation, while a discussion involving an analysis of the energetics along the series is presented in Sec. III. Our conclusions are stated in Sec. IV.

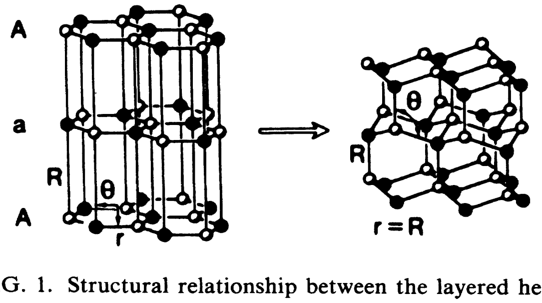

FIG. 1. Structural relationship between the layered hexagonal phase (h-BeO) and the wurtzite (w-BeO) structures.

II. CALCULATION AND RESULTS

Our calculations are based on the all-electron full-potential augmented-plane-wave method[16] (FLAPW) and make use of the local-density approximation (LDA) to the density-functional theory as parametrized by Hedin and Lundqvist.[17] We perform a semirelativistic calculation in which the core states are calculated fully relativistically and self-consistently, whereas the valence states are treated nonrelativistically. The expansion of the potential and of the charge densities inside the muffin-tin (MT) spheres included terms up to $l_{\max}=8$; the MT spheres radii used for B, C, Be, N, O were 1.30, 1.30, 1.35, 1.30, 1.45 a.u. and convergency tests suggested to include wave functions up to $k_{\max}=4.5$ a.u.

Figure 1 displays the geometrical relationship between the structures investigated in this work. Starting from the layered phase and decreasing the interlayer bond length (R), the dense wurtzite phase is achieved by buckling the honeycomb layers (changing θ) into chair configurations and simultaneously stretching the intralayer bond length (r). More details about the choice of variables which characterizes this transition have been given elsewhere.[11,14] Since nothing is known about BeO in the layered structure, our study began with the determination of the interatomic distances between Be and O in this phase through total-energy minimization. At this stage several tests were performed on the sampling of the irreducible Brillouin zone (BZ). For this step, as well as in the determination of the energy barrier, we used 12 special k points.[18] We obtained a bond length for the monolayer equal to 1.54 Å which is very similar to the summation of Slater's atomic radii[19] for Be and O ($r_{\mathrm{Be}}=1.0$ Å and $r_{\mathrm{O}}=0.6$ Å). This same relationship is known to hold very well for layered BN, graphite, and BC_3. Therefore in the graphitic limit the variables which characterize the transition assume the following values: $R=3.33$ Å,[20] $\theta=90°$, and $r=1.55$ Å, while in the wurtzite phase $R=r=1.63$ Å,[2] and $\theta=109.47°$. This set of values corresponds to the ideal ratio $c/a=1.633$ for the wurtzite structure, which is slightly different from the experimental ratio $c/a=1.623$,[2] but were chosen this way in order to make systematic comparisons with previous calculations for BN and C systems. The nearest-neighbor distances for all the phases considered in this work are given in Table I.

With this convention in mind, the internal structural energy per molecule is given as a function of the selected variables $E(R,r,\theta)$. Any of them could be arbitrarily

TABLE I. Nearest-neighbor distance in Å (Ref. 2) for the compounds in the wurtzitelike (dense) and graphitelike (layered) phases.

	C	BN	BeO
Dense	1.54	1.56	1.63
Layered	1.42	1.45	1.54[a]

[a] This work.

selected as the independent variable, but in practice R, which can be modified by uniaxial stress, is selected. Therefore the other variables r and θ become functions of R and are determined by minimizing the total energy with respect to them at each fixed value R. This gives rise to three functions $E(R)$, $r(R)$, and $\theta(R)$, which are, respectively, the minimum internal energy at a given R, and the values of r and θ at which this minimum occurs. These three functions are displayed in Fig. 2.

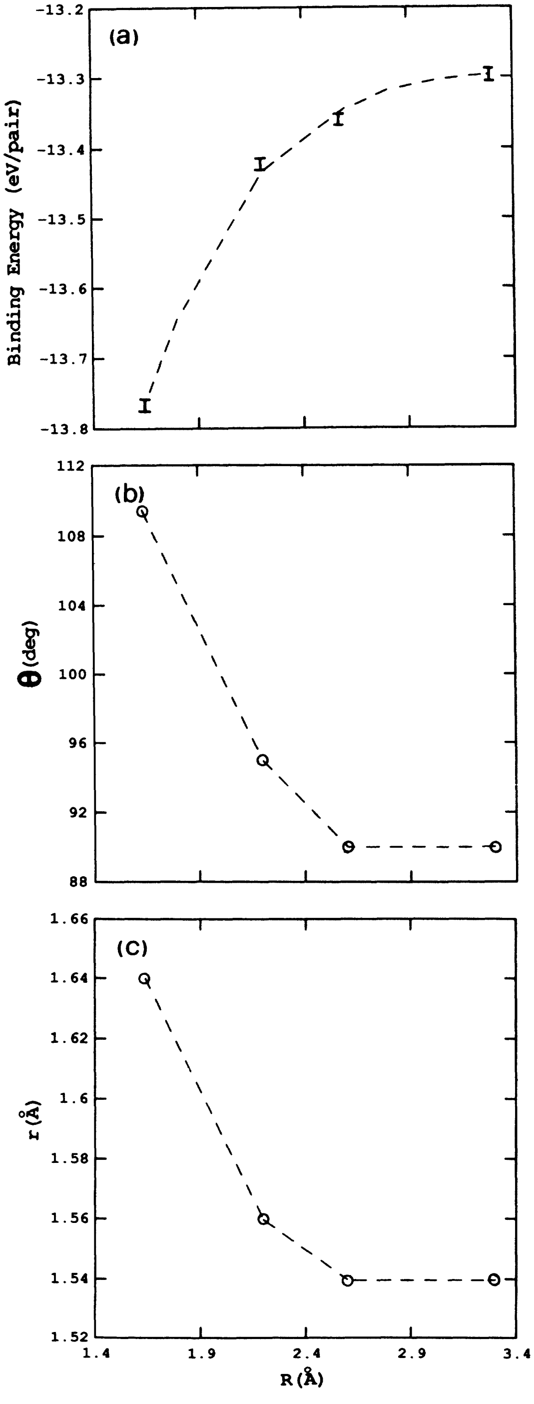

FIG. 2. (a) Cohesive energy per molecule of BeO, (b) buckling angle, and (c) bond length within layers, as functions of the bond length between layers along the minimum-energy path between w-BeO and h-BeO. The left side corresponds to the dense limit and the right side corresponds to the layered limit.

As shown in Fig. 2(a), the layered phase is structurally unstable towards the described deformation. Despite the fact that we have minimized the energy for only two values of R along the path, it is clear that the layered form does not correspond to a metastable atomic configuration. We calculated two intermediary points: the first value of R, 2.2 Å, corresponds to the interlayer separation, at which the maximum of the barriers is reached for similar transitions in BN and graphite, while the second value, 2.6 Å, was chosen to investigate a possible shift of the barrier. Even at this value of the interlayer separation, the internal energy is lower than that of the layered phase, which leaves almost no room (within the uncertainty of the calculation)[21] for an effective barrier.

III. DISCUSSION

Despite the difference in energies between the layered and the dense forms, which already suggests the instability of the layered form, the search for the barrier was an unavoidable step, simply because of previously known trends along the isoelectronic series. The results are summarized in Fig. 3. This figure also displays similar barriers for the C and BN systems, and were obtained by pseudopotential calculations.[11,14] Compared to the graphite → diamond transition, the BN system displays smaller activation energies, which is consistent with the observed trends for covalent systems, namely, decreasing cohesion, bulk modulus and phonon frequencies with increasing polarity of the bond.

Figure 3 displays the energy excess of the atomic configurations with respect to the dense phases. The absolute values of the cohesion along the series for the two

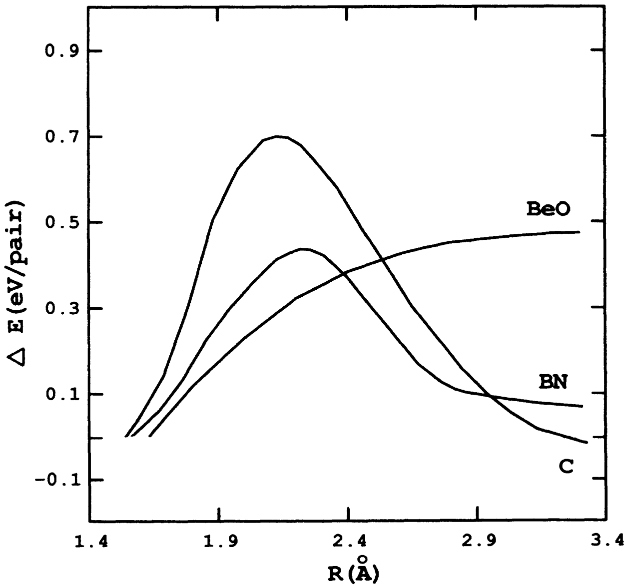

FIG. 3. Internal energy barriers (relative to the total energies of the dense phases) along the minimum-energy paths between the layered and the dense phases of C (from Ref. 11), BN (from Ref. 10), and BeO (this work).

extreme phases is shown in Table II.[22] These values were calculated using the same set of 30 k points in the irreducible BZ for the dense and the layered phases, which have the same space-group symmetry D_{6h}^4, and the Lehmann-Taut tetrahedron method of integration.[23] Some of our binding energies exceed those of previous pseudopotential calculations[11-15] by more than 1 eV per pair, a difference which seems to originate in the different treatment given to the core states. Our value for graphite, however, agrees well with previous all-electron FLAPW calculations for the graphite monolayer.[24] Actually our values slightly underestimate the correct all-electron LDA value for the binding energy of these systems since structural parameters, like c/a ratios, have not been optimized.

Figure 3 and Table II indicate that the cohesion of the layered structure is more strongly affected by the increase of bond polarity than that of the dense phase. To improve our understanding of this point we plotted in Fig. 4 the difference ($\Delta E = E^d - E^l$) between the components (kinetic E_{kin}, Coulomb E_{Coul}, and exchange and correlation E_{xc}) of the total energy of the two phases along the series of compounds. However, since the members of the series differ not only in polarity but also in their bond lengths, we included a fictitious member in which only polarity is changed, i.e., BN with the lattice constants of C (BN/C). In this way we can separate the effect of these two distinct changes in the inhomogeneous electron gas.

The changes in E_{kin} and in E_{xc} (described by the LDA) in the first step of the sequence can be easily interpreted if we reason that the main differences between the electronic charge densities of the two phases, as well as their main implications, lie in the two-dimensional and higher-density character of the charge in the layered phase versus the three-dimensional and lower-density character of the charge density of the dense phase ("dense" in the sense of number of atoms per unit volume). If this is the case, in the homopolar system (C), the dense and layered phases can be modeled, respectively, by a homogeneous electronic distribution ρ_d and an alternation of slabs of electronic densities $\rho = \rho_l$ and $\rho = 0$, with $\rho_l > \rho_d$, as is the case in diamond and graphite. The change of polarity only can be envisioned as a disproportionation of the regions of constant densities $\rho_{d,l}$ into alternating uniform regions of densities $\rho_{d,l}^A = \rho_{d,l} - \Delta\rho_{d,l}$ and $\rho_{d,l}^B = \rho_{d,l} + \Delta\rho_{d,l}$. For instance, starting with C and increasing the polarity, we see that the difference in E_{kin} ($\Delta E_{\text{kin}} = E_{\text{kin}}^d - E_{\text{kin}}^l$) decreases, while the difference in E_{xc} increases (see Fig. 4). We note that these two changes could be attributed essentially to the functional forms of these energy densities in the homogeneous electron gas in the absence of gradient corrections, i.e., $E_{\text{kin}} \approx \rho^{2/3}$ and $E_{\text{xc}} \approx -\rho^{4/3}$, if $\Delta\rho_l \approx \Delta\rho_d$.

The changes ΔE_{kin} and ΔE_{xc} in the next step of the sequence (BN/C → BN) are more subtle in view of the fact that the bond lengths of the two phases relax differently and that the electron gas is already sufficiently inhomogeneous for us to reason in terms of homogeneous systems. Nevertheless, we note that the observed increase in ΔE_{kin} and decrease in ΔE_{xc} could be attributed to the functional form of these energy densities in the homogeneous electron gas if in each region (A,B) of the layered phase the charge density decreased by an amount sufficiently larger than in the corresponding region of the dense phase under lattice relaxation, i.e., $\rho_d^{>(A,B)} - \rho_d^{(A,B)} < \rho_l^{>(A,B)} - \rho_l^{(A,B)}$ (note that the superscript $>$ stands for larger nearest-neighbor distances). Since the relaxation in the nearest-neighbor distance of the layered phase is larger than that of the dense phase (see Table I), this may be a plausible interpretation.

The net effect of this two-step transformation is an overall increase of ΔE_{xc} and ΔE_{kin} in going from C to BN, as well as in going from BN to BeO. This means that these contributions to the total energy favor, respectively, inhomogeneities and larger interatomic distances typical of the more polar systems. If they were dominant, the layered phases would become more stable relative to the dense phases as polarity increases along the series. It is actually the behavior of the Coulomb energy in the two phases with increasing bond polarity that gradually destabilizes the layered phase along the series and is ultimately responsible for the nonexistence of layered BeO. This contribution, generically described by "Coulomb energy," is of course composed of more elementary terms like electron-electron, electron-core, and core-core interaction energies, among which the core-core term is the one that dominates the behavior of the difference in E_{Coul} along the series analyzed here.

TABLE II. Cohesive energies in eV per molecule along the series for the wurtzitelike (dense) and graphitelike (layered) phases obtained in this work.

	C	BN	BeO
Dense	17.01	15.18	13.77
Layered	16.95	15.07	13.29

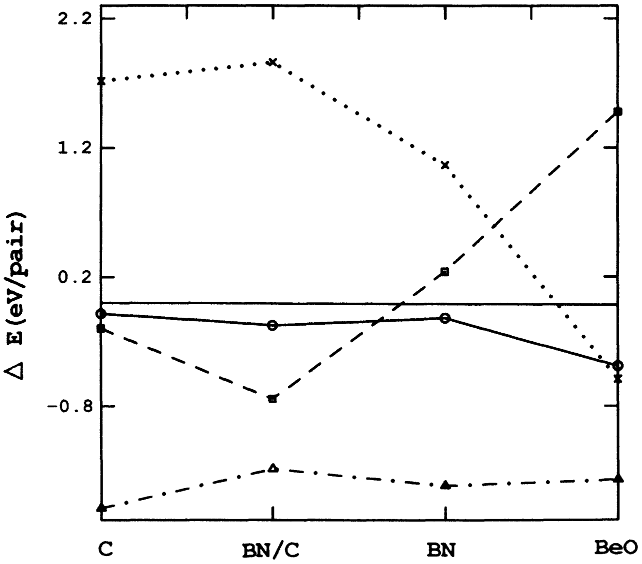

FIG. 4. Energy difference ($\Delta E = E^d - E^l$) between the layered and the dense phases of BeO, separated in its components. ——, total energy; — — —, kinetic energy; · · · ·, Coulomb energy; and —·—·—, exchange and correlation energy.

III. CONCLUSIONS

We have systematically studied the series of first-row compounds C, BN, and BeO in the dense wurtzitelike and the layered graphitelike phases through a first-principles, total-energy, all-electron LDA calculation. The aim was to understand the mechanism that helps the formation of the layered form in C and BN systems and hinders its formation in BeO. On the basis of the kinetic and exchange correlation energies, which favor, respectively, larger interatomic distances and inhomogeneities in the electron gas, the layered form becomes more favorable relative to the dense phase as the bond polarity increases. It is the Coulomb energy which is ultimately responsible for the destabilization of the layered phases in more polar systems and prohibits the formation of layered BeO.

On the other hand, the proposed synthesis of BeO by CVD may remain a viable process for the synthesis of this material in the dense wurtzite form, which has the largest energy gap (7.8–10.7 eV) (Ref. 25) among the first-row compounds.

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[20] This chosen value of the interlayer distance is equal to that of BN, which is also similar to that of graphite (3.35 Å), however the layers were separated by three times this distance during the determination of the intralayer bond length.

[21] The uncertainty in the values of $E(R,r,\theta)$ at a certain R are caused essentially by the values of E at the neighboring points of the two-dimensional (2D) mesh in the variables r and θ.

[22] These values were obtained by subtracting the total spin-polarized atomic energies of the constituent atoms as well as the zero-point motion (E_{zp}), estimated according to the Debye model, from the total crystalline energies ($E_{\text{zp}}=\frac{9}{4}k_B\theta_D$ per molecule, with $\theta_D^{\text{BeO}}=1280$, $\theta_D^{\text{BN}}=1700$, and $\theta_D^{\text{C}}=2000\,^{\circ}\text{C}$). As previously noted, E_{zp}'s of the layered and the dense phases are essentially equal, despite the differences in the phonon spectrum of the phases. See Ref. 12.

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