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Ab initio study of graphite → diamondlike transitions in BN

Renata M. Wentzcovitch, S. Fahy, Marvin L. Cohen, and Steven G. Louie
Department of Physics, University of California, and Materials and Chemical Sciences Division,
Lawrence Berkeley Laboratory, Berkeley, California 94720
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We have investigated the variation of the structural energy along two transition paths from the layered to the highly condensed phases of BN using the first-principles total-energy pseudopotential method. Along the structural paths considered, the symmetries of the initial layered phases have been maintained, leading from the rhombohedral and hexagonal graphitic phases, which differ in their stacking sequences, into the zinc-blende and wurtzite phases, respectively. Constraining the interlayer distances, the total energies were minimized by allowing the hexagonal rings to stretch and buckle into chair conformation. The paths obtained in this way have activation energy barriers approximately 40% smaller than those in graphite→diamond transitions of C, and approximately equal to 0.38 eV/pair for both processes considered when the zero-point motion energy contribution is neglected. The charge densities indicate that strong bonding between the hexagonal layers occurs only in the final stage of the transitions, after the barriers have been crossed, and the structures collapse into the tetrahedrally coordinated phases. From the point of view of electronic structure, at all stages along the transitions, BN displays gaps (calculated within the local-density approximation) larger than 3.5 eV, a minimum which is reached when the activation energy barrier is near a maximum.

I. INTRODUCTION

Recent advances in the technology of layered materials[1] have stimulated renewed interest in the physics of graphite and layered BN. New graphitic forms, in which C is replaced by B and/or N, allow a larger range of controlled properties as well as new possibilities for intercalation chemistry. At the same time these advances call for more basic and comparative studies of the relationship between graphite and layered BN.

A question of interest in the study of the high-pressure properties of graphite and layered BN is that of the nature of the transformation process from these materials into the fourfold-coordinated phases. A study of this problem requires a general understanding of the bonding and electronic structure of C and BN in their layered and fourfold-coordinated phases. Moreover, in view of the existence of the novel graphite-based materials, an understanding of these transitions acquires additional importance for future investigations aimed at producing new substances with controlled physicochemical properties.

It is known that, when applied to graphite or layered BN, high pressures and high temperatures produce synthetic diamonds[2] and zinc-blende or wurtzite BN.[3] From the experimental point of view, the syntheses of these dense phases are relatively well established. Besides the variety of the starting materials, their production depends on the experimental conditions involved, such as pressure, temperature, and the presence of catalysts. Reasonably accurate pressure-temperature phase diagrams for C and BN are available. On the other hand, from the theoretical microscopic point of view, the role played individually by these factors is not well understood. In particular there are puzzling questions about the relationship between the structural orientations of the parent and the newly formed phases.[4]

The purpose of this paper is to report a microscopic first-principles investigation of the role of mechanical stresses in the structural transformations of layered forms of BN into their dense modifications, the zinc-blende and the wurtzite phases. We use the total-energy pseudopotential method in the localized basis formalism[5,6] to obtain accurate values of the internal energies of the BN compound along specific structural transition paths. Similar studies already exist for the graphite to diamond transitions and provide us with useful cases[7–9] for comparison of aspects of the transition, such as the energy barriers for the transition and the formation of bonds linking the original graphitic layers.

The most common form of layered BN is the hexagonal phase (h-BN), which does not have an equivalent form in graphite, and from this, both dense phases have been synthesized. The formation of the wurtzite phase (w-BN) under static compression has been shown to require smaller temperatures than the formation of the zinc-blende phase.[10] This is similar to the syntheses of hexagonal and cubic diamond from graphite.[2] From the rhombohedral form of BN (r-BN),[11] the synthesis of zinc-blende BN (z-BN) is achieved under the same circumstances in which wurtzite BN is produced from hexagonal BN.[12] This indicates that the stacking sequence also plays an important role in the transformations, and supports models in which the transformations proceed by diffusionless mechanisms with well-defined epitaxial relationships between the parent and the newly formed phases.

Despite many similarities between the h-BN→wBN transition, which will be described in the next section, and the graphite → hexagonal-diamond transition, their microscopic mechanisms appear to be different. This is essentially because of the difference in the stacking of the initial layered phases of BN and that of (bernal) graphite. As pointed out by Bundy and Kasper,[13] to achieve the observed epitaxial relationship between the parent and the daughter phases, the graphite layers should deform into "boat" instead of "chair" configuration. A distortion of this kind, combined with intralayer bond stretching and interlayer bond compressing, results in a hexagonal diamond phase whose *c* axis is perpendicular to the graphitic *c* axis. The possibility of a similar mechanism being operative in the *h*-BN→*w*-BN transition was raised by Riter,[4] who suggested that even though it would be necessary to have a lateral displacement of layers in the initial phase, on the basis of the deformation energies of individual layers, this mechanism should involve smaller activation energies for the transition. This point will not be addressed in the present study because a comparative calculation would require larger unit cells and prohibitive costs.

In the next section we report details of the calculations and the results of the present study. This is followed by a comparison with previous work on the graphite to diamond transition. Some conclusions are presented in Sec. III.

II. CALCULATIONS AND RESULTS

The geometrical relationships between the structures explored in this work are displayed in Fig. 1. In these transformations, the symmetries of the original phases remain unchanged along the transformation paths, and the transitions can be characterized simply by three internal structural parameters. The first case, shown in Fig. 1(a), has symmetry C_{3v} and corresponds to the rhombohedral to zinc-blende (*r*-BN→*z*-BN) transition. The second case corresponds to the hexagonal to wurtzite (*h*-BN→*w*BN) transition, with symmetry D_{6h}^4. The starting graphitic phases differ in their stacking sequences: *r*-BN has a three-layer sequence, *ABCABC*, . . . , while *h*-BN has a two-layer sequence *AaAa* , ... By decreasing the interlayer bond lengths, buckling the honeycomb layers into chair configurations, and simultaneously stretching the intralayer bond lengths, the denser zinc-blende and wurtzite forms are achieved. In the graphitic limit, the three variables which characterize the structures assume the values: buckling angle $\Theta = 90°$, intralayer bond length $r = 1.45$ Å, and interlayer bond length $R = 3.34$ Å. In the dense limit they are $\Theta = 109.47°$, $r = R = 1.57$ Å.[14]

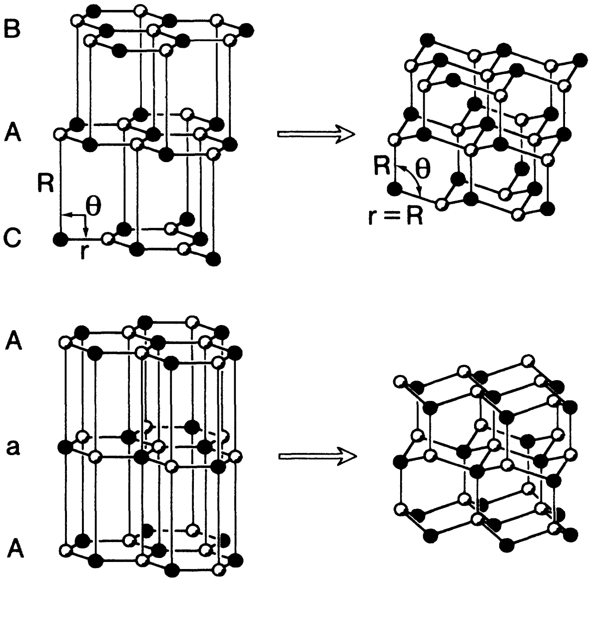

FIG. 1. Structural relationship between the layered phases and the fourfold-coordinated structures considered in this work. (a) Rhombohedral BN to zinc-blende transition. (b) Hexagonal BN to wurtzite transitions.

Following this convention, the internal structural energy per molecule becomes a function of three selected variables, $E(R,r,\Theta)$. Once one of them is chosen to be the independent variable, we obtain the values of the other two by minimizing the total energy with respect to them. A convenient independent variable is the interlayer bond length *R*, which in practice can be modified by application of stress along the soft [0001] "graphitic" direction. It should be noted that a different independent variable could have been chosen, giving rise to a different transformation path. For example, to study the effect of hydrostatic pressures, the cell volume *V* is the appropriate independent variable, which in the present case is a function of the three chosen variables $V(R,r,\Theta)$.

Our convention gives rise to three functions of *R*: $E_{\min}(R)$, $r_{\min}(R)$, and $\Theta_{\min}(R)$. They are shown in Fig. 2, and correspond, respectively, to the minimum value $E(R,r_{\min},\Theta_{\min})$ of the internal energy at a given *R*, the value of *r* at which this minimum occurs, and the value of Θ at the same minimum. The two curves in Fig. 2(a) correspond to the two transitions studied: the solid line corresponds to the *r*-BN→*z*-BN transition, in which the structural energy minimizations were done as mentioned above, while the dashed line corresponds to *h*-BN→*w*-BN transition, in which the same values of the parameters *R*, *r*, and Θ used in the *r*-BN→*z*-BN transition were used for the hexagonal structures.

The total energies were calculated within the local-density-functional theory,[15] with the Wigner approximation[16] for the exchange-correlation energy. The interaction between the electrons and the ion cores was described by first-principles pseudopotentials[17] whose configurations have been reported elsewhere.[18] The wave functions were expanded in Bloch sums of Gaussian orbitals,[5] of the form

$$f(\mathbf{r}) = e^{-ar^2} r^l Y_{lm}(\theta,\phi) \ . \tag{1}$$

The chosen basis set consisted of four radial decays *a* with four orbitals *s*, p_x, p_y, and p_z, for each decay, for both B and N.[19] The crystal potential, with plane-wave components up to 64 Ry, was iterated to full self-consistency using the scheme of Chan *et al.*[6] Along the *r*-BN→*z*-BN transition, the Brillouin-zone averages were sampled using a uniform grid containing 25 *k* points along the irreducible Brillouin zone. For the h-BN→w-BN transition, the uniform grid used contained 30 k points.

A close inspection of Fig. 2 shows that there are striking similarities between the present transitions and the equivalent ones in C.[8,9] A common feature of the transitions in the BN and the C systems is the sudden change in behavior of the interlayer bond lengths $r(R)$ and buckling angle $\Theta(R)$. As the layers approach each other (decreasing R), the angle Θ, which in the graphitic limit is very insensitive to the interlayer distance R, suddenly starts changing at a faster rate below a critical value of R. This happens at the point where the interaction between layers starts increasing, and the energy barrier starts to rise; i.e., when the interlayer bond length R is around 2.6 Å. The behavior of the intralayer bond length $r(R)$ is quite similar, but the sudden change in behavior does not happen until a later stage, closer to the top of the barrier, which corresponds to an interlayer bond length of approximately equal to 2.2 Å. At this point the bonds start buckling quickly, while the structures collapse into the dense forms.

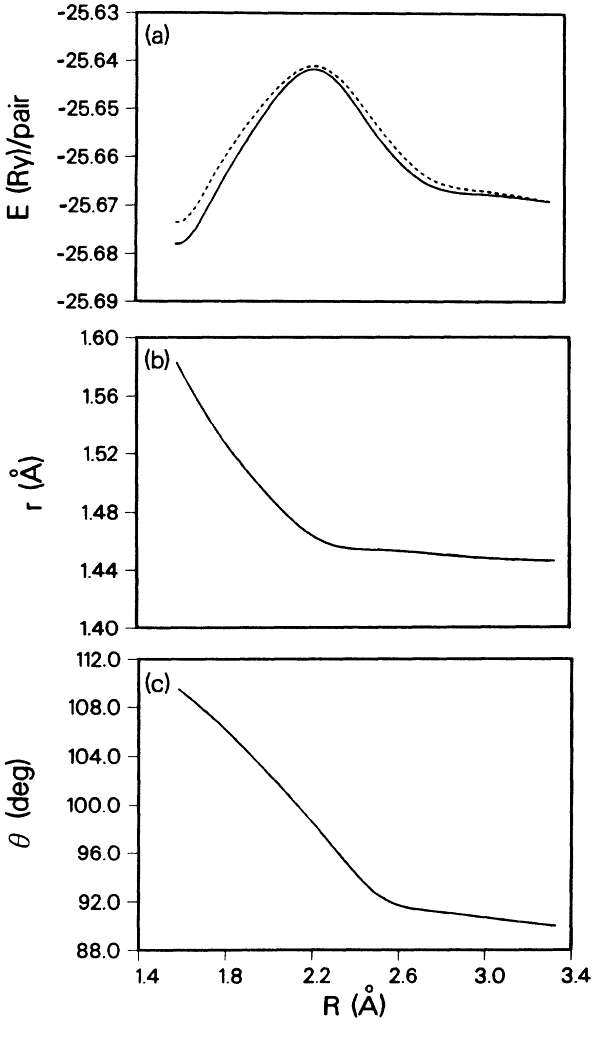

FIG. 2. (a) Total energy per BN molecule in the r-BN→z-BN (solid line) and h-BN→w-BN (dashed line) transitions, (b) bond length within layers, and (c) buckling angle as functions of the bond length between layers for the path which minimizes the total energy for each value of the interlayer bond length. The left side corresponds to the dense limit, while the right corresponds to the layered limit.

Compared to the graphite→diamond transitions, the BN system requires smaller activation energies. The heights of the barriers in the present calculation are approximately 0.39 eV/pair while in the C system they are 0.66 eV/pair. This result is consistent with an overall trend of covalent systems: Whenever covalency is decreased by introducing some ionic character to the bond, the cohesive energies decrease, as well as their vibrational frequencies and bulk moduli. This effect is also strongly manifested in the relative binding energies of the layered and the dense phases of BN. It is well known that the graphite's cohesive energy, 14.748 eV/pair, is slightly larger than diamond's 14.698 eV/pair.[8,20] Our calculation indicates that the partially ionic character of BN depletes the binding energy of the layered phases more strongly than the dense phases when compared to the purely covalent phases of C. In particular we obtain a difference in cohesion, $E^z_{\mathrm{coh}}-E^r_{\mathrm{coh}}$, between the phases of 0.12 eV/pair when the crystal zero-point motion is not taken into account. This is not an obvious result, since the dense phases, which are the more stable according to our results, are not the usual forms found in nature, but are synthesized from the layered phases.

The large difference in densities of the layered and the fourfold-coordinated structures, suggests that the observed stability of the layered phases may be accounted for by their lower zero-point motion vibrational energy, E_{ZP}'s, as compared with that of the dense phases. Despite the important difference of the details in the phonon spectrum of the two phases, an approximate estimate of these energies can be done by using the Debye model. Inspection of the specific heat of the layered phases at low temperatures[21,22] shows that instead of following the T^3 dependence on the temperature T, typical of three-dimensional systems, it follows a T^2 law derivable from a two-dimensional (2D) Debye model. The fitted Debye temperature consistent with the 2D Debye model for layered BN is 598 K, in contrast to 1700 K for the dense phases. The expressions for the E_{ZP}'s in the 2D and the 3D Debye models are, respectively, $2k_B\Theta_D$ and $\frac{9}{4}k_B\Theta_D$ eV per pair, which yield $E^r_{\mathrm{ZP}}=0.10$ and $E^z_{\mathrm{ZP}}=0.33$ eV/pair. When these values are added to the calculated energies, the relative stability of the layered phases is recovered with a difference in cohesion $E^z_{\mathrm{coh}}-E^r_{\mathrm{coh}}=-0.11$ eV/pair. The cohesion of the zine-blende and wurtzite structures are, respectively, 13.5 and 13.4 eV/pair, which are comparable to previous results obtained by pseudopotential plane-wave calculations.[18,23]

It is interesting to compare the estimated E_{ZP}'s of different phases of BN with those of the graphite and diamond phases of C, which can be directly evaluated from existent phonon DOS's.[24,25] These homopolar phases, however, have very similar E_{ZP}'s ($E^{\mathrm{gr}}_{\mathrm{ZP}}=0.33$ and $E^{\mathrm{dia}}_{\mathrm{ZP}}=0.36$ eV/pair), despite a substantial difference in their phonon energy distribution. This indicates that the

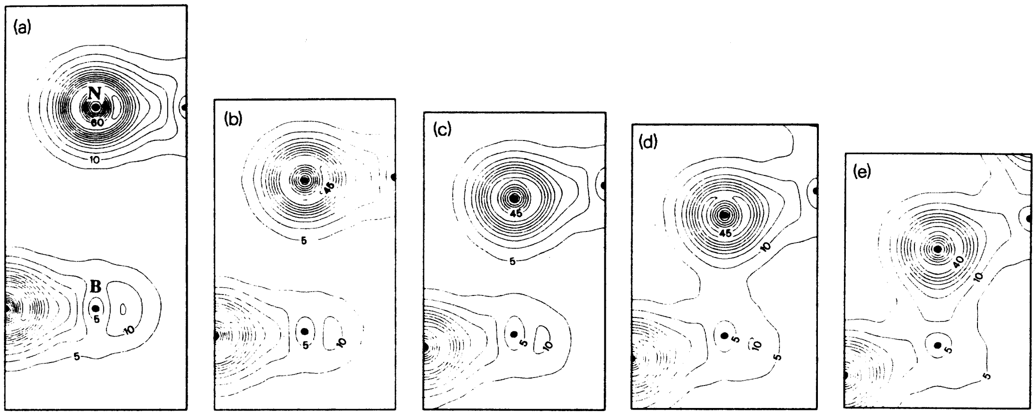

FIG. 3. Charge density in the {1100} planes for various points along the path in the r-BN→z-BN transition. They correspond to interlayer bond lengths of (a) 3.34 Å, (b) 2.50 Å, (c) 2.25 Å, (d) 2.00 Å, and (e) 1.56 Å.

evaluation of E^{r}_{ZP} based on the 2D Debye model and using Θ_D's fitted to low-temperature specific-heat data may not be sufficiently accurate and other corrections to the cohesive energies should be considered. For example, the basis set used in the calculation, in particular the orbital sizes, may be less appropriate to deal with layered BN and the total energies in this phase may be less converged. We conclude that the reason for the preponderance of the layered form of BN over the dense form at room temperature is a question which could be clarified when thermodynamical data [$S(T)$, $H(T)$, etc.] from 0 K to room temperature become available for the two forms of BN and allow a more realistic comparison of their free energies.

The above discussion brings up an important question concerning the influence of the zero-point motion in the energy barrier's height. These energies are expected to vary strongly along the transition with a value in the dense limit which is almost as large as the activation barrier. Given the difficulty in estimating this energy in intermediate stages along the transition, where some bonds are breaking and new ones are forming, we do not include this effect in our calculation. However, we estimate that a deviation of up to 50% in the barrier height is possible.

Another point of interest is the reconstruction of bonds during the transition. Figure 3 contains charge-density plots in the $(1\bar{1}00)$ plane, which is perpendicular to the hexagonal plane, at various stages along the rB→z-BN transition path. This plane contains the σ bonds, derived from sp^2 orbitals, and the π bonds in the graphitic limit, as well as sp^3 bonds in the dense limit. Since the transition was studied by constraining the interlayer bond length, this figure shows the "sequence of events" as the layered phases are compressed along the c axis. Figures 3(a)–3(c) correspond to the right-hand side of the barrier drawn in Fig. 2(a). We see that up to the top of the barrier, which corresponds to Fig. 3(c), the integrity of the graphitic bonding is preserved. The σ bonds remain undisturbed and almost no charge is added to the region between the planes, indicating that, despite an increasing interaction between π orbitals in adjacent planes, it is still not enough to disturb substantially the sp^2-p_z configuration of the layered phase. The formation of bonds linking the layers happens in the succeeding Figs. 3(d) and 3(e), which correspond to the left-hand side of the barrier in Fig. 2(a). In this region of the transition the layered structures are collapsing into the dense phases. The lowering of the total energy in this region is followed by a corresponding rearrangement of the sp^2 bonds into sp^3. Although we have not calculated the corresponding charge densities in the h-BN→w-BN transition, the bond formation is expected to be very similar. This is what was found in the graphite→diamond transition.[8]

Finally, our study reveals that, along the r-BN→z-BN or z-BN→w-BN transition paths, the band gaps behave in a similar manner, and at no points along the paths do the structures become metallic. Initially, the LDA (local-density approximation) gap is approximately 4.6 eV in the rhombohedral structure; around the top of the barrier it decreases to approximately 3.5 eV, followed by a final opening to 4.5 eV in the zinc-blende structure.

III. CONCLUSIONS

We have performed a total-energy calculation of the transitions from the layered (hexagonal and rhombohedral) phases to the highly condensed phases (zinc blende and wurtzite) in the BN semiconductor compound. The activation barriers have been computed along structural transition paths compatible with the crystalline symmetries of the parent and the newly formed phases and have shown very similar energetic features. Compared to similar transitions in C (graphite→ diamond transition), the energy barriers in BN, 0.38 eV/pair, are 40% smaller, which is consistent with its larger heteropolarity. From the point of view of electronic structure, none of the structures along the considered transition paths have metallic character. The fundamental gap remains large throughout the transition, with values around 4.6 eV in the graphitic limit and 4.5 eV in the dense limit, despite a small decrease to 3.5 eV near the top of the structural energy barrier. Inspection of the charge densities indicate that interlayer bonds are developed in the later stage of the transitions, once the barriers are overcome and the layered structures are collapsing into those of the dense phases. The difference in the vibrational zero-point energy is found to be important for stability of the layered phases of BN compared to the dense fourfold-coordinated phases.

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[19] The choice of the basis set was done in the following way: For each atom kind the decays were chosen to be in geometric progression. A full minimization of the energy with respect to the smallest and the largest decays was performed at the two end points of the transitions, which demonstrated the set of the decays to be very similar. For N, a constant set of decays proved to be satisfactory along the path, while for B, the decays for the layered phases were found to be smaller than those for the denser phases. The smallest and the largest N decays were 0.23 and 5.8, respectively, while the corresponding B decays in the dense phases were 0.17 and 5.3, and those in the layered phases were 0.15 and 5.0. For the intermediate structures, the B decays were linearly interpolated from those at the two extreme of the transition as functions of the interlayer distance. This procedure was chosen in order to minimize the uncertainty in the total energies along the transition paths. The minimization of the decays in the layered structure compared to those corresponding to the dense phases improved the binding energy of the layered phases by approximately 0.03 eV per molecule.

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