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First-principles study of the stability of BN and C

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First-principles total energy calculations are performed to study the phase stability of BN and C at low temperature. These are done using density functional theory (DFT) within the local density approximation (LDA) and the generalized gradient approximation (GGA). We find that for both materials LDA calculations predict dense cubic structures as the ground state structures, while the GGA calculations predict less dense hexagonal layered structures as the ground states. Our calculated results provide a stringent test for the validity of the functional used for the DFT calculations. Accurate experimental measurements of thermodynamic properties for BN and C at low temperature are needed to clarify the stability issues for these materials.

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I. INTRODUCTION

Cubic BN (borazone) has outstanding physical and chemical properties such as extreme hardness, very high thermal conductivity and melting temperature, wide band gap and low dielectric constant. In contrast to diamond, it is also stable against oxidation and acid-resistant. These fascinating features have made it suitable for many applications in modern microelectronic devices and machine tools.[1] However, growth of high quality cubic BN is rather difficult because it is not the observed stable phase of BN at standard conditions. Recent progress in growth techniques has rekindled interest in investigating the phase stability of BN, both theoretically and experimentally.[1–10] BN crystallizes in three main allotrope phases: (1) Dense cubic, c-BN phase, in the zinc-blende structure (space group T_d^2). (2) Dense hexagonal, w-BN phase, in the wurtzite structure (space group C_{6v}^4). (3) Layered hexagonal, h-BN phase (space group D_{6h}^4), which has a stacking sequence $AaAa\ldots$, i.e., a B atom in a subsequent layer is placed directly below the N atom in the previous layer (see Fig. 1). Other layered allotrope phases, which have different stacking sequences along the c direction, also exist. These layered structures all have sp^2 bonding character and their structural properties are very similar to each other, because the layer-layer van der Waals interaction is very weak in this system.

Experimentally,[1] at standard conditions, the only stable allotrope phase observed is h-BN. c-BN can be synthesized in the laboratory under pressure and converts to the h-BN phase when heated in vacuum to 1700 K. w-BN is found to be unstable under any growth conditions. Traditionally, it was believed that h-BN is the ground state of BN,[11] similar to the situation for C, where the layered hexagonal graphite structure is found to be more stable than the cubic diamond structure.[12–14] However, recent measurements of Solozhenko[8–10,15] suggest that c-BN might be the ground state of BN. Theoretically, the ground state stability of BN has been studied extensively,[2–7] using density functional theory (DFT) within the local density approximation (LDA).[16] The majority of these LDA calculations were performed using pseudopotential methods. They showed unambiguously that c-BN has a lower total energy than h-BN. Only the orthogonalized linear combination of atomic orbital (OLCAO) calculation of Xu and Ching[5] found that h-BN has a lower total energy than c-BN. The observed phase stability of the h-BN is then attributed to the lower zero-point motion vibrational energy of h-BN relative to c-BN. However, a recent theoretical analysis of Albe[3] and Kern *et al.*[2] suggested that the difference of the zero-point energy between these two phases is too small (<10 meV) to compensate for the static total energy difference. Thus they predict that the ground state of BN is c-BN, similar to that proposed by Solozhenko.[15]

To clarify this issue, we have performed all electron DFT total energy calculations using the generalized gradient approximation[17,18] (GGA) as well as using the LDA. It is well known from extensive prior work that the GGA generally yields substantially better cohesive energies than the LDA.[2,19–21] In some cases, the GGA also predicts correctly the ground state phases of materials where the LDA produces incorrect orderings. For example, the GGA predicts correctly the ferromagnetic bcc ground state for Fe, whereas the LDA predicts incorrectly a close packed ground state for Fe.[19] The GGA also predicts a large total energy difference between the dense stishovite and the stable α-quartz structure, in excellent agreement with experiment, while the LDA prediction is too small.[22] Relative to the LDA, the GGA consistently predicts a larger lattice constant and a smaller bulk

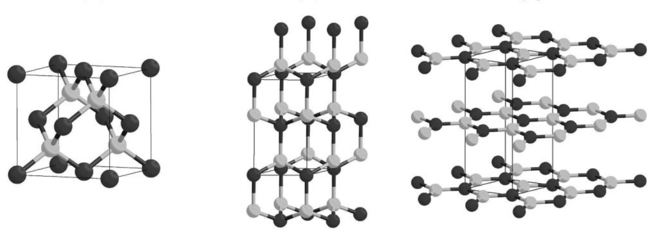

FIG. 1. Crystal structure of BN in (a) the cubic zinc-blende phase, (b) the wurtzite phase, and (c) the hexagonal phase.

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modulus. These results indicate that the GGA has a tendency to lower the total energy of materials with less dense structures more than for a corresponding dense structure. Because c-BN and h-BN have very different equilibrium volumes and local atomic bonding, the GGA could have significant effects on the relative stability of c-BN and h-BN. Indeed, we find that the GGA lowers the atomic total energies of B and N more than the solid BN, so the cohesive energy of BN is reduced to 6.9 eV from the LDA value of 8.2 eV, in much better agreement with experimental value of 6.6 eV. The GGA also lowers the total energy of the less dense h-BN more than the dense c-BN. Thus, the GGA predicts that h-BN is the ground state of BN. This is consistent with the early experimental phase diagram,[11] but contradicts recent experimental suggestions[8–10,15] and LDA predictions.[2,3] Furthermore, the GGA also predicts a huge increase of the interlayer distance in h-BN, reflecting the fact that the GGA is inadequate for describing the weak interlayer van der Waals coupling between the sp^2-bonded planes.[23] However, the change of the total energy associated with the overestimation of the interlayer distance is small (~ 16 meV/atom) compared to the energy difference between c-BN and h-BN. Thus, this error in the calculated structural parameters of h-BN does not change the conclusion that h-BN is predicted by GGA to be the ground state structure of BN.

II. METHOD OF CALCULATIONS

The total energy calculation is performed using the DFT as implemented in the full-potential linearized augmented plane wave (FLAPW) method.[24] We used muffin-tin radii of $R_{\mathrm{MT}}=1.35$ a.u. for all the atoms reported here and basis set cutoff of $R_{\mathrm{MT}}K_{\mathrm{max}}=8.0$. The Brillouin-zone integrations were performed using 60 special[25] k points for the cubic structure and 40 special k points for the hexagonal structure. Convergence tests indicated that the total energy differences are converged to better than 2 meV/atom with these choices. These tests included basis set convergence, k-point convergence, sphere and interstitial mesh densities, and linearization effects (tested by adding local orbitals). To calculate the structure parameters, we first search for the minimum total energy at each volume with respect to all cell parameters. The static lattice ground state properties were extracted from these calculated minimum total energies at each volume, fitting to Murnaghan's equation of state.[26] For the LDA calculations, we used the Ceperley-Alder exchange correlation potentials.[27] For the GGA, we use the parameter-free form given by Perdew and Wang (PW91).[17] Similar results are obtained when the PBE form of the GGA[18] is used. The implementation of the GGA in the FLAPW program is described in detail in Ref. 19. The total energies for the atoms were calculated using either an atomic program or the FLAPW program with a supercell approach. Tests for the LDA calculations show that these two apporaches give identical results.

III. RESULTS

Table I presents our calculated equilibrium lattice parameters a, c/a and V, the bulk moduli B, the pressure coefficients of the bulk modulus B', the cohesive energies E_c, and the total energy differences ΔE relative to the cubic phase for BN in three different phases. Our calculated results are compared with previous comprehensive LDA calculations of Albe,[3] Furthmüller *et al.*,[4] and Wentzcovitch *et al.*[6] and available experimental data.[6,28–32]

A. The LDA results for BN

Our LDA calculated results are consistent with previous LDA pseudopotential calculations. We find that (1) the calculated structural parameters are in good agreement with experimental values. The LDA underestimates slightly the equilibrium volumes. In agreement with experimental data, the w-BN and the c-BN have similar volumes, while the volume of the h-BN is about 51% larger than the volume for c-BN. (2) The calculated bulk moduli and the pressure coefficients of the bulk modulus are also in good agreement with experiment. Note that the bulk modulus of h-BN is an order smaller than those of c-BN and w-BN. To get the correct bulk modulus for the highly anisotropic h-BN, it is very important to search for the optimized cell parameters at each volume as described above. Otherwise, erroneous results for the bulk modulus can occur due to fitting errors.[4] (3) The LDA overestimates the cohesive energy of BN. The overbinding in the calculation is characteristic of the LDA. Our results are consistent with the calculated results of Furthmuller *et al.*[4] and Kern *et al.*,[2] but the calculated cohesive energy of Albe is much smaller, possibly due to an inconsistency with their atomic total energy calculation which was performed using different method. (4) The LDA predicts that the c-BN phase has the lowest total energy. The w-BN total energy is 17 meV/atom above that for c-BN, whereas that of h-BN is 72 meV/atom above that for c-BN. These results are similar to previous calculations.

B. The GGA results for BN

The results obtained using the GGA functional for BN are also presented in Table I. We find that (1) the GGA increases the equilibrium lattice parameters relative to the LDA. For the c-BN and the w-BN phases, the agreement with experimental values is improved. For the h-BN phase, although the calculated in-plane lattice parameter a is in good agreement with experimental value, unfortunately, the GGA predicted c/a ratio is drastically increased from the LDA value of 2.580 to 3.336, much larger than the experimental value of 2.660. However, the total energy associated with the increase of the interlayer distance is very small. Reducing the c/a ratio from 3.336 to 2.660 increases the total energy by only 16 meV/atom, indicating that h-BN is essentially a 2-dimension system with very weak bonding between the hexagonal layers. (2) The GGA predicts a smaller bulk modulus than the LDA, mainly due to the increase in the predicted equilibrium volume. (3) The GGA corrects the over-binding of the atoms in the LDA calculation. The predicted cohesive energy is in much better agreement with experimental values. (4) The cohesive energy differences between c-BN and w-BN are very similar in both the LDA and the GGA calculations. However, unlike the LDA calculation that predicts the dense c-BN to be the most stable structure, the GGA calculation predicts that the h-BN is more stable. This result is consistent with the general trend that the GGA

TABLE I. Calculated equilibrium structural parameters and cohesive energies of BN. Results are compared with previous LDA calculations and available experiment data (Refs. 6,28–32).

	K. Albe (LDA)	Furthmüller (LDA)	Wentzcovitch (LDA)	LAPW (LDA)	LAPW (GGA)	Expt.
cubic-BN						
V (Å^3/atom)	5.797	5.718	5.860	5.750	5.994	5.930
a (Å)	3.593	3.576	3.606	3.583	3.633	3.615
E_c (eV/atom)	6.47	8.152	7.15	8.153	6.930	6.6
B (GPa)	395	397	367	401	369	369–400
B'	3.65	3.59	3.6	3.96	3.00	4.0
wurtzite-BN						
V (Å^3/atom)	5.813	5.731		5.785	6.014	5.966
a (Å)	2.532	2.521		2.525	2.557	2.553
c/a	1.654	1.652		1.660	1.662	1.656
E_c (eV/atom)	6.481	8.172	7.177	8.136	6.912	
B (GPa)	394	401		408	366	
B'	3.68	3.59		3.22	3.74	
ΔE (eV/atom)	0.011	0.020	0.027	0.017	0.018	
hexagonal-BN						
V (Å^3/atom)	8.747	8.613		8.673	11.515	9.042
a (Å)	2.496	2.468		2.495	2.517	2.504
c/a	2.600	2.590		2.580	3.336	2.660
E_c (eV/atom)	6.527	8.207	7.21	8.081	7.006	
B (GPa)	30.1	261		26.7	2.13	36.7, 29.9
B'	10.1	3.66		10.72	9.6	5.6, 9.3
ΔE (eV/atom)	0.057	0.055	0.06	0.072	-0.075	

lowers the total energy of a less dense structure more than a dense structure.[20,22] The GGA result agrees with traditional[11] phase diagram of BN, but the LDA results are closer to recent experimental phase diagram of BN.[15] Since no accurate thermodynamic data at low temperature is available for BN, it is not completely clear which result is closest to reality.

C. The results for C

To help verify that the GGA results for BN are not spurious, we have performed similar calculations for C, for which more reliable experimental data exists. Corresponding to c-BN, w-BN, and h-BN structures, we investigated the relative stability of the diamond, hexagonal diamond, and graphite structures (see Fig. 2). These structures can be obtained by replacing both B and N by C. For the graphite structure, however, the stacking sequence is $ABAB$, instead. The calculated results are shown in Table II. We find that the effect of the GGA for C is very similar to that for BN. Relative to the LDA calculated results, the GGA increases the lattice constants and reduces the bulk moduli. Although the GGA produces a much better agreement with experimental data for the cohesive energy, the calculated c/a ratio for graphite using GGA is much too large[33] compared to experimental data. Again, the GGA lowers the total energy of the less dense graphite structure much more than the dense diamond structure. The predicted total energy difference for graphite is lowered from the LDA value of 15 meV/atom to -145 meV/atom. Of this, 15 meV/atom can be attributed to the overestimation of the c/a ratio in the GGA calculations. Experimentally, the enthalpy differences between diamond and graphite, measured from the heat of combustion, is about -19 meV/atom at standard conditions.[12–14] Taking into account the volume difference between the two structures and assuming that the vibrational zero point energy and entropy are similar for the two structures, the estimated total energy difference ΔE for graphite is about -40 meV/atom. Therefore, it seems to us that although the GGA predicts correctly the ground state phase, it overestimated the stability of the graphite structure. Of course, a final conclusion can be reached only when accurate thermodynamic data from 0 K to room temperature become available for the two forms of C.

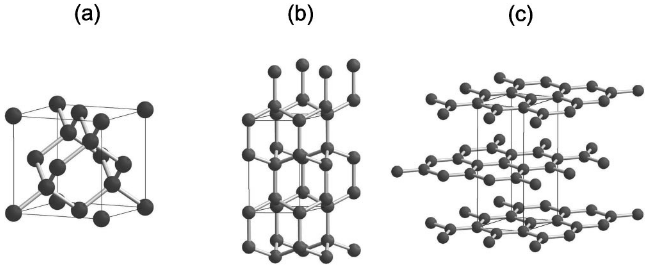

FIG. 2. Crystal structure of C in (a) the cubic diamond phase, (b) the hexagonal diamond phase, and (c) the hexagonal graphite phase.

Recently, Chacham and Kleinman[34] studied the stability of C using the GGA and a pseudopotential method. Using the PBE functional[18] of the GGA, they found that for graphite the equilibrium c/a ratio is 2.73 and the total energy differ-

TABLE II. Calculated equilibrium structural parameters and cohesive energies of C. Results are compared with previous LDA calculations and available experiment data (Refs. 14,36–40).

	Furthmüller (LDA)	Fahy/Yin (LDA)	LAPW (LDA)	LAPW (GGA)	Expt.
diamond					
V (Å^3/atom)	5.488	5.583	5.522	5.731	5.673
a (Å)	3.528	3.548	3.535	3.579	3.567
E_c (eV/atom)	9.026	8.17	9.011	7.766	7.37
B (GPa)	460	444	465	430	443
B'	3.67	3.24	3.44	3.38	4.0
hexagonal diamond					
V (Å^3/atom)	5.504	5.602	5.542	5.756	5.61
a (Å)	2.480	2.50	2.480	2.516	2.51
c/a	1.666	1.656	1.678	1.670	1.638
E_c (eV/atom)	8.998	8.140	8.987	7.748	
B (GPa)	462	440	462	446	
B'	3.66	3.5	3.62	2.80	
ΔE (eV/atom)	0.028	0.030	0.024	0.018	
graphite					
V (Å^3/atom)	8.609	9.312	8.554	13.540	8.797
a (Å)	2.440	2.47	2.447	2.470	2.46
c/a	2.738	2.724	2.706	4.150	2.730
E_c (eV/atom)	9.027		8.996	7.911	7.374
B (GPa)	286	236.1	26.8	0.417	
B'	3.57		13.22	9.70	
ΔE (eV/atom)	-0.000	0.000	0.015	-0.145	

ence between the graphite and the diamond structures is -22 meV/atom. Although these values seem to be in excellent agreement with experiment data, they are very different from our calculated value of $c/a=4.15$ and ΔE(graphite) $=-145$ meV/atom. They also contradict with another GGA pseudopotential calculation[33] which found that the c/a ratio is 3.6. On the other hand, a third calculation by Lee and Martin,[35] also using the PBE functional, yielded a value of 2.735, close to experiment. To see whether the difference is caused by using different GGA functional, we have repeated our calculations using the PBE functional of GGA. We find that the results are nearly identical to that obtained by using the PW91 functional of GGA.[17] Therefore, the discrepancy between our calculated results and the one obtained by Chacham and Kleinman is not understood.

IV. SUMMARY

In summary, we have performed first principles LDA and GGA total energy calculations to study the stability of BN and C. We show that for both materials LDA calculations predicts the dense cubic structures as the ground state structures, while the GGA calculations predict the hexagonal layered structures as the ground states. We find that, in general, GGA lowers the total energy of a less dense structure more than that of a dense structure, thus the phase transition pressure predicted by GGA is higher than that predicted by LDA. Our calculated results also put a stringent test on the validity of the functional used for the DFT calculations. Accurate experimental measurements of thermodynamic properties for BN and C at low temperature are needed to clarify the stability issues for these materials.

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