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Chemical anisotropy in diamondlike BC_2N: First-principles calculations

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We present first-principles calculations of elastic constants for several diamondlike BC_2N (d-BC_2N) structures. Our results show that for the fully relaxed d-BC_2N structures, although the deviations of their lattice constants from those of cubic lattices are small (about 1%), the differences among the elastic constant components, that should be the same for cubic lattices, can reach 75% due to the chemical anisotropy of the d-BC_2N structures, which will affect the spectra of acoustic phonons of these d-BC_2N structures and so their bulk moduli determined by Brillouin scattering experiments. For calculations, in which exact cubic symmetry is imposed on these d-BC_2N structures during the structural relaxations, our tests show that large residual stresses of 4–5 GPa exist in such constrained cubic d-BC_2N structures that are not fully relaxed. Any results derived by assuming such exact cubic symmetry on these d-BC_2N structures may not be reliable.

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Considerable efforts have been made to describe the structures of recently synthesized diamondlike BC_2N (d-BC_2N) for its potential applications as a superhard material with high-temperature thermal stability.[1–6] Recently, Kim *et al.*[7] reported a first-principles calculation on the high- and low-density d-BC_2N by constraining the structures to exact cubic symmetry and claimed that the calculated bulk moduli are in excellent agreement with the available experimental data and consequently the structures of the synthesized high- and low-density d-BC_2N are determined. Exact cubic symmetry was also assumed in the analysis of the experimental x-ray diffraction results of the synthesized d-BC_2N samples.[8] However, these d-BC_2N structures are not exactly cubic due to the differences in chemical properties of boron, carbon, and nitrogen atoms. Here we report the first-principles calculations of elastic constants of these d-BC_2N structures, which show that the differences among the elastic constant components, that should be the same for cubic lattices, can reach 75%, even though the deviations of their lattice constants from those of exact cubic lattice structures are about 1%. The chemical anisotropy of the d-BC_2N structures will affect, among other things, the spectra of acoustic phonons, and so the bulk moduli determined by Brillouin scattering experiments.[9]

We study the d-BC_2N structures denoted as BC_2N-1, BC_2N-2, and BC_2N-3 in Ref. 1, which recently have been assigned to the high-density (BC_2N-1 and BC_2N-2) and low-density (BC_2N-3) structures of d-BC_2N (Ref. 7) synthesized experimentally.[8,10,11] The crystal lattices and orientations of the unit (or super) cells of the d-BC_2N structures are given in Fig. 1. In our calculations we used the PARATEC code[12] with all the calculation parameters being the same as those used in Ref. 1, where we employed the *ab initio* pseudopotential and local-density approximation (LDA) with a plane-wave basis set.[13–15] The norm-conserving Troullier-Martins pseudopotentials[16] were used with cutoff radii of 1.3, 1.3, and 1.5 a.u. for N, C, and B, respectively. The exchange-correlation functional of Ceperley and Alder[14] as parameterized by Perdew and Zunger[17] was used. The total energy of the structures was minimized by relaxing the structural parameters using a quasi-Newton method.[18] The total-energy and stress calculations used an eight-atom zinc-blende-structured unit cell,[1] an $8\times8\times8$ Monkhorst-Pack[19] k-point grid, and a 100 Ry energy cutoff. The energy convergence of the calculation is on the order of 10^{-6} eV for the eight-atom cells in Fig. 1 with the residual stresses in the fully relaxed structures less then 0.05 GPa.

In Table I, we compare the calculated lattice constants for the d-BC_2N structures studied by several different groups using different density-functional theory (DFT) first-principles calculation packages (such as PARATEC, CASTEP, CERIUS, and VASP) within both generalized gradient approximation (GGA) and LDA. Most of the reported results are in good agreement with those obtained in our previous work.[1] This shows that, when properly performed, different DFT packages should and would lead to essentially the same structural results. In particular, most of the reported calculations show differences (close to 1%) among the three lattice constants for each and every d-BC_2N structure studied here while only one single lattice constant is used in Ref. 7 to approximate the d-BC_2N structures by exact cubic lattices which require their lattice constants $a=b=c$ and $\alpha=\beta=\gamma=90°$ during the structural relaxations. The fully relaxed structures of d-BC_2N have the following crystal symmetry: BC_2N-1 has a monoclinic supercell, BC_2N-2 is orthorhombic, and BC_2N-3 is tetragonal. A small and orthorhombic unit cell[23] can be defined for BC_2N-1 with the lattice vectors $\vec{a}_0=\vec{R}_{C2}-\vec{R}_{C1}$, $\vec{b}_0=\vec{R}_{C3}-\vec{R}_{C1}$, and $\vec{c}_0=\vec{b}$ (see Fig. 1).

The elastic constants of d-BC_2N are calculated with the energy-strain scheme by applying controlled strains to the fully relaxed d-BC_2N structures and then relaxing the ion positions while keeping the strained lattice constants unchanged.[24] The elastic constants are determined by the second-order derivatives of the total energy changes in the

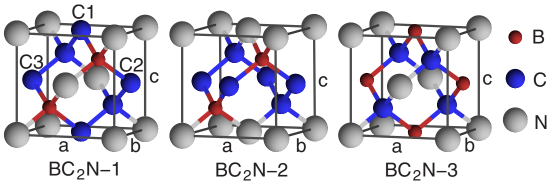

FIG. 1. (Color online) The structures of d-BC_2N.

TABLE I. Comparisons of the calculated lattice constants (a, b, c) of d-BC$_2$N (in the unit of Å).

Structure	Ours (a, b, c)	Others (a, b, c)
BC$_2$N-1 monoclinic (supercell)	3.570, 3.609, 3.570 (α=89.5°)[a]	3.61[b]
		3.572, 3.607, 3.572 (α=89.42°)[c]
		3.579, 3.612, 3.579 (α=89.32°)[d]
BC$_2$N-2 orthorhombic	3.568, 3.613, 3.564[a]	3.61[b]
		3.570, 3.610, 3.566[c]
		3.554, 3.599, 3.553[e]
BC$_2$N-3 tetragonal	3.584, 3.634, 3.584[a]	3.64[b]
		3.589, 3.635, 3.589[c]

[a] Reference 1.
[b] Reference 7.
[c] Reference 20.
[d] Reference 21.
[e] Reference 22.

d-BC$_2$N structures with respect to the applied strains. The total energy-strain curves are obtained by fitting the calculated total energy changes as functions of applied strains in a polynomial up to the second order in the applied strains with several discrete values of strains limited within ±1%. Table II gives the calculated elastic constants of the d-BC$_2$N structures and how the strains are applied for the calculation of different C_{ij}. For BC$_2$N-1, there are several other nonzero C_{ij} with values less than 30 GPa that are not listed in Table II. Existing results of the elastic constants of d-BC$_2$N (Refs. 22 and 23) are also listed in Table II for comparison. The results in Table II show the effects of chemical anisotropy on the mechanical properties of d-BC$_2$N, where even though the differences caused by the chemical anisotropy of the d-BC$_2$N structures among the lattice constants are small (about 1%), the differences among the elastic constant components, that should be the same for cubic lattices, are about 10% for BC$_2$N-1 (supercell) and BC$_2$N-2, and reach 75% among $\{C_{12}, C_{23}$, and $C_{31}\}$ for BC$_2$N-3. Our calculation predicted much less anisotropy in the elastic constants of BC$_2$N-2 than those obtained in Ref. 22, which gives a bulk modulus of 459.4 GPa using $E(V)$ relation and 441 GPa using C_{ij} with the formula we use below.[25] Both are higher than the other results listed in Table III and almost equal to that of diamond (463.7 GPa),[22] while all synthesized d-BC$_2$N samples show much lower bulk moduli compared to that of diamond.[8,10]

In Table III, we compare the bulk moduli of the d-BC$_2$N structures calculated from elastic constants we obtained by the formula[25] $B_0=[(C_{11}+C_{22}+C_{33})+2(C_{12}+C_{23}+C_{31})]/9$, and those obtained by the fittings of the energy-volume points given in our previous work and by several other groups using different DFT first-principles calculation packages (such as PARATEC, CASTEP, CERIUS, VASP, and ABINIT) within both GGA and LDA. Most of the results agree well, indicating the consistence of various calculation methods and codes. In the above formula[25] to calculate the bulk modulus from elastic constants, the differences in the changes in different lattice constants with respect to the change in volume

TABLE II. The calculated elastic constants of d-BC$_2$N (in the unit of GPa), applied nonzero strains, and second-order derivatives of total energy changes with respect to the applied strains. For BC$_2$N-1, elastic constants in both the supercell and unit cell are given (see Fig. 1 and the text). Previous results of BC$_2$N-1 and BC$_2$N-2 are also listed for comparison.

	BC$_2$N-1			BC$_2$N-2		BC$_2$N-3		
	Super	Unit	Other[a]	Unit	Other[b]	Unit	Applied strain	$d^2(\Delta E/V)/d\delta^2$
C_{11}	907.8	975.0	1002.9	906.0	916.0	861.7	$e_1=\delta$	C_{11}
C_{22}	921.5	1083.5	1106.1	920.1	1064.2	945.1	$e_2=\delta$	C_{22}
C_{33}	907.8	921.5	938.1	900.5	939.0	861.7	$e_3=\delta$	C_{33}
C_{44}	484.6	509.9	528.6	502.3	460.3	462.6	$e_4=2\delta$	$4C_{44}$
C_{55}	500.7	459.0	496.5	501.8	524.0	500.1	$e_5=2\delta$	$4C_{55}$
C_{66}	484.3	379.3	384.9	504.2	627.5	462.6	$e_6=2\delta$	$4C_{66}$
C_{12}	159.5	27.8	27.1	138.8	120.2	156.7	$e_1=-e_2=\delta$	$C_{11}+C_{22}-2C_{12}$
C_{23}	159.5	166.6	168.5	157.1	205.3	156.7	$e_2=-e_3=\delta$	$C_{22}+C_{33}-2C_{23}$
C_{31}	149.2	152.3	153.4	156.5	199.6	89.1	$e_3=-e_1=\delta$	$C_{33}+C_{11}-2C_{31}$

[a] Reference 23.
[b] Reference 22.

TABLE III. Comparisons of the bulk moduli of d-BC_2N (in the unit of GPa) calculated by the elastic constants we obtained, and those by the fittings of the energy-volume points given in our previous work and by several other groups.

	Ours	Others
BC_2N-1	408.2 (399.7[a])	342.4[b], 383.3[c], 402.1[d], 397.6[e],409.0[f]
BC_2N-2	403.6 (400.1[a])	344.7[b], 459.4[g], 380.7[d], 400.2[e]
BC_2N-3	385.9 (369.9[a])	289.6[b], 362.9[d]

[a] Reference 1.
[b] Reference 7.
[c] Reference 21.
[d] Reference 28.
[e] Reference 2.
[f] Reference 23.
[g] Reference 22.

are neglected. This is expected to be a good approximation for the d-BC_2N structures which deviate only slightly from those of cubic lattices. For the tetragonal BC_2B-3, for instance, we obtain $\mu = d(b/a)/dV \times V/(b/a) = -0.045$, which gives $B_0 = 384$ GPa using a more complex formula[26] compared to $B_0 = 386$ GPa using the above simple formula.[25] Another possible error in the calculated bulk modulus may come from the fact that the phonon contribution to the total energy of the crystal is neglected in the DFT calculation. Even at zero temperature, the total energy of the crystal should include the phonon zero-point energy which depends on the distribution of the phonon frequencies. Changes in the crystal volume will change the phonon frequencies and so the bulk modulus of the crystal through phonon contributions to the crystal total energy. Previous studies[27] have shown that phonon zero-point energy and finite-temperature contributions to bulk moduli of some metals can be as large as 20%. However, for less compressible materials, such as d-BC_2N where thermal effects at ambient conditions are weak, we expect that the volume dependence of the phonon frequencies do not introduce significant contributions to bulk moduli. As the phonon zero-point energy and thermal effects are not included in the DFT-based bulk modulus calculations whether one uses the fittings of energy-volume or energy-strain (C_{ij}) points, in principle, these two methods should have the same accuracy, as is shown in Table III, if the correct structure is adopted in both methods. In Ref. 7, the bulk moduli for the d-BC_2N structures are obtained by $B_0 = (C_{11} + 2C_{12})/3$, which comes as a special case of the general formula[25] $B_0 = [(C_{11} + C_{22} + C_{33}) + 2(C_{12} + C_{23} + C_{31})]/9$. The special formula is valid only for structures with exact cubic symmetry where $C_{11} = C_{22} = C_{33}$, $C_{44} = C_{55} = C_{66}$, and $C_{12} = C_{23} = C_{31}$, and is not applicable for the d-BC_2N structures, especially for BC_2N-3 where the differences among $\{C_{12}, C_{23}$, and $C_{31}\}$ reach 75% (see Table II above). Therefore, using (C_{11}, C_{12}), (C_{22}, C_{23}), or (C_{33}, C_{31}) in the special formula, which are equivalent under true cubic symmetry, will obviously result in significant differences in the calculated bulk moduli. From our calculated elastic constants in Table II, the difference in the bulk moduli obtained using different sets of C_{ij} in the above special formula valid only for cubic lattices is about 3% for BC_2N-1 (supercell) and BC_2N-2, and reaches 21% for BC_2N-3. When the artificial cubic symmetry is imposed, the calculation errors are expected to increase since the anisotropic distribution of different B, C, and N atoms (i.e., chemical anisotropy) in the unit cell will lead to residual stresses, as we will discuss below, which will complicate the calculation of elastic constants.

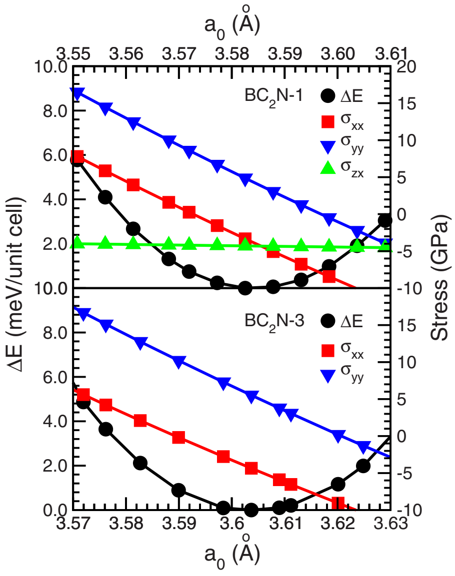

FIG. 2. (Color online) The calculated total-energy difference (left scale) relative to the lowest energy, and stresses (right scale) of BC_2N-1 (top panel) and BC_2N-3 (bottom panel) as functions of lattice constant obtained by the constrained relaxation of cubic symmetry ($a = b = c$ and $\alpha = \beta = \gamma = 90°$). The symmetries of the structures require that the stress $\sigma_{zz} = \sigma_{xx}$ and all the other stress components not shown in the figure to be zero.

To see the effects of the lattice symmetry on the structural relaxation, we calculated total energy and stresses of BC_2N-1 and BC_2N-3 as functions of lattice constant a by imposing the exact cubic symmetry ($a = b = c$ and $\alpha = \beta = \gamma = 90°$) while relaxing the atomic positions until all the forces on atoms become zero. The calculated external stresses needed to maintain the assumed cubic symmetry of the d-BC_2N structures are plotted in Fig. 2. Calculated results for BC_2N-2 are about the same as those for BC_2N-1 because of their similarities and are not given. It is obvious from Fig. 2 that large residual stresses of about 4–5 GPa remain in the structures at the minimum energy if the exact cubic symmetry constraint is imposed in the structural relaxation. For any accurate first-principles calculations, it is important, not only to check the energy convergence, but also the stress convergence. A residual stress below 0.1 GPa is usually considered acceptable for the equilibrium structures of the low compressible B, C, and N compounds. Anything above this level indicates that the structure has not been properly relaxed and further calculations performed on such structures would not be reliable. Our test calculations show (see Fig. 2) that the d-BC_2N structures with the exact cubic symmetry constraint contain residual stresses 40–50 times the acceptable level. Consequently, without a full structural relaxation that removes the residual stresses and a proper account of all C_{ij}'s in the correct formula for bulk moduli for the three d-BC_2N structures that have different and reduced (from cubic) symmetries, the calculated results and any conclusions, such as the structural assignments based on such calculations, may contain errors.

In summary, crystal structures and elastic constants of several different d-BC_2N structures were studied. Our results show that for the fully relaxed d-BC_2N structures, although the deviations of their lattice constants from those of exact cubic lattices are small (about 1%), the differences caused by the chemical anisotropy of the d-BC_2N structures among the elastic constant components, that should be the same for cubic lattices, are about 10% for BC_2N-1 (supercell) and BC_2N-2, and reach 75% for BC_2N-3 among its $\{C_{12}, C_{23}, \text{and } C_{31}\}$, which is expected to affect the spectra of acoustic phonons of these BC_2N structures and so their bulk moduli determined by Brillouin scattering experiments,[9] etc. The bulk modulus calculated with the special formula applicable only to cubic lattices will have an error of 20% for the BC_3N-3 structure. Our test calculations also show that, apart from ignoring differences among elastic constant components that are equivalent only for cubic lattices, imposing exact cubic symmetry for the nominally cubic d-BC_2N structures also induces large residual stresses in such constrained cubic d-BC_2N structures. The stress differences among different stresses components can be as large as 10 GPa, which will further complicate the calculation of elastic constants in these constrained cubic d-BC_2N. Our calculations confirm that the DFT-based bulk modulus calculations, whether one uses the fittings of energy-volume or energy-strain (C_{ij}) points, should have the same accuracy, if the correct structure is adopted in both methods.

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