

## ARTICLES

Origin of Superhardness in Icosahedral B<sub>12</sub> Materials

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Received: June 2, 2004; In Final Form: June 27, 2004

Boron-rich phases with icosahedral symmetry are quite intriguing. It is important to understand the origin of hardness of boron-rich materials. By starting from a chemical bond viewpoint, a simple method for evaluating hardness of boron-rich phases is presented. This method has been applied to some materials such as  $\alpha$ -B<sub>12</sub>, B<sub>13</sub>C<sub>2</sub>, and B<sub>12</sub>X<sub>2</sub> (X = O, P, As), and the predicted hardnesses are in agreement with available experimental values. The results show that this approach provides a powerful tool for predicting superhardness when searching for novel superhard materials in boron-rich phases by first principles.

## 1. Introduction

Superhard materials are useful in a variety of industrial applications. Man-made diamonds offer an alternative but fail to cut iron-based metals because of chemical interactions. It would be useful to develop other materials that avoid the above-mentioned technical problems. Most of the boron-rich phases with a three-dimensional boron network structure are of low density, high hardness, and high thermal stability. For example, boron carbide exhibits many attractive properties, even surpassing diamond and cubic boron nitride at temperatures over 1100 °C. Therefore, intense interest has been focused on the physical and chemical properties of these materials because of potential industrial applications.<sup>1–9</sup>

The boron-rich materials have received more attention, partly because of novel superhard materials based on the icosahedron. Therefore, the prediction of hardness for boron-rich systems is of importance.

With the development of the first-principles approach, it has always been a goal of materials researchers to design a new superhard material completely on the basis of theory. However, hardness is too complex to be described by first principles. Recently, a new definition of the hardness of covalent crystals has been presented.<sup>10</sup> In our opinion, the hardness of covalent crystals is intrinsic and equivalent to the sum of resistance of each bond per unit area to indentation. According to this idea, the hardness of covalent crystals should have the following form<sup>10</sup>

$$H_v \text{ (GPa)} = 14(N_a e^{-1.191f_i})E_h \quad (1)$$

where  $E_h$  is the covalent energy gap, which characterizes the strength of the covalent bond;  $N_a$  is the covalent bond number per unit area; and  $f_i$  is the ionicity of the bonds.

In the present paper, we extend our calculation to icosahedral crystals and present an evaluation method for hardness to show how the method is applied and demonstrate that the procedure

is transferable to various boron-rich crystals such as  $\alpha$ -B<sub>12</sub>, B<sub>12</sub>As<sub>2</sub>, B<sub>12</sub>P<sub>2</sub>, B<sub>12</sub>O<sub>2</sub>, and boron carbide.

## 2. Theoretical Methods

**2.1. Chemical Bond Parameters.** Boron can form many interesting structures. Boron-rich crystals always have complex structure because of the connectivity arrangement of the boron icosahedra. Reviews concerning bond covalency and its application have been made by Phillips, Van Vechten, and Levine.<sup>11,12</sup> It is known that PVL (Phillips–Van Vechten–Levine) theory can deal only with binary crystals. Zhang has pointed out that the properties of a crystal can be described by chemical bond parameters and any complex crystal can be decomposed into different kinds of pseudobinary crystals.<sup>13</sup> These binary crystals are related to each other, and every binary crystal includes only one type of chemical bond, but the properties of these pseudobinary crystals are different from those of real binary crystals, although their chemical bond parameters can be calculated in a similar way. In the theory, the “crystal formula” of a substance is a combination of subformulas of chemical bonds. The subformula of any kind of chemical bond A–B in the multibond crystal A<sub>a</sub>B<sub>b</sub>... can be expressed by the following formula

$$[N(B-A)a/N_{CA}]A[N(A-B)b/N_{CB}]B \quad (2)$$

where A, B, ..., represent different elements or different sites of the same element in the crystal formula;  $a, b, \dots$ , represent the numbers of the corresponding element;  $N(B-A)$  represents the number of B ions in the A ion coordination group; and  $N_{CA}$  represents the nearest coordination number of an A ion. After decomposing the complex crystal into different kinds of pseudobinary crystals that form an isotropic system and introducing an effective charge of valence electron by Pauling bond valence method, PVL theory<sup>11,12</sup> can be used directly to calculate the chemical bond parameters in a complex crystal compound.

In analogy with the work of PVL, The average energy gap  $E_g^\mu$  for each bond  $\mu$  can be separated into homopolar  $E_h^\mu$

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and heteropolar  $C^\mu$  parts. The homopolar gap  $E_h^\mu$  can be interpreted as being produced by the symmetric part of the total potential  $1/2(V_A + V_B)$ , while the ionic or charge-transfer gap  $C^\mu$  results from the effect of the antisymmetric part  $1/2(V_A - V_B)$ . The average valence–conduction band gap is given by the ionicity  $f_i^\mu$  and covalency  $f_c^\mu$  of any type of

$$(E_g^\mu)^2 = (E_h^\mu)^2 + (C^\mu)^2 \quad (3)$$

chemical bond are defined as follows

$$f_i^\mu = (C^\mu)^2 / (E_g^\mu)^2 \quad \text{and} \quad f_c^\mu = (E_h^\mu)^2 / (E_g^\mu)^2 \quad (4)$$

where

$$E_h^\mu = 39.74 / (d^\mu)^{2.48} \text{ (eV)} \quad (5)$$

and  $d^\mu$  is the bond length. For any binary crystal  $AB_n$ -type compounds, the heteropolar  $C^\mu$  part is defined as

$$C^\mu = 14.4b^\mu [(Z_A^\mu)^* + \Delta Z_A^\mu - n(Z_B^\mu)^*] [\exp(-k_s^\mu r_0^\mu) / r_0^\mu] \text{ (eV)} \quad (6)$$

with

$$r_0^\mu = (d^\mu) / 2 \quad (7)$$

$$k_s^\mu = (4k_f^\mu / \pi a_B)^{1/2} \quad (8)$$

$$(k_f^\mu)^3 = 3\pi^2 N_e^\mu \quad (9)$$

$$N_e^\mu = (n_e^\mu)^* / v_b^\mu \quad (10)$$

$$(n_e^\mu)^* = [(Z_A^\mu)^* / N_{CA} + (Z_B^\mu)^* / N_{CB}] \quad (11)$$

$$v_b^\mu = (d^\mu)^3 / \sum_\nu [(d^\nu)^3 N_b^\nu] \quad (12)$$

where  $v_b^\mu$  is the bond volume,  $(n_e^\mu)^*$  is the number of effective valence electrons per bond of type  $\mu$ ,  $N_e^\mu$  is the number of valence electrons of type- $\mu$  bonds per cubic angstrom,  $k_f^\mu$  is the Fermi wavenumber of the valence electron in the binary crystal composed of only one type of bond  $\mu$ ,  $k_s^\mu$  is the Thomas–Fermi screening wavenumber of the valence electron in the binary crystal composed of only one type of bond  $\mu$ ,  $a_B$  is the Bohr radius, and  $n$  is the ratio of element B to element A in the subformula.  $\Delta Z_A^\mu$  is a correction factor from d electron effects such as the crystal field stable energy and the Jahn–Teller effect.<sup>14,15</sup>  $b^\mu$  is proportional to the square of the average coordination number  $N_c^\mu$

$$b^\mu = \beta (N_c^\mu)^2, \quad N_c^\mu = N_{CA} / (1 + n) + n N_{CB} / (1 + n) \quad (13)$$

where  $b^\mu$  depends on a given crystal structure. The typical value of  $\beta$  is 0.089 within 10%.<sup>13</sup>

**2.2. Hardness of Multicomponent Compound Systems.** The hardness of a pseudobinary compound composed of  $\mu$ -type bonds can be calculated as follows<sup>10,15</sup>

$$H_v^\mu \text{ (GPa)} = 8.82 (N_e^\mu)^{2/3} E_h^\mu e^{-1.191 f_i^\mu} \quad (14)$$

or

$$H_v^\mu = 350 (N_e^\mu)^{2/3} e^{-1.191 f_i^\mu} / (d^\mu)^{2.5}$$

The hardness of multicomponent compound systems can be expressed as an average of the hardnesses of all binary systems in the solid. Hardness surely involves the cooperative softening of many bonds. When there are differences in the strength among different types of bonds, the trend toward breaking the bonds will start with the softer ones. Therefore, the hardness  $H_v$  of complex crystals should be calculated by a geometric average of all bonds as follows

$$H_v = [\prod_\mu (H_v^\mu)^{n^\mu}]^{1/\sum n^\mu} \quad (15)$$

where  $n^\mu$  is the number of bonds of type  $\mu$  composing the actual complex crystal.

### 3. Calculation and Discussion

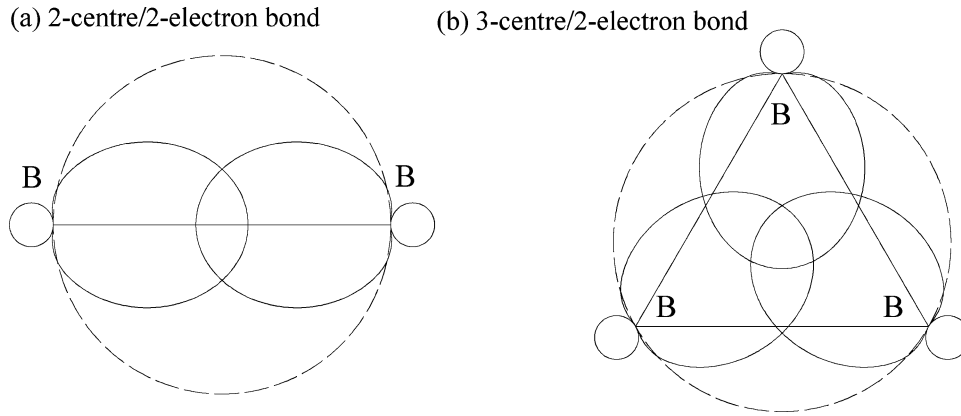
**3.1. Three-Center Bonds.** The above approach allows one to predict the hardness of materials accurately. However, when it is applied to boron-rich phases, some problems arise. The distinct feature of the chemical bonding of boron solids is three-center or icosahedral bonding. The icosahedra are linked by covalent bonds. The atoms in the icosahedra are held together by peculiar delocalized three-center bonds. The first problem in extending eq 1 or eq 14 to boron-rich systems is how the bond length of the three-center bonds is to be determined. For two-center/two-electron bonds, the bond length is defined as the distance between two nuclei of bonding atoms. In Figure 1, we employ  $sp_x$  hybrid orbitals to show a sketch of a two-center/two-electron bond and a three-center/two-electron bond. In three-center/two-electron bonds, the lengths of the lines between pairs of atoms cannot yet be considered as the bond lengths.<sup>12</sup> In our opinion, we can approximately take the diameter of the circle shown in Figure 1 as the bond length of the three-center/two-electron bond. If the distances between pairs of atoms in the three-center/two-electron bond are all equal and denoted  $l$ , then the bond length of three-center/two-electron bonds  $d_{3c2e}$  can be expressed as

$$d_{3c2e} = (2/\sqrt{3})l \quad (16)$$

**3.2.  $\alpha$ -Rhombohedral Boron.** The  $\alpha$ -rhombohedral form of boron is the simplest of the boron-rich solids. The  $B_{12}$  icosahedron is, in general, quite regular. The rhombohedral unit cell has  $a = 5.057 \text{ \AA}$ ,  $\alpha = 58.06^\circ$ , and  $Z = 1$ .<sup>16</sup> The 36 valence electrons of each  $B_{12}$  unit are distributed as follows: 26 electrons form the 10 three-center/two-electron bonds (denoted BBB1) and 3 normal two-center/two-electron bonds (denoted BB1) within the icosahedron and 6 electrons share with 6 other electrons from 6 neighboring icosahedra in adjacent planes to form the rhombohedrally directed normal two-center/two-electron bonds (denoted BB2); this leaves 4 electrons which is just the number required for the 6 equatorial three-center/two-electron bonds (denoted BBB2). Thus  $\alpha$ -boron has four bond types. According to the above-mentioned crystallographic data,  $B_{12}$  can be decomposed into the sum of pseudobinary crystals as follows<sup>13,14</sup>

$$B_{12} = 10(\text{BBB1}) + 3(\text{BB1}) + 2(\text{BBB2}) + 3(\text{BB2})$$

where the coefficient is the number of bonds in the cell. On the basis of the current method, the calculated hardness values of  $\alpha$ -rhombohedral boron with typical structures are listed in Table 1. As shown in Table 1, our calculated values agree well with the available experimental ones. The results are very acceptable.



**Figure 1.** Sketches of (a) a two-center/two-electron bond and (b) a three-center/two-electron bond.

**TABLE 1: Hardness and Parameters Related to the Hardness Calculations of  $\alpha$ -Rhombohedral Boron**

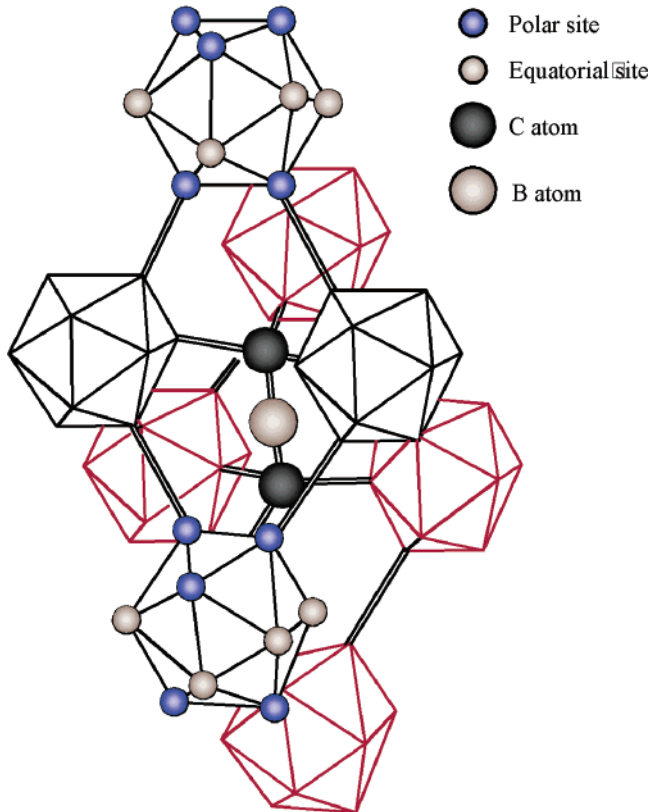
bond type	$d^\mu$	$\nu_b^\mu$	$N_e^\mu$	$E_h^\mu$	$f_i^\mu$	$H_v^\mu$	$H_{\text{vcalc}}^a$ (GPa)	$H_{\text{vexpt}}^b$ (GPa)
BB1	1.77	4.268	0.468	9.64	0.000	51.3	32.0	34 <sup>c</sup>
BBB1	2.044	6.575	0.304	6.749	0.000	26.9		
BB2	1.71	3.850	0.519	10.51	0.000	59.9		
BBB	2.338	9.84	0.204	4.836	0.000	14.7		

<sup>a</sup> Calculated microhardness. <sup>b</sup> Experimental microhardness. <sup>c</sup> Reference 17.

**TABLE 2: Hardness and Parameters Related to the Hardness Calculations of B<sub>13</sub>C<sub>2</sub>**

bond type	$d^\mu$	$\nu_b^\mu$	$N_e^\mu$	$E_h^\mu$	$f_i^\mu$	$H_v^\mu$	$H_{\text{vcalc}}^a$ (GPa)	$H_{\text{vexpt}}^b$ (GPa)
BB1	1.796	4.837	0.413	9.301	0.000	45.5	42.0	41.5 <sup>c</sup>
BBB1	2.074	7.449	0.269	6.502	0.000	23.9		
BB2	1.732	4.271	0.468	10.301	0.000	54.8		
BC	1.61	3.485	0.383	12.198	0.004	56.7		
B <sub>2</sub> C	1.423	2.406	1.246	16.568	0.008	169.3		

<sup>a</sup> Calculated microhardness. <sup>b</sup> Experimental microhardness. <sup>c</sup> Reference 6.



**Figure 2.** Atomic structure of B<sub>13</sub>C<sub>2</sub>.

**3.3. Boron Carbides B<sub>13</sub>C<sub>2</sub>.** Boron carbides are among a number of materials with crystal structures derived from that of  $\alpha$ -rhombohedral boron. The crystal structure of boron carbide, B<sub>13</sub>C<sub>2</sub>, is built up of B<sub>12</sub> icosahedra linked together by C–B–C chains; see Figure 2. The lattice constants are  $a = 5.197$  Å,  $\alpha = 65^\circ 35'$ , and  $Z = 1$ , and the space group is  $R3m$  (No. 166).<sup>1,16</sup> The incorporation of carbon in boron carbide was understood to supply the extra two electrons to the crystal of  $\alpha$ -boron,

replacing the weak three-center bond with strong covalent bonds. There are five distinct types of bond in B<sub>13</sub>C<sub>2</sub>: (1) three-center/two-electron bonds (BBB1) within the icosahedron, (2) two-center/two-electron bonds (BB1) within the icosahedron, (3) BB2 bonds connecting to adjacent icosahedra at 1.732 Å, (4) B–C bonds between carbon atoms and boron atoms of the icosahedron, and (5) B<sub>2</sub>C bonds within the chain. A view of the array of icosahedral B<sub>12</sub> units found in the crystal is shown Figure 2. B<sub>13</sub>C<sub>2</sub> can be decomposed into the sum of pseudobinary crystals as follows

$$\text{B}_{13}\text{C}_2 = 10(\text{BBB1}) + 3(\text{BB1}) + 3(\text{BB2}) + 6(\text{BC}) + 2(\text{B}_2\text{C})$$

B–C bonds are polar covalent bonds and have little ionicity. The calculated hardness and parameters related to the hardness calculations of B<sub>13</sub>C<sub>2</sub> are listed in Table 2. The calculated hardness is in agreement with experiment.

**3.4. Boron Suboxide.** B<sub>12</sub>O<sub>2</sub> has the same space group ( $R3m$ ;  $a = 5.15$  Å,  $\alpha = 62.90^\circ$ ) as B<sub>13</sub>C<sub>2</sub>.<sup>18</sup> It consists of a rigid three-dimensional network of boron icosahedra. Each of the two oxygen atoms links to three B<sub>12</sub> icosahedra, whereas the oxide atoms are nonbonding. The inter-icosahedral distance is shorter than the intra-icosahedral average distance. The inter-icosahedral distance is 1.664 Å, and the average intra-icosahedral distance is 1.798 Å. According to different bonding statuses, B<sub>12</sub>O<sub>2</sub> can be decomposed into the sum of pseudobinary crystals as follows

$$\text{B}_{12}\text{O}_2 = 10(\text{BBB1}) + 3(\text{BB1}) + 3(\text{BB2}) + 6(\text{BO}_{4/3})$$

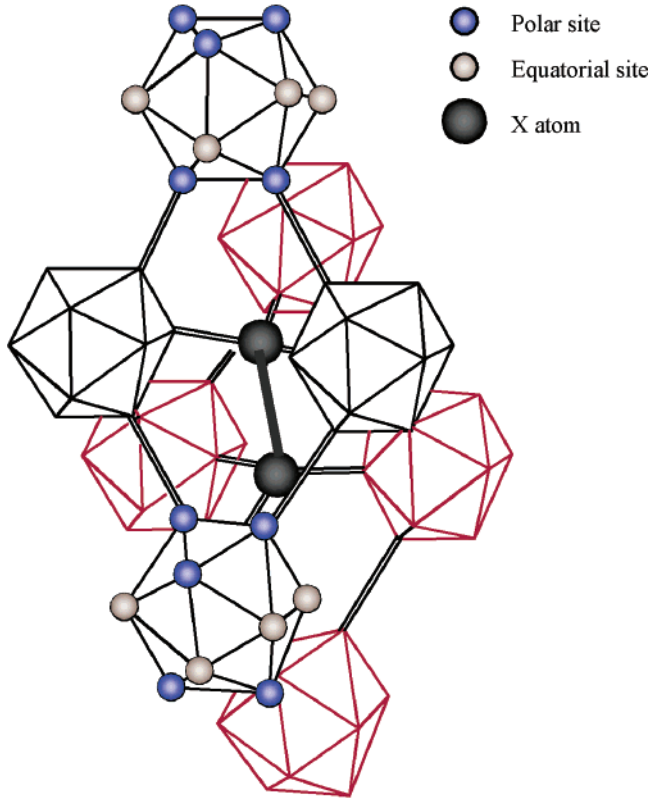
The calculated results for hardness and chemical bond parameters are shown in Table 3. From Table 3, it can be seen that the calculated hardness agrees with the measured value.

**3.5. B<sub>12</sub>P<sub>2</sub> and B<sub>12</sub>As<sub>2</sub>.** Icosahedral borides are materials based on 12-atom boron clusters in which boron atoms occupy the 12 vertices of the icosahedron. Figure 3 illustrates the rhombohedral unit cell with the space group  $R3m$  of two simple

**TABLE 3: Hardness and Parameters Related to the Hardness Calculations of  $B_{12}O_2$** 

bond type	$d^u$	$v_b^u$	$N_e^u$	$E_h^u$	$f_i^u$	$H_v^u$	$H_{vcalc}^a$ (GPa)	$H_{vexp}^b$ (GPa)
BB1	1.798	4.270	0.468	9.276	0.000	49.3	44.6	45 <sup>c</sup>
BBB1	2.076	6.573	0.304	6.494	0.000	25.9		
BB2	1.664	3.385	0.591	11.240	0.000	69.8		
$BO_{4/3}$	1.476	2.362	1.073	15.132	0.460	83.7		

<sup>a</sup> Calculated microhardness. <sup>b</sup> Experimental microhardness. <sup>c</sup> Reference 7.

**Figure 3.** Atomic structure of  $B_{12}X_2$  ( $X = P, As$ ). Two pnictide atoms are bonded to one another to form a two-atom chain.

icosahedral boride insulators:  $B_{12}P_2$  ( $a = 6.000 \text{ \AA}$ ,  $c = 11.857 \text{ \AA}$ ,  $Z = 3$ ) and  $B_{12}As_2$  ( $a = 6.169 \text{ \AA}$ ,  $c = 11.900 \text{ \AA}$ ,  $Z = 3$ ).<sup>1,19</sup> These crystals are composed of 12-boron-atom icosahedra and two-atom chains ( $P_2$  or  $As_2$ ) that reside between icosahedra. As shown in Figure 3, in  $B_{12}P_2$  and  $B_{12}As_2$ , each pnictide atom forms four bonds. Each pnictide atom bonds to a boron atom in each of the three adjacent icosahedra, and the two pnictide atoms bond with one another. According to the above theory,  $B_{12}X_2$  ( $X = P, As$ ) can be decomposed into the sum of pseudobinary crystals as follows

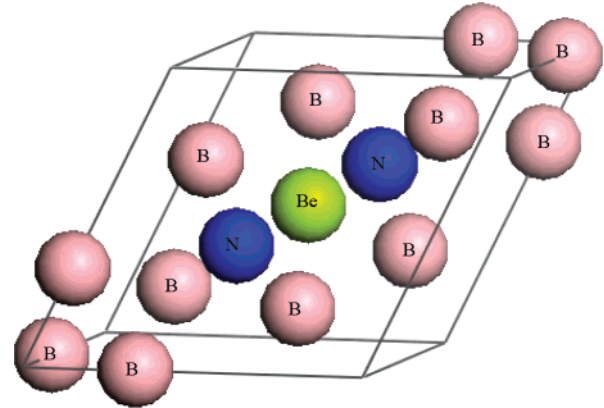
$$B_{12}X_2 = 10(BBB1) + 3(BB1) + 3(BB2) + 6(BX) + (XX)$$

Their chemical bond parameters and predicted hardnesses of  $B_{12}P_{12}$  and  $B_{12}As_{12}$  have been calculated and are listed in Table 4. According to eq 14, three conditions should be met for a superhard material: higher bond density or electronic density, shorter bond length, and greater degree of covalent bonding. In the above examples, the average bonding electronic densities,  $N_e^u$ , of  $B_{12}As_2$ ,  $B_{12}P_2$ , and  $B_{12}O_2$  are 0.346, 0.390, and 0.575, respectively. Correspondingly, their hardnesses increase monotonically. In other word, the hardnesses of boron-rich phases were changed by the addition of adding other elements to the  $B_{12}$  systems. This would be a possible route for designing novel superhard materials.

**TABLE 4: Hardness and Parameters Related to the Hardness Calculations of  $B_{12}X_2$  ( $X = P, As$ )**

crystal	bond type	$d^u$	$v_b^u$	$N_e^u$	$E_h^u$	$f_i^u$	$H_v^u$	$H_{vcalc}^a$ (GPa)
$B_{12}P_2$	BB1	1.80	4.12	0.49	9.25	0.00	50.6	32.9
	BBB1	2.08	6.36	0.31	6.46	0.00	26.2	
	BB2	1.67	3.29	0.61	11.14	0.00	70.7	
	BP	1.91	4.92	0.36	7.98	0.22	27.4	
	PP	2.24	7.94	0.42	5.38	0.00	26.6	
$B_{12}As_2$	BB1	1.81	4.40	0.45	9.12	0.00	47.2	28.6
	BBB1	2.09	6.77	0.30	6.39	0.00	25.3	
	BB2	1.77	4.11	0.49	9.64	0.00	52.8	
	BAAs	2.00	5.94	0.30	7.12	0.23	21.4	
	AsAs	2.39	10.13	0.33	4.58	0.00	19.3	

<sup>a</sup> Calculated microhardness.

**Figure 4.** Atomic structure of  $B_{12}N_2Be$ .**TABLE 5: Optimized Parameters for  $B_{12}N_2Be$  with the  $B_{13}C_2$  Structure**

crystal system	rhombohedral		
space group	$R\bar{3}m$ (No. 166)		
atoms per unit cell	3		
atom positions	18(h)	B	(0.1600, 0.8400, 0.6435)
	18(h)	B	(0.1088, 0.8916, 0.8876)
	6(c)	N	(0, 0, 0.3746)
	3(b)	Be	(0, 0, 0.5)
cell constants ( $\text{\AA}$ )	$a = 5.4159$	$c = 12.3458$	
$\alpha, \beta, \gamma$	90, 90, 120		

**3.6. Designing Novel Superhard Materials.** With the increasing capabilities of first-principles methods, the computer-based design of materials has played an important role in materials science research. Because first-principles calculations are not limited to physically realizable states of a material, it is reasonably simple to change the crystal structure of the material, move or substitute an atom, and so forth, and then to evaluate the effect of these modifications on the properties.<sup>20</sup>

In this section, using the semiempirical formula for hardness and first-principles calculations, an example of searching for novel superhard materials is presented. We study the hardness of a novel  $B_{12}N_2Be$  structure obtained from a full geometry relaxation of the substituted  $B_{13}C_2$ .  $B_{12}N_2Be$  phases can be constructed by replacing carbon atoms at  $(0, 0, z)$  with nitrogen atoms and boron atoms at  $(0, 0, 1/2)$  with Be atoms; see Figure 4. Calculations of the ground-state geometries for the above compounds were carried out in the framework of density functional theory (DFT) with the Material Studio.<sup>21</sup> Optimizations are performed with CASTEP code. The interactions between the ions and the electrons are described by using Ultrasoft Vanderbilt pseudo-potential, and the electron–electron interaction is treated within the local density approximation LDA by the Ceperley–Alder exchange correlation potential. The calculations were performed using an energy cutoff of 280 eV



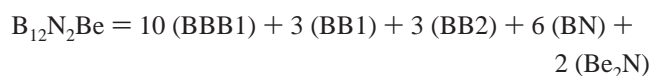
**TABLE 6: Hardness and Parameters Related to the Hardness Calculations of B<sub>12</sub>N<sub>2</sub>Be**

bond type	$d^{\mu}$	$v_b^{\mu}$	$N_e^{\mu}$	$E_h^{\mu}$	$f_i^{\mu}$	$H_v^{\mu}$	$H_{\text{vcalc}}^a$ (GPa)
BB1	1.724	3.621	0.552	10.259	0.000	61.1	48.7
BBB1	2.058	6.159	0.325	6.636	0.000	27.7	
BB2	1.783	4.005	0.499	9.470	0.000	52.5	
BN	1.518	2.472	0.719	14.115	0.187	80.0	
Be <sub>2</sub> N	1.547	2.616	1.019	13.468	0.019	117.6	

<sup>a</sup> Calculated microhardness.

for the plane-wave basis set. The optimization of the lattice parameters and the ion relaxation were performed iteratively until the minimum on the total energy was met; see Table 5 for the optimized parameters.

According to different bonding status and optimized parameters, B<sub>12</sub>N<sub>2</sub>Be can be decomposed into the sum of pseudobinary crystals as follows



The calculated hardness and parameters related to the hardness calculations of B<sub>12</sub>N<sub>2</sub>Be are listed in Table 6. The predicted hardness for B<sub>12</sub>N<sub>2</sub>Be is the highest among the boron-rich solids mentioned above.

#### 4. Conclusion

In conclusion, starting from the chemical bond viewpoint, a simple method for predicting the hardnesses of boron-rich phases has been presented. The predicted hardnesses of boron carbide and boron suboxide crystal are in good agreement with their measured values. One can expect that boron-rich materials

formed by adding some element to boron icosahedra have great potential as new superhard materials for industrial use.

**Acknowledgment.** The authors thank Prof. Philip Nash of Illinois Institute of Technology, Chicago, IL, for his careful correction of the English in this manuscript. The authors acknowledge financial support from The DFYU-B87 Foundation of Yanshan University.

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