

Lattice Anomalies of MBC ($M = H, Li, Na$) Under Anisotropic Compression

Kazuaki KOBAYASHI, Masao ARAI and Taizo SASAKI

Computational Materials Science Center, National Institute for Materials Science, Namiki 1-1, Tsukuba-shi, Ibaraki 305-0044

Fax: 81-29-852-7449, e-mail: kobayashi.kazuaki@nims.go.jp

Recently, we theoretically found the lattice anomaly of LiBC under anisotropic compression. Lattice constant c of LiBC contracts under a , b -axis compression although lattice constant c generally expands under a , b -axis compression. This contraction of lattice constant c implies a kind of negative Poisson ratios. From an analysis of model calculations, an electrostatic interaction between negatively and positively ionized layers and a size of a cation atom are very important key points for the lattice anomaly. In this study, we investigate MBC ($M = H, Li, Na$) under anisotropic compression by first-principles calculations. As a result, the contraction of lattice constant c for HBC when $P_{xy} = 50$ GPa is larger than that for LiBC. In contrast, there are no lattice anomalies of NaBC under anisotropic compression.

Key Words: HBC, first-principles, electronic structure, lattice anomaly, anisotropic compression

1. INTRODUCTION

LiBC has been theoretically predicted to be a superconductor (T_c over 90 K) if holes are doped.¹⁾ On the other hand, we found that LiBC shows a lattice anomaly under anisotropic compression.^{2,3)} Lattice constant c contracts under a , b -axis compression. The lattice constant change is quite small as 0.014 Å when $P_{xy} = 50$ GPa. Already, in spite of thorough studies of the lattice anomaly for LiBC and related compounds,²⁻⁴⁾ we did not obtain the behavior of the lattice anomaly with the exception of LiBC. In this paper, we try to investigate and search some compounds which exhibit a larger contraction of c -axis under a , b -axis compression.

The purpose of this study is to investigate electronic and lattice changes of boron-carbide compounds under various compression conditions. The important point to note is that it is possible to optimize the structure under anisotropic compression for the above compounds using the first-principles molecular dynamics (FPMD) method. In this study, we investigate the possibility of a lattice anomaly for hexagonal boron-carbide compounds (HBC, LiBC and NaBC with $P6_3/mmc$ symmetry) under anisotropic compression. We calculate the electronic and lattice properties of HBC, LiBC and NaBC under various compression conditions ($P = 0, 50$ GPa as hydrostatic, $P_{xy} = 50$ GPa as biaxial a , b -axis, $P_z = 50$ GPa as uniaxial c -axis).

We have considered the reason of this anomalous behavior for LiBC as follows.³⁾ The first point is the electrostatic interaction between hexagonal Li and B-C layers. LiBC is non-metallic when $P = 0$ GPa and $P_{xy} = 50$ GPa. LiBC consists of alternately (A - B) stacked B-C layers and Li layers intercalated between B-C layers, as shown in Fig. 1. The Li layer is positively ionized and the B-C layer is negatively ionized. They electrostatically interact each other. The positively and negatively

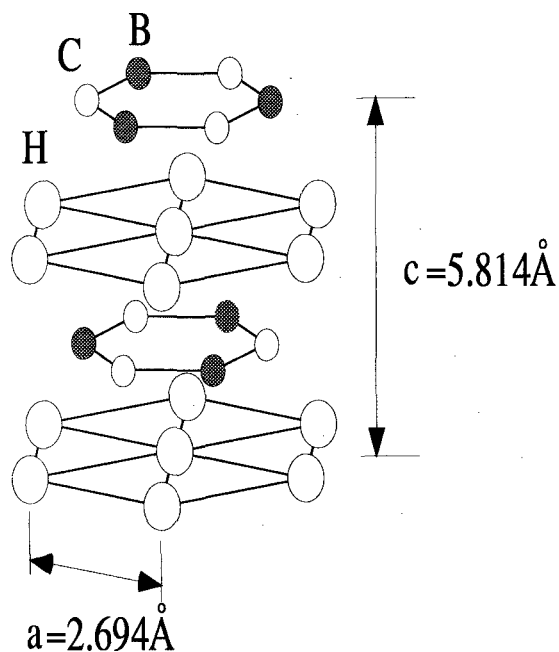


Fig. 1. Crystal structures of HBC. This structure is same as LiBC and NaBC. The values of a and c are equilibrium lattice constants using FPMD ($N_k = 259k$, $E_{cut} = 144$ Ry).

ionized charge densities of Li and B-C layers would increase with P_{xy} if the further charge transfer between layers were absent. Therefore, a , b -axis compression increases the attractive electrostatic interaction between Li and B-C layers, which may be the driving force of the c -axis contraction. The electrostatic interaction between the positively and negatively ionized layers would be re-

duced by a redistribution of the electron density if the system was metallic. In contrast, the hypothetical phase of LiBC, where the stacking of B-C layers is a primitive ($A-A$) type, becomes semimetallic.^{1,3} We obtained the same lattice anomaly of $A-A$ stacked LiBC.³ Therefore, increasing of the electrostatic interaction under a , b -axis compression is not the necessary and sufficient condition for the contraction of lattice constant c .

The second point is a size of a cation atom.⁵ It is very important to investigate a relation between the size of the cation atom and the lattice contraction of c -axis under a , b -axis compression. It was found that there is no lattice anomaly for NaBC under anisotropic compression in spite of the fact that NaBC is non-metallic when $P = 0$ GPa in our previous study.³ A size of a Na atom is larger than that of a Li atom. The larger size of the cation atom (Na) could be unfavorable to contract lattice constant c under a , b -axis compression. Since a size of a hydrogen (H) atom is smaller than that of the Li atom, it is expected that the lattice contraction of HBC under a , b -axis compression will be larger than that of LiBC.

In the past, first-principles approaches using the density functional theory^{6,7} under anisotropic compression have not often been attempted because of the lack of corresponding experiments at a sufficiently low temperature. It is expected that first principles calculations may predict new physical properties and behavior of materials under anisotropic compression. Therefore, we believe that it is very important to investigate differences in the electronic and lattice properties under various compression conditions.

2. METHOD OF CALCULATION

The present calculation (FPMD) is based on the local density approximation in the density functional theory with the Wigner interpolation formula⁸ and generalized gradient approximation (GGA-PBE)⁹ for the exchange-correlation. The optimized pseudopotentials (H, Li, B and C) by Troullier and Martins (TM)^{10,11} are used. Nonlocal parts of the pseudopotentials are transformed to the Kleinman-Bylander separable forms¹² without ghost bands. A partial core correction (PCC)¹³ is considered for the Li and Na pseudopotentials.

The number of sampling k -points (N_k) is 95 for HBC, NaBC, LiBC, 259 for HBC in the irreducible Brillouin zone (BZ). The wave function is expanded in plane waves, and the energy cutoff (E_{cut}) is 81 Ry for HBC, LiBC, NaBC and 144 Ry for HBC with the maximum number of plane waves being about 7500 for HBC. The number of atoms in a unit cell is 6. The number of k -points is fixed during the cell optimization. The details of the calculation process with the cell optimization were reported in our previous works.^{3,14} Our treatment follows the hydrostatic, uniaxial (c -axis) and biaxial (a , b -axis) compression conditions given in the present studies. All systems maintain the crystal symmetry under compression.

We perform the electronic structure calculation using CASTEP code¹⁵ in order to compare with our calculated results.

Table I. Optimized lattice constants[Å], the c/a ratios of HBC, LiBC and NaBC. "*" indicates the number of k -points is 259 and the energy cutoff is 144 Ry. "*²" and "*³" indicate the results using CASTEP(LDA) and (GGA-PBE),¹⁵ respectively. "*⁴" indicates other theoretical results.¹⁶

	GPa	c	a	c/a
HBC	$P = 0$ GPa	5.796	2.694	2.15
HBC(*)	$P = 0$ GPa	5.814	2.694	2.16
HBC(PBE)	$P = 0$ GPa	5.837	2.672	2.18
HBC(* ²)	$P = 0$ GPa	5.829	2.678	2.18
HBC(* ³)	$P = 0$ GPa	5.886	2.673	2.20
HBC	$P = 50$ GPa	4.968	2.589	1.92
HBC	$P_{xy} = 50$ GPa	5.759	2.573	2.24
HBC(*)	$P_{xy} = 50$ GPa	5.776	2.573	2.24
HBC	$P_z = 50$ GPa	4.865	2.700	1.80
LiBC	$P = 0$ GPa	6.950	2.735	2.54
LiBC(* ²)	$P = 0$ GPa	6.797	2.710	2.51
LiBC(* ³)	$P = 0$ GPa	6.946	2.713	2.56
LiBC	(Exp ¹⁷)	7.058	2.752	2.56
LiBC	$P = 50$ GPa	5.870	2.617	2.24
LiBC	$P_{xy} = 50$ GPa	6.936	2.590	2.68
LiBC	$P_z = 50$ GPa	5.636	2.761	2.04
NaBC	$P = 0$ GPa	8.400	2.801	3.00
NaBC(* ²)	$P = 0$ GPa	8.120	2.775	2.93
NaBC(* ³)	$P = 0$ GPa	8.280	2.785	2.97
NaBC(* ⁴)	$P = 0$ GPa	8.266	2.778	2.98
NaBC	$P = 50$ GPa	7.157	2.648	2.70
NaBC	$P_{xy} = 20$ GPa	8.428	2.711	3.11
NaBC	$P_{xy} = 50$ GPa	8.501	2.609	3.26
NaBC	$P_z = 50$ GPa	6.834	2.833	2.41

3. RESULT AND DISCUSSION

The optimized lattice properties in the present calculation are tabulated in Table I. The results of lattice properties for HBC, LiBC using FPMD agree well with those obtained by CASTEP. Equilibrium lattice constant c of NaBC using FPMD slightly disagrees with that obtained by CASTEP. Our calculated equilibrium lattice constant c of NaBC with LDA⁸ is the largest and the value of it from Ref. 15 is slightly smaller than that obtained by CASTEP(GGA-PBE). Equilibrium lattice constant c of NaBC is very sensitive to the calculational parameters (N_k , E_{cut} , etc.). There are also no lattice anomalies of NaBC in the results by CASTEP. From Table I, the c/a ratios of HBC, LiBC and NaBC decrease when $P = 50$ GPa and $P_z = 50$ GPa. They increase when $P_{xy} = 50$ GPa. Thus, there is no difference of the trend as for the variation of c/a ratio under the various compression conditions. The lattice contraction of c -axis for HBC when $P_{xy} = 50$ GPa is 0.037 Å. It is larger than the value (0.014 Å) of the lattice contraction for LiBC.

It was found in the previous work¹⁸ that the lattice constant (c -axis) under a , b -axis compression is sensitive to the number of k -points. As for LiBC, it has been concluded that a sufficient convergence was obtained at 95 k -points.³ A larger number of k -points (259) for HBC is used in order to check the convergence of the lattice properties. The deviations of the total energies, equilibrium lattice constants c and the contractions of lattice constant c when $P_{xy} = 50$ GPa for HBC at 95 k -points, 81 Ry and 259 k -points, 144 Ry are less than about 10.5

meV, 0.018 Å and 0.01 Å, respectively. Therefore, it can be concluded that a sufficient convergence is obtained at 95 k-points.

The electronic band structures of HBC and LiBC when $P = 0, 50$ GPa, $P_{xy} = 50$ GPa and $P_z = 50$ GPa are shown in Fig. 2 and Fig. 3, respectively. The electronic band structures of NaBC when $P = 0, P_{xy} = 20, 50$ GPa and $P_z = 50$ GPa are shown in Fig. 4. The bandwidths increase as the pressure increases in all cases. HBC is semimetallic when $P = 0, 50$ GPa, $P_{xy} = 50$ GPa and $P_z = 50$ GPa. LiBC is non-metallic when $P = 0, 50$ GPa, $P_{xy} = 50$ GPa and $P_z = 50$ GPa. NaBC is non-metallic when $P = 0, 50$ GPa and $P_z = 50$ GPa, semimetallic when $P_{xy} = 20, 50$ GPa.

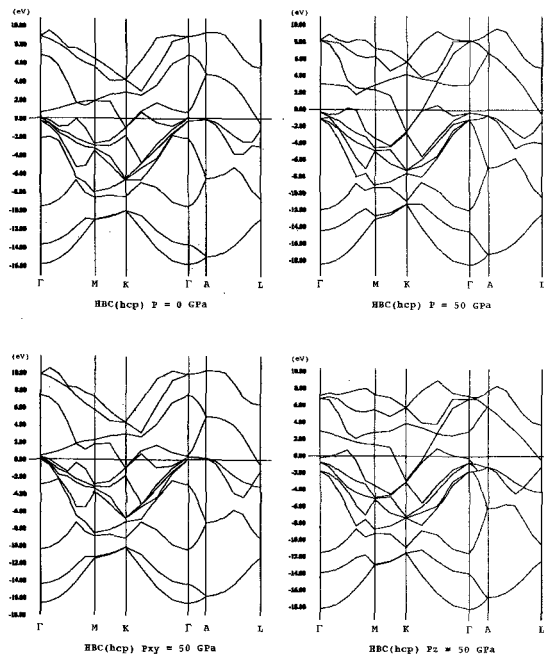


Fig. 2. Energy band structures of HBC when $P = 0, 50, P_{xy} = 50$ and $P_z = 50$. The Fermi level is indicated by the horizontal line.

The electronic structures of HBC, LiBC and NaBC broadly resemble each other although dispersions of individual bands near the Fermi level differ between them. Hydrostatic compression does not modify the electronic band structure qualitatively. The semimetallic character of HBC is invariable under various compression conditions. The variation of the electronic band structure for LiBC under present compression conditions is small. In contrast, the electronic band structure of NaBC is sensitive to compression. A band gap of NaBC disappeared and became semimetallic when $P_{xy} = 20, 50$ GPa. The band gap for NaBC expands when $P = P_z = 50$ GPa. There are σ bands at the $A-\Gamma$ line close to the Fermi level as shown in Fig. 2, Fig. 3 and Fig. 4. Most σ bands are occupied and other σ bands of HBC and NaBC slightly

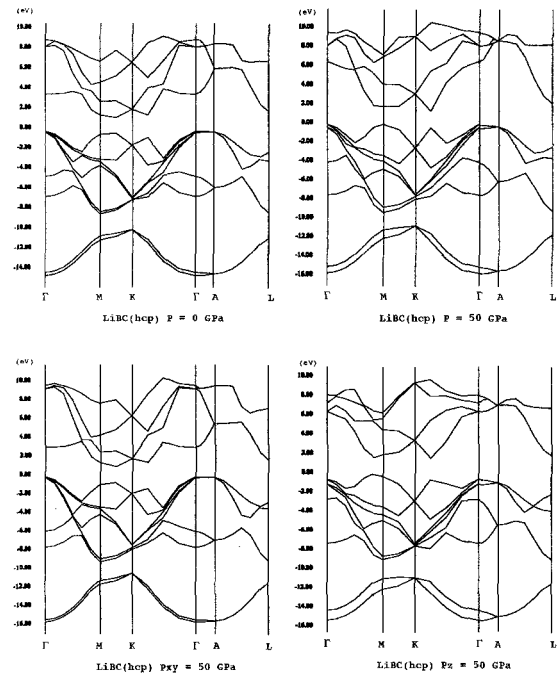


Fig. 3. Energy band structures of LiBC when $P = 0, 50, P_{xy} = 50$ and $P_z = 50$.

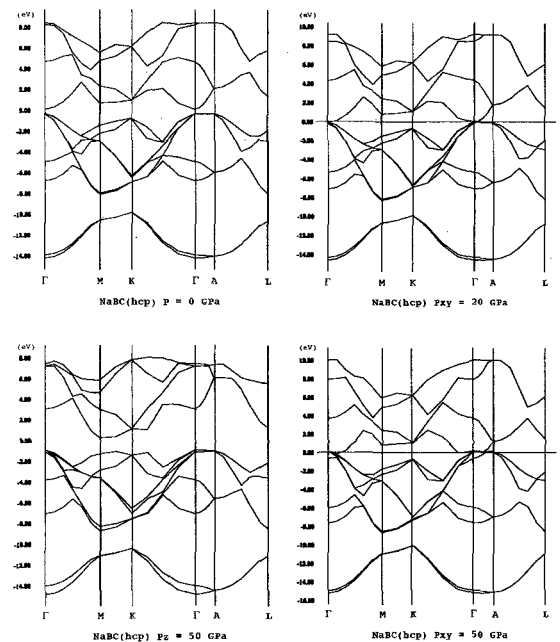


Fig. 4. Energy band structures of NaBC when $P = 0, P_{xy} = 20, 50$ and $P_z = 50$. The Fermi level is indicated by the horizontal line.

cross or touch the Fermi level.

4. SUMMARY

We calculated the electronic and lattice properties of HBC, LiBC and NaBC under various compression conditions using FPMD. Like the case of LiBC,³⁾ we found the lattice anomaly of HBC under a , b -axis compression. The value of the lattice contraction for HBC is larger than that for LiBC. We think that the smaller atomic size of hydrogen is the main reason of this larger contraction nevertheless HBC is semimetallic. NaBC does not imply the anomaly of lattice properties under anisotropic compression. The size of the cation atom plays a important role in which the contraction occurs or not under anisotropic compression. HBC is semimetallic under all calculated compression conditions. NaBC becomes semimetallic when $P_{xy} = 20, 50$ GPa. The electronic structures of NaBC when $P = 0, 50$ GPa and $P_z = 50$ GPa are non-metallic. The values of the bandgap for NaBC when $P = P_z = 50$ GPa become larger than that when $P = 0$ GPa. It is necessary to consider the disagreement of calculated lattice constants c for NaBC using FPMD and CASTEP in a future next task.

It may be impossible to neglect the quantum effect of hydrogen in a HBC solid since hydrogen is the lightest atom in the periodic table. At present, it is not clear that the quantum effect of hydrogen will enhance the lattice anomaly of the c -axis contraction or not. It is necessary to consider the quantum effect for HBC by means of the first-principles path-integral molecular dynamics method¹⁹⁻²¹⁾ in future. We believe that the study of anisotropic compression will be increasingly important in the near future.

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