Lattice Anomaly of MgB(*h*-BN) under Anisotropic Compression

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We have examined the lattice and electronic properties of a hypothetical compound of magnesium boride (MgB) with a hexagonal boron-nitride (*h*-BN) type crystal structure using the first-principles molecular dynamics (FPMD) method. We found a lattice anomaly of MgB(*h*-BN) under uniaxial *c*-axis compression. Lattice constant *a* contracts 0.0017 and 0.0051 nm under *c*-axis compression with *P_z* = 50 and 100 GPa, respectively. This contraction implies that the Poisson ratio of MgB(*h*-BN) is negative.

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1. Introduction

We found that LiBC and HBC show a lattice anomaly under anisotropic compression.¹⁻³⁾ Their *c* lattice constants contract under *a*, *b*-axis compression (*P_{xy}*). The lattice constant changes are quite small 0.0014 nm for LiBC and 0.0037 nm for HBC when *P_{xy}* = 50 GPa. After thorough studies of the lattice anomalies of LiBC and related compounds,¹⁻⁴⁾ we have only observed this lattice anomaly in LiBC and HBC.

Very recently, we found that a hypothetical compound of MgB with a hexagonal BN (*h*-BN with *P*6₃/mmc) crystal structure implies a lattice anomaly of the *a*-axis under *c*-axis compression (*P_z*). Lattice constant *a*(*b*) of MgB(*h*-BN) contracts under *c*-axis compression, which indicates a negative Poisson ratio. Our interest in MgB(*h*-BN) originated in our study of magnesium boride phases under various compression conditions.⁴⁾ This has been obtained from the Mg₂B₂ phase with Wurtzite crystal structure by structural transformation under uniaxial *c*-axis compression as shown in Fig. 1.

In this study, we investigate a lattice anomaly of the hypothetical magnesium boride compound (MgB(*h*-BN)) under anisotropic compression. The purpose of this study is to investigate electronic and lattice changes of MgB(*h*-BN) under various compression conditions. The important point to note is that it is possible to optimize the structure under anisotropic compression using the first-principles molecular dynamics (FPMD) method. We calculated the electronic and lattice properties of MgB(*h*-BN) under various compression conditions (*P* = 0, 50 GPa as hydrostatic, *P_{xy}* = 50 GPa as biaxial *a*, *b*-axis, and *P_z* = 50 and 100 GPa as uniaxial *c*-axis).

We have pointed out that the contraction of lattice constant *c* for LiBC and HBC under *a*, *b*-axis compression is related to an electrostatic interaction between the cation and B-C layers, and the size of cation atoms.^{2,3,5)} In contrast, MgB(*h*-BN) contracts along *a*(*b*)-axis under *c*-axis compression. In MgB(*h*-BN), each layer consists of an equal number of Mg and B atoms and is not ionized so the lattice anomaly of MgB(*h*-BN) has no relation to inter-layer electrostatic interactions.

In the past, first-principles approaches using the density functional theory^{6,7)} (DFT) under anisotropic compression

have not often been attempted because of the lack of corresponding high-pressure experiments at sufficiently low temperatures. It is expected that such approaches may predict novel physical properties and behaviors of materials under anisotropic compression. Therefore, we believe that it is very important to investigate the electronic and lattice properties of materials 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⁾ for exchange-correlation. The optimized pseudopotentials (Mg and B) by Troullier and Martins (TM)^{9,10)} are used. Nonlocal parts of the pseudopotentials are transformed to the Kleinman-Bylander separable forms¹¹⁾ without ghost bands. A partial core correction (PCC)¹²⁾ is used for the Mg pseudopotential.

The number of sampling *k*-points (*N_k*) is 259 in the irreducible Brillouin zone (BZ). The wave function is expanded in plane waves, and the energy cutoff (*E_{cut}*) is 81 Ry with the maximum number of plane waves being about 5500. The number of atoms in a unit cell is 4. The number of *k*-points is fixed during cell optimization. Our treatment follows the hydrostatic, uniaxial (*c*-axis) and biaxial (*a*, *b*-axis) compression conditions given in the present studies. Unit cell parameters are optimized using the stresses¹³⁾ acting on them. A structural optimization of internal atoms in the unit cell is performed using Hellmann-Feynman forces. In fact, internal atoms do not displace because of a constraint of the crystal symmetry in MgB(*h*-BN). The system of MgB(*h*-BN) maintains crystal symmetry under compression. The *c/a* ratio in the FPMD calculation is a variable parameter within the symmetry constraint for MgB(*h*-BN). The details of the calculation process with cell optimization have been reported in our previous publications.^{2,4,14)}

3. Results and Discussion

The optimized lattice properties from the present calculation are tabulated in Table 1. Previous results for HBC³⁾ and LiBC²⁾ are also tabulated for comparison with the results of the present study. From Table 1, *c/a* ratios of MgB(*h*-BN) increase when *P* = 50 GPa and *P_{xy}* = 50 GPa. They decrease

Fig. 1 Crystal structures of MgB(Wurtzite) and MgB(h-BN).

when $P_z = 50$ and 100 GPa. In the present study, we have found that lattice constant $a(b)$ shows anomalous behavior under c -axis compression. This is different from the c -axis lattice anomalies of HBC³⁾ and LiBC.²⁾ Lattice constant $a(b)$ of MgB(h-BN) contracts by 0.0017 and 0.0051 nm when $P_z = 50$ and 100 GPa, respectively. It is confirmed that lattice constant a contracts when $P_z = 200$ GPa. There are no anomalies under hydrostatic and a , b -axis compressions. The lattice expansion on the a , b -axis for HBC and LiBC under c -axis compression is very small. Generally, the lattice constant change on the a , b -axis is small for a variation of lattice constant c because intra-layer (B-C) bonding is strong and rigid.

It was found in previous work¹⁷⁾ that the lattice constant under anisotropic compression is sensitive to the number of k -points. We have investigated this sensitivity to the number

Table 1 Optimized lattice constants[nm], the c/a ratios of MgB(h-BN), HBC³⁾ and LiBC.²⁾ “PBE” indicates the generalized gradient approximation (GGA-PBE).¹⁵⁾

	GPa	c	a	c/a
MgB(h-BN)	$P = 0$ GPa	0.4564	0.4099	1.11
MgB(h-BN)	$P = 50$ GPa	0.4074	0.3530	1.15
MgB(h-BN)	$P_{xy} = 50$ GPa	0.4655	0.3479	1.34
MgB(h-BN)	$P_z = 50$ GPa	0.4010	0.4082	0.98
MgB(h-BN)	$P_z = 100$ GPa	0.3746	0.4048	0.93
HBC	$P = 0$ GPa	0.5796	0.2694	2.15
HBC(PBE)	$P = 0$ GPa	0.5837	0.2672	2.18
HBC	$P = 50$ GPa	0.4968	0.2589	1.92
HBC	$P_{xy} = 50$ GPa	0.5759	0.2573	2.24
HBC	$P_z = 50$ GPa	0.4865	0.2700	1.80
LiBC	$P = 0$ GPa	0.6950	0.2735	2.54
LiBC	$P = 50$ GPa	0.5870	0.2617	2.24
LiBC	$P_{xy} = 50$ GPa	0.6936	0.2590	2.68
LiBC	$P_z = 50$ GPa	0.5636	0.2761	2.04
LiBC	(Exp ¹⁶⁾)	0.7058	0.2752	2.56

of k -points for magnesium boride phases and concluded that sufficient convergence is obtained at 259 k -points in this study.

The electronic band structures of MgB(h-BN) when $P = 0$, 50 GPa, $P_{xy} = 50$ GPa and $P_z = 50$ GPa are shown in Fig. 2. They are metallic under all calculated compression conditions in this study. The electronic band structure when $P_z = 100$ GPa is also metallic. They broadly resemble each other although their dispersions of individual bands near the Fermi level differ. The bandwidths increase as the pressure increases in all cases. The electronic bands at the A -point near the Fermi level are almost invariant under compression. In contrast, the electronic bands around the K -point near the Fermi level change under compression by a greater amount than those at the A -point. The lowest unoccupied band at the L -point when $P = 0$ GPa shifts slightly to a lower energy and becomes the occupied band when $P_z = 50$ GPa as shown in Figs. 2(a) and (d). These changes near the Fermi level may induce a structural phase transformation, although that is not treated in the present study. Furthermore, the changes may be related to the a , b -axis contraction under c -axis compression.

As we mentioned in the introduction, the origin of the anomalous contraction of lattice constant a under c -axis compression is unknown. From the crystal structure of MgB(h-BN) as shown in Fig. 1, there is no electrostatic interaction between Mg-B layers. For comparison, we calculate the energy band structure with lattice constant a set at its value when $P = 0$ GPa while c is fixed at its value when $P_z = 50$ GPa. The obtained energy band structure is almost identical to the one when $P_z = 50$ GPa since the contraction of 0.0017 nm is quite small.

One electronic band crosses the Fermi level at the Γ - A line when $P = 0$ GPa as shown in Fig. 2(a). This band shifts to lower energy when $P_z = 50$ GPa as shown in Fig. 2(d). Its occupation increases as a result of shifting to lower energy, so that the bonding of Mg and B in the intra-layer is strengthened by the larger number of bonding electrons. This may be the driving force of the a , b -axis contraction.

Fig. 2 Energy band structures of MgB(*h*-BN) when $P = 0, 50$ GPa, $P_{xy} = 50$ GPa and $P_z = 50$ GPa. The Fermi level is indicated by the horizontal line.

4. Summary

We calculated the electronic and lattice properties of the hypothetical material MgB(*h*-BN)⁴⁾ under various compression conditions using FPMD. As in the case of LiBC,²⁾ we found a lattice anomaly in MgB(*h*-BN) under *c*-axis compression. The values of the lattice contraction for MgB(*h*-BN) are 0.0017 and 0.0051 nm when $P_z = 50$ and 100 GPa, respectively. This anomaly shows that the Poisson ratio of MgB(*h*-BN) is negative.

In previous studies, we found the anomalous behavior of lattice constant *c* under *a*, *b*-axis compression for the

hexagonal layered materials HBC and LiBC.^{1–3)} The mechanism of the anomaly has been partially described in earlier reports.^{2,3,5)} In contrast, the present study shows that the origin of the lattice anomaly in MgB(*h*-BN) under *c*-axis compression has not been adequately explained. It is impossible to describe the contraction of lattice constant *a*(*b*) using the inter-layer interaction and the size of the cation atom.^{2,3,5)} The lattice contraction of *a*(*b*)-axis under *c*-axis compression may be attributed to the larger number of bonding electrons due to increased occupation of the band at the Γ -A line near the Fermi level. Our next task is to clarify the origin of this effect.

The anomalous behavior of MgB(*h*-BN), HBC and LiBC has been thoroughly checked for accuracy with the DFT-LDA calculation. Intensive examination leads to the conclusion that these anomalies are correct, at least within the DFT-LDA(GGA for HBC and LiBC) calculation. However, the values of the lattice contraction of MgB(*h*-BN), HBC and LiBC are quite small on the order of 0.001 nm. Thus, further investigation is necessary and the search for new materials which show larger lattice contractions should be pursued. We believe that the study of anisotropic compression will be increasingly important in the near future.

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