Mechanical and electronic properties of superhard ReB_2

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Considering the effect of spin-orbit coupling, we have studied the equation of state, elastic properties, and the electronic structures of ReB_2 by first-principles plane-wave basis pseudopotential calculations. Our calculated results show that ReB_2 has high bulk modulus (356 GPa), large shear modulus (293 GPa), and great elastic constant c_{44} (284 GPa), and thus support that ReB_2 is ultraincompressible and a potentially superhard material. Besides the compact crystal structure, the electronic mechanisms of its hardness can be understood from the highly directional covalent bonds and the optimal filling of the bonding states.

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Superhard materials have been a subject of permanent interest due to their importance in both fundamental science and technique applications. Two kinds of materials are believed to be powerful superhard candidates. One includes strong covalent compounds of C, B, N, and O, such as diamond,[1] cubic boron nitride (*c*-BN),[2] B_6O,[3] and BC_2N.[4] The other kind of hard materials is offered by incorporating light elements into heavy transition metals and optimizing covalent bonding and valence-electron density.[5,6] Therefore, transition-metal boride, carbide, nitride, or oxide might be the most interesting candidate as a very hard material.[7–10] Since Os has the highest valence-electron density and the least compressibility among the transition metals,[11–14] it is natural that OsB_2 becomes one typical example and has been extensive studied recently.[6,15,16] Nevertheless, it was found that OsB_2 is only a hard material but not a superhard one, perhaps because the Os lattice excessively expands upon the incorporation of B atoms to form OsB_2 and there are extra freedoms of atomic position in orthorhombic OsB_2. In searching for even harder materials, very recently, Chung *et al.*[17] have successfully synthesized rhenium diboride (ReB_2) and reported that it is an ultraincompressible superhard material. ReB_2 forms in hexagonal lattice (space group $P6_3/mmc$, No. 194) and there are 2 f.u. per unit cell, with two Re atoms occupying the 2*c* Wyckoff site (1/3, 1/3, 1/4) and four B atoms holding the 4*f* position (1/3, 2/3, *z*).[18] Compared with OsB_2, ReB_2 has shorter metal-metal bond length, less internal parameters, and higher hardness.

In order to fully clarify mechanical and electronic properties of ReB_2, the theoretical calculations that can provide further details are highly desirable. So far, only the existing theoretical report addressing the elastic properties was made by Hao *et al.*[19] Their calculations provided useful information for the understanding of mechanical characters of ReB_2. However, it is well known that Re is one of the 5*d* transition metals with high valence-electron density, and thus Re has strong spin-orbit coupling (SOC). Their calculations have not included the effect of SOC. Furthermore, less attention has been paid to the band structure of ReB_2. In this Brief Report, we carry out systematic studies for the equation of states (EOS), elastic constants, and the electronic structure of ReB_2 from first-principles calculations, including the effect of SOC.

Calculations on ReB_2 are conducted by the BSTATE code[20] using first-principles plane-wave basis pseudopotential method based on the density functional theory and employing the local density approximation (LDA-PW91)[21] for the exchange-correlation energy. The 2*s* and 2*p* states of B and 5*d* states of Re are treated by the Vanderbilt ultrasoft pseudopotential,[22] while the norm-conserving scheme[23] is used for other states. To include the effect of SOC, we perform the calculations using the relativistic fully separable pseudopotential in the framework of noncollinear magnetism.[24,25] The special *k* points of $12\times12\times8$ mesh are generated using the Monkhorst-Pack scheme[26] and the cutoff energy of 30 Ry for the plane-wave expansion is used. The calculated lattice constants and bulk modulus and its first pressure derivative are estimated through a least-squares fit of calculated total energy versus volume to the third-order Birch-Burnaghan EOS.[27] For the hexagonal systems, structure (c/a ratio) optimizations are performed for each fixed volume. The elastic constants are obtained by similar methods of Refs. 28 and 29. The shear modulus, Young's modulus, and Poisson's ratio are calculated according to the Voight-Reuss-Hill bounds.[30]

TABLE I. Calculated equilibrium lattice parameters a_0 (Å), c_0 (Å), bulk modulus B_0 (GPa), and its pressure derivative (B_0'), compared with available data for diamond, *c*-BN and ReB_2.

	a_0	c_0	B_0	B_0'
Diamond	3.532		469	3.59
	3.567[a]		446[a]	3.0[a]
c-BN	3.590		402	3.62
	3.610[b]		392[b]	3.79[b]
ReB_2	2.872	7.405	359	4.09
(SOC)	2.877	7.415	357	4.15
(SOC+relaxed)	2.874	7.412	356	4.14
	2.870[c]	7.395[c]	369[c]	
	2.900[d]	7.478[d]	360[d]	4.0[d]

[a]Experiment (Ref. 1).
[b]PW-PP (GGA) (Ref. 2).
[c]PW-PP (LDA) (Ref. 19).
[d]Experiment (Ref. 17).

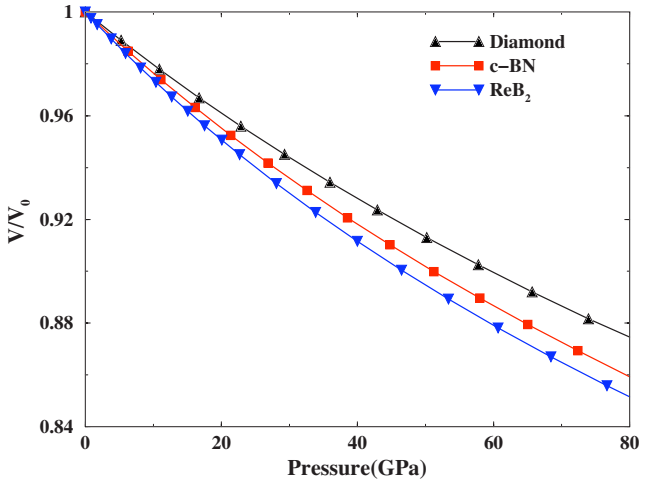

FIG. 1. (Color online) The calculated volume-pressure data (EOS) of diamond, c-BN, and ReB_2.

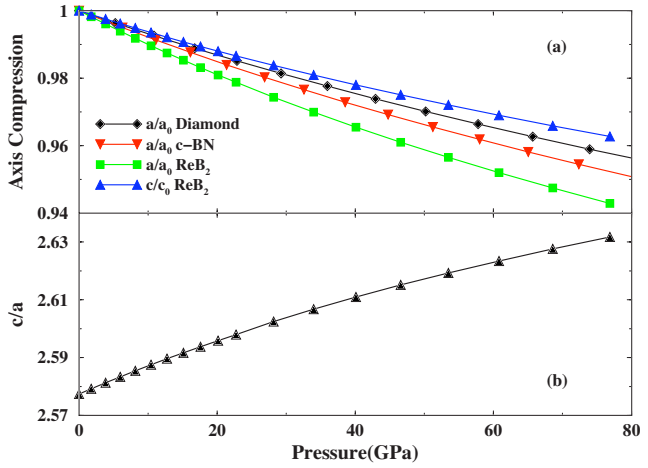

FIG. 2. (Color online) (a) The calculated axis compression of diamond, c-BN, and ReB_2 and (b) the axial ratio c/a of ReB_2 as a function of pressure.

Table I presents our results of lattice constants and bulk modulus and its pressure derivative of ReB_2, diamond, and c-BN, in comparison with other available data. First, we can see that the calculated data of diamond and c-BN are in good agreement with the other theoretical or experimental values[1,2,7] within LDA and generalized gradient approximation (GGA) errors, substantiating the accuracy of our calculations. Then, let us see EOS of ReB_2. The equilibrium lattice constants calculated both in the absence and in the presence of SOC are very close with the available value[17,19] within an error of 1%. The bulk moduli for the cases with and without SOC are 359 and 356 GPa, respectively, which are in excellent agreement with the experimental data (360 GPa) (Ref. 17) and the previous calculated value (369 GPa) (Ref. 19) but are smaller than those of diamond (469 GPa) and c-BN (402 GPa). To further compare the compressibililty of ReB_2, diamond, and c-BN under pressure, the volume compressions as a function of pressure are plotted in Fig. 1. We can explicitly see that ReB_2 is more compressible than diamond and c-BN, although they are all ultraincompressible materials.

Elastic constants, shear modulus, Young's modulus, and Poisson's ratio are essential for understanding the macroscopic mechanical properties of solids and for designing hard materials. These properties of ReB_2, diamond, and c-BN are calculated and listed in Table II. For ReB_2, we perform three series of calculation: (1) excluding SOC and fixing atomic internal coordinate, (2) including SOC and fixing atomic internal coordinate, and (3) including SOC and relaxing atomic internal coordinate. It is found that the maximum deviation for cases (1) and (2) is about 10%, and that the maximum difference between (2) and (3) totals to about 15%. Compared with the results of Hao *et al.*,[19] our calculated c_{12} is larger by 13%, while our c_{13} is smaller by 15%. Our other calculated values are basically consistent with those of Hao *et al.*[19] The elastic constants c_{11} or c_{33} measure the a- or c-direction resistance to linear compression, respectively. We find that c_{11} of ReB_2 (679 GPa) is comparable to that of c-BN (818 GPa), while c_{33} for ReB_2 (1083 GPa) rivals c_{11} for diamond (1106 GPa). Also, there is substantial anisotropy in the compressibility of ReB_2. The anisotropic behavior is observed from the axial compressions [Fig. 2(a)] and the axial ratio c/a as function of pressure [Fig. 2(b)]. As seen in Fig. 2(a), the a axis is more compressible than the c axis, and the c axis of ReB_2 is even more incompressible than the analogous axis of diamond under pressure from the calculational perspective. Hardness is a macroscopic concept. Besides the bulk modulus, the shear modulus and the elastic

TABLE II. Calculated elastic constants c_{ij} (GPa), shear modulus G (GPa), Young's modulus E (GPa), and Poisson's ratio ν, compared with available data for diamond, c-BN, and ReB_2.

	c_{11}	c_{33}	c_{44}	c_{12}	c_{13}	G	E	ν
Diamond	1106		604	151		550	1186	0.079
	1020[a]		553[a]	133[a]		509[a]		
c-BN	818		479	194		403	907	0.124
ReB_2	716	1108	290	151	133	310	725	0.171
(SOC)	708	1144	275	149	120	305	714	0.172
(SOC+relaxed)	679	1083	284	170	137	293	691	0.181
	685[b]	1088[b]	282[b]	151[b]	158[b]	295[b]	699[b]	0.185[b]

[a]FLAPW (GGA) (Ref. 7).
[b]PW-PP (LDA) (Ref. 19).

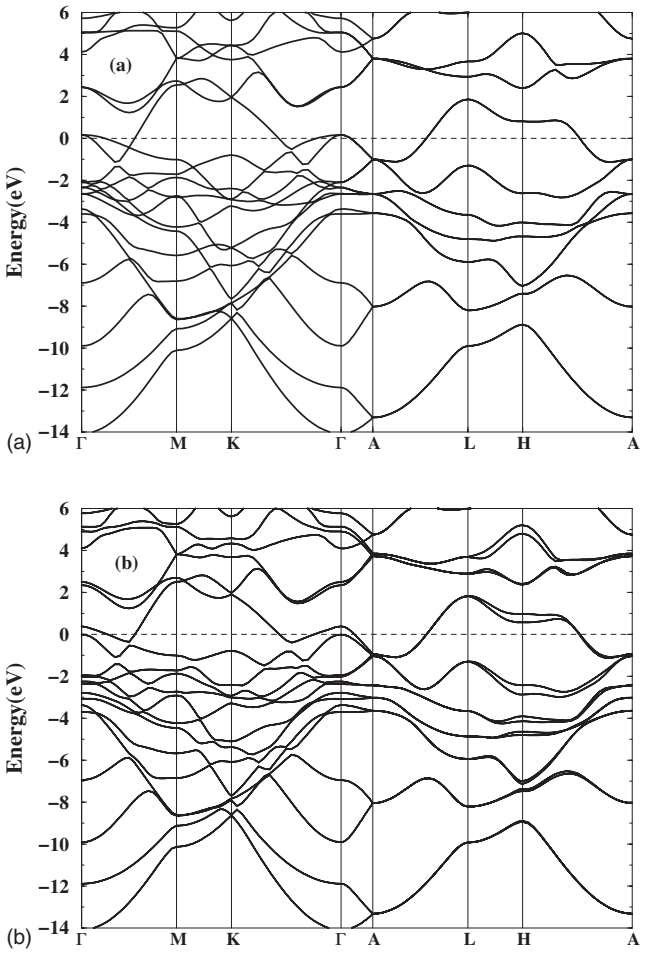

FIG. 3. (a) Band structure of ReB_2 from the LDA calculation excluding SOC. (b) Band structure of ReB_2 from the LDA calculation including SOC. $\Gamma=(0,0,0)$, $M=(0.5,0,0)$, $K=(1/3,1/3,0)$, $A=(0,0,0.5)$, $L=(0,0,0.5)$, and $H=(0.5,0,0.5)$.

constant c_{44} are also the most important parameters indirectly governing the indentation hardness. The shear modulus G and the elastic constant c_{44} of ReB_2 are calculated to be 293 GPa and 284 GPa, respectively. Both values are exceptionally high, exceeding the counterparts of OsB_2 ($G=174$ GPa, $c_{44}=61$ GPa)[15] and approaching 70% of those of c-BN ($G=403$ GPa, $c_{44}=479$ GPa). Therefore, the present calculations show that ReB_2 is an ultraincompressible material and has a potential to be a superhard material.

In order to gain a deeper insight into the hardness of ReB_2, the electronic properties such as band structure, the density of states (DOS), and the charge density are calculated in the absence and in the presence of SOC at the experimental lattice constants. Figures 3(a) and 3(b) display the band structures for the cases with and without SOC, respectively, while Fig. 4 presents the total and projected DOS with SOC. We note that there are several bands crossing the Fermi level in Fig. 3 and the substantially large total DOS at the Fermi level in Fig. 4, indicating well metallic feature in ReB_2. This metallicity might make ReB_2 a better candidate for hard conductors at extreme conditions of high temperatures and high pressures. Both band structures in Figs. 3(a) and 3(b) have main features in common, but SOC makes some degenerate

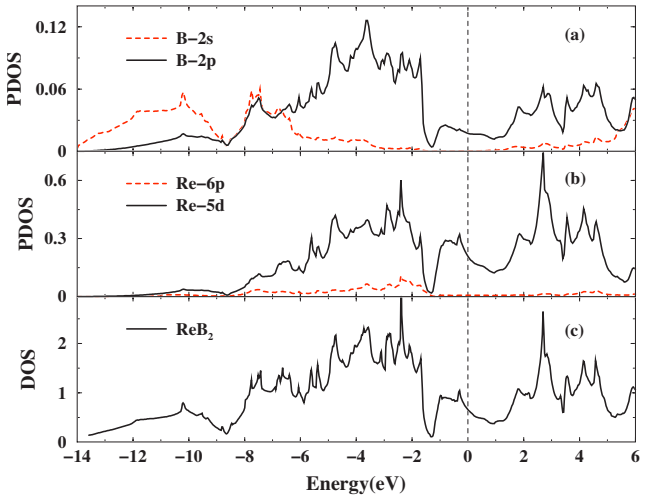

FIG. 4. (Color online) Total and projected density of states of ReB_2 from the LDA calculation including SOC. The vertical dashed line at zero is the Fermi energy level.

symmetry points (such as Γ, M, and K) or lines (L-H-A) split.

As seen in Figs. 3 and 4, the lowest four bands can be mostly attributed to B 2s states. Above these bands, the electronic structure is governed by a strong hybridization between the Re 5d and B 2p states, which indicates the strong covalent bonding of Re-B. The covalency can be clearly seen through the charge density of ReB_2 in Fig. 5. Neighbor B atoms form very powerful covalent bonds. The bonding between the Re atoms and their neighbor B atoms is also highly directional. According to Chen *et al.*,[16] the Re-B bond should

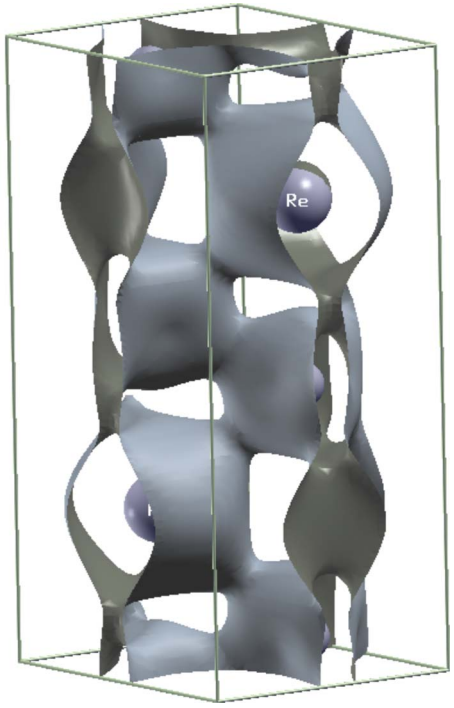

FIG. 5. (Color online) The charge density for ReB_2 within a primitive cell. The bondings of Re-B and B-B exhibit high directionality, indicating strong covalent characters.

be a considerable amount of covalent character rather than ionic one, similar to OsB_2. The highly directional covalent bonds resist elastic and plastic deformations, counteract the creation and movement of dislocations, and achieve the superhardness of ReB_2. On the other hand, we have found that the mostly occupied region (−7.5–1 eV) may be viewed as the bonding states of the hybridization complex formed by the Re 5*d* and B 2*p* states, while the unoccupied higher region (above 1 eV) the corresponding antibonding states. This optimal filling of the bonding states formed by 5*d*-2*p* hybridization also has important contribution to the hardness of ReB_2.

In summary, the mechanical and electronic properties of ReB_2 are investigated by the first-principles calculations. The calculated bulk moduli with and without SOC are 359 and 356 GPa, respectively, which well agree with the experimental value (360 GPa). Considering the effect of SOC and atomic internal coordinate relaxed, our calculated shear modulus G (293 GPa) and the elastic constant c_{44} (284 GPa) are exceptionally high. Therefore, it is supported by our results that ReB_2 is ultraincompressible and a potentially superhard material. At the same time, the ReB_2 is found to have metallic features, similar to OsB_2. Besides the dense lattice structure, the electronic mechanisms of the hardness of ReB_2 can be understood from the highly directional covalent bonds and the optimal filling of the bonding states.

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