Research Letter

Structural, Elastic, and Electronic Properties of ReB_2 : A First-Principles Calculation

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The structural, elastic, and electronic properties of the hard material ReB_2 have been investigated by means of density functional theory. The calculated equilibrium structural parameters of ReB_2 are in agreement with the experimental results. Our result of bulk modulus shows that it is a low compressible material. Furthermore, the elastic anisotropy is discussed by investigating the elastic stiffness constants. The charge density and the electronic properties indicate that the covalent bonding of Re-B and B-B plays an important role in formation of a hard material. The good metallicity and hardness of ReB_2 might serve as hard conductors.

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1. INTRODUCTION

Superhard materials are useful in a variety of industrial applications for fast machining and drilling. Intense experimental and theoretical efforts have been focused on the possibility of synthesizing and designing novel superhard material [1, 2]. Recently, the ultra-incompressible hard material OsB_2 has been synthesized successfully in experiment [3]. However, the Os lattice expands by approximately 10% upon the incorporation of B atoms to form OsB_2 and undergoes a distortion to an orthorhombic phase. In searching for much more hard materials, Chung et al. attempted to use the element Re, which lays directly next to the left of Os in the periodic table of the elements. They successfully synthesized the hard material ReB_2 under ambient conditions [4], for which the incorporation of B into the interstitial sites of Re to form ReB_2 brings only 5% expansion of the Re lattice and the bulk modulus of ReB_2 is 360 GPa rivaling that of the diamond (442 GPa) [5]. Thus, ReB_2 is considered to be one of the most promising candidates for improving the mechanical properties of OsB_2 .

The pure Re has a large bulk modulus of 360 GPa while its hardness is only 1.3–3.2 GPa [6]. The high bulk modulus of Re is mainly due to the high valence electron density, while the low hardness is related to the metallic bonds *because they are the same in all directions and therefore poor at resisting either plastic or elastic shape deformations*. How-

ever, the ReB_2 is an ultra-incompressible (360 GPa) as well as a hard (30.1–55.5 GPa) material [4]. Though first-principles quantum mechanical calculations can provide robust explanations of ReB_2 properties, a few results have been reported [7]. Therefore, it is interesting to understand the microcosmic mechanism of the hardness-related properties of ReB_2 from the basic point of view of physics and applications.

In this work, we performed density functional calculations on ReB_2 to study its structural, elastic, and electronic properties related to the electron configuration of this material. The equilibrium structural parameters, bulk modulus, and elastic stiffness constants were calculated and compared with experimental results, and its elastic anisotropy and compressibility were discussed. The charge density, band structure, and density of states (DOS) of ReB_2 were also calculated for investigating the electronic properties of ReB_2 .

2. METHODS AND MODELS

The density functional calculations on the structural, elastic, and electronic properties of ReB_2 were performed using the CASTEP code [8]. Both lattice and internal coordinates were optimized to get the equilibrium structure for ReB_2 . The exchange-correlation function was treated by both the generalized gradient approximation (GGA-PBE) [9] and the local density approximation (LDA-CAPZ) [10, 11]. The Vanderbilt ultrasoft pseudopotential [12] was used with the cutoff

energy of 350 eV, and the k -point meshes of $10 \times 10 \times 4$ for hexagonal ReB_2 were generated using the Monkhorst-Pack scheme [13]. The energy convergence was checked with increasing cutoff energy to 400 eV, which brought only 10 meV error. In the geometry optimization, all forces on atoms were converged to be less than $0.03 \text{ eV/\AA}$; the maximum ionic displacement was within $0.001 \text{ \AA}$, and the total stress tensor was reduced to the order of 0.05 GPa . For ReB_2 , the experimental structure was used as the initial structure for the calculations [14].

3. RESULTS AND DISCUSSIONS

ReB_2 has a hexagonal lattice (space group $P63/\text{mmc}$, No.194) with the experimental lattice parameters $a = b = 2.900$ and $c = 7.478 \text{ \AA}$ [14]. In the hexagonal structure, two Re atoms occupy the $2a$ Wyckoff sites and four B atoms occupy the $4f$ sites, as shown in Figure 1. The calculated lattice constants of ReB_2 within both LDA and GGA are shown in Table 1, which shows that the optimized lattice constants are larger using GGA method than that of using LDA method. In addition, the calculated lattice parameters of a and c with GGA are in good agreement with the experimental data [14], differing only by 0.66% and 0.92%, respectively. By contrast, the results using LDA are larger than the experimental values by 1.0% and 1.1. The calculated densities within both LDA and GGA are 13.08 and 12.96 g/cm^3 with an error about 3.1% and 2.2% compared with the experimental value 12.68 g/cm^3 , respectively [14]. The calculated elastic constants C_{ij} of ReB_2 at zero pressure are also shown in Table 1. All of them satisfy the criteria for stability of hexagonal structure based on the Born-Huang criterion [15, 16], which indicates that this structure of the material is stable. The calculated values for bulk modulus using LDA and GGA are 360 and 353 GPa, respectively, both of which are in good agreement with the experimental results (360 GPa) [4]. This value rivals that of diamond (442 GPa) [5], indicating the incompressibility characteristic of hexagonal ReB_2 .

The elastic anisotropy (A) of crystals can exert great effects on the properties of physical mechanisms, such as anisotropic plastic deformation, crack behavior, and elastic instability. Thereby, it is important to calculate elastic anisotropy in order to obtain a deep understanding for the properties of such material. For hexagonal ReB_2 , the anisotropy of shear anisotropy ratio was calculated by $A = C_{44}/C_{66}$ [17], and the results using the LDA and GGA approached 1.02. Additionally, the knowledge of elastic coefficients also provides a method to evaluate the linear compressibility. The ratio for linear compressibility coefficients k_c/k_a of hexagonal crystal is defined as $k_c/k_a = (C_{11} + C_{12} - 2C_{13})/(C_{33} - C_{13})$ [18]. A value of 1.0 implies the isotropic compressibility, and the deviation from 1.0 is the value that measures the anisotropy for the linear compressibility along the c and a directions. The k_c/k_a of ReB_2 is 0.58 for LDA and 0.57 for GGA, respectively, which means that the compressibility along the c axis is *much* smaller than that along the a axis, coinciding with the calculated elastic constants very well along different axes (shown in Table 1). In addition, the percentages of anisotropy in compressibility and shear were also

FIGURE 1: The crystal structure for ReB_2 . Black and grey balls represent Re and B atoms, respectively.

TABLE 1: Calculated structural parameters of ReB_2 using LDA and GGA: $a(\text{\AA})$, $b(\text{\AA})$, $c(\text{\AA})$, density ρ (g/cm^3), elastic constants C_{ij} (GPa), bulk modulus B (GPa), and shear anisotropy $A = C_{44}/C_{66}$, the ratio for linear compressibility coefficients k_c/k_a , and anisotropic factors A_G and A_B compared with the experimental results.

	LDA	GGA	Expt. ^{(a), (b)}
$a(b)$	2.870	2.881	2.9 ^(a)
c	7.395	7.409	7.478 ^(a)
ρ	13.08	12.96	12.68 ^(a)
C_{11}	686	678	—
C_{33}	1080	1071	—
C_{44}	282	272	—
C_{12}	155	144	—
C_{13}	152	148	—
C_{66}	266	267	—
B	360	353	360 ^(b)
A	1.02	1.02	—
k_c/k_a	0.58	0.57	—
$A_G[\%]$	1.36	1.55	—
$A_B[\%]$	1.91	1.91	—

^(a) See [13].

^(b) See [4].

calculated by bulk modulus factors $A_B = (B_V - B_R)/(B_V + B_R)$ and shear modulus factors $A_G = (G_V - G_R)/(G_V + G_R)$ [19], respectively, in which B and G represented the bulk and shear modulus, and the subscripts V and R denoted the Voigt and Reuss approximations. For hexagonal ReB_2 , $A_B = 1.91\%$ and $A_G = 1.36\%$ with LDA calculation and $A_B = 1.94\%$ and $A_G = 1.55\%$ with GGA calculation, respectively. These results indicate that ReB_2 is slightly anisotropic in compressibility, which is consistent with the experimental phenomenon [4].

FIGURE 2: (a) The total charge density contour (unit in $e/\text{\AA}^3$) for ReB_2 . (b) The difference charge density contour (unit in $e/\text{\AA}^3$) for ReB_2 . The charge density shown here is the result from GGA calculations. The bonding between Re and B exhibits the strong directionality throughout the plane. Black and grey balls represent Re and B atoms, respectively.

It is known that the hardness of a material is mainly determined by the bonding type in the system. To investigate the chemical bonding characteristic of the system, the electronic structure of ReB_2 such as the electron density, band structure, and density of states (DOS) was calculated with GGA and LDA at zero pressure. We find that the band structure, density of states, and charge density calculated by both the LDA and GGA methods at the corresponding theoretical equilibrium lattice constants show the similar patterns, and hence we just give the GGA results in this paper. The total charge density plot (the plot in the plane including B1, B2, B3, B4, Re1, and Re2) is shown Figure 1 as well as Figures 2(a) and 2(b). There are some electrons between Re atoms and their neighbor B atoms, and a strong directional bonding exists between them, indicating covalent bonding in ReB_2 . To shed more light on the bonding characteristic of ReB_2 , we plot the difference charge density (the difference between total density and superposition of atomic densities) in Figure 2(b). Clearly, two neighbor B atoms form a very strong covalent bond, which indicates that the formation of these directional covalent bonds leads to the high hardness. *Population analysis in CASTEP is performed using a projection of the plane wave states onto a localized basis using a technique described by Sanchez-Portal et al. [20], and population analysis of the resulting projected states is then performed using the*

Mulliken formalism [21]. This technique is widely used in the analysis of electronic structure calculations performed with linear combination of atomic orbitals (LCAO) basis sets. From the Mulliken population analysis for ReB_2 , the net charges of B and Re are -0.32 and 0.65 , respectively. It indicates a charge transfer from Re to B atoms, which revealed a partial ionic contribution to the Re-B bonding. On the other hand, along the c axis, metal atoms form linear chains and the metal-metal distance is very large and nearly equals the half of the cell parameter of the c axis, that is, $3.075 \text{ \AA}$. This might be an implication of certain weak metallic bonding between metal atoms. Therefore, our result suggests that the bonds of ReB_2 are of the unusual mixtures of covalent, ionic, and metallic bonding, as observed in OsB_2 [22].

The band structure of ReB_2 is shown in Figure 3 and the dashed line represents the Fermi level E_F . It can be seen that the occupied and unoccupied levels form one band and the levels near E_F are crossing and extended, indicating a metallic characteristic in ReB_2 . Since the metallicity is uncommon in superhard materials, that is, most of the superhard materials are insulators or semiconductors [23], this special characteristic of ReB_2 will put it in a favorable position in the future application for electron conductivity. Figure 4 is the total DOS (TDOS) of ReB_2 and partial DOS (PDOS) of B-2s, B-2p, Re-5p, and Re-5d with GGA calculation. Figure 4(e)

FIGURE 3: The band structure of ReB_2 . The dashed line represents the Fermi level.

FIGURE 4: Total DOS of ReB_2 and partial DOS of B-2s, B-2p, Re-5p, and Re-5d from the GGA calculations. The dashed line represents the Fermi level.

shows that E_F locates in the extended states with substantially density of states, which implies some good metallicity of ReB_2 . Additionally, in the DOS (see Figure 4(e)), the deep valley near the E_F , named as pseudogap, can be ascribed to the strong hybridization that leads to a separation of the bonding states. The partial DOS in Figure 4 shows that the total DOS near E_F is mainly contributed by the strong hybridization between the Re-5d and B-2p states, and the contributions of Re-5p and B-2s states are quite small. This strong hybridization of Re-5d and B-2p states also indicates the strong covalent bonding of Re-B. It is obvious that both of the analyses of charge density and DOS demonstrate the covalent bonding characteristic of ReB_2 , which is responsible for the high bulk modulus and hardness.

4. CONCLUSIONS

The results and analysis of the structural, elastic, and electronic properties for ReB_2 demonstrate that the hexagonal ReB_2 with the experimental structural parameters is found to

be metallic, which is uncommon in hard materials and suggests that ReB_2 is a potential hard conductor. Its bulk modulus calculated by LDA and GGA is large enough to compare with that of diamond. The bonds of ReB_2 are of the unusual mixtures of covalent, ionic, and metallic bonding. The electron structure indicates that the covalent bonding of Re-B and B-B is mainly responsible for the high hardness.

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