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All-electron study of ultra-incompressible superhard material ReB_2: structural and electronic properties*

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This paper investigates the structural and electronic properties of rhenium diboride by first-principles calculation based on density functional theory. The obtained results show that the calculated equilibrium structural parameters of ReB_2 are in excellent agreement with experimental values. The calculated bulk modulus is 361 GPa in comparison with that of the experiment. The compressibility of ReB_2 is lower than that of well-known OsB_2. The anisotropy of the bulk modulus is confirmed by c/a ratio as a function of pressure curve and the bulk modulus along different axes along with the electron density distribution. The high bulk modulus is attributed to the strong covalent bond between Re-d and B-p orbitals and the wider pseudogap near the Fermi level, which could be deduced from both electron charge density distribution and density of states. The band structure and density of states of ReB_2 exhibit that this material presents metallic behavior. The good metallicity and ultra-incompressibility of ReB_2 might suggest its potential application as pressure-proof conductors.

Keywords: first-principles, incompressibility, electronic property
PACC: 7115A, 7115H, 7115J, 6430

1. Introduction

Superhard materials are widely used in many fields ranging from cutting and polishing tools to wear-resistant coatings.[1−4] Design and synthesis of novel and robust superhard materials are of great interests to the material science community. Up to now, although diamond remains the known hardest material with many demands, it is not an effective tool for cutting steel and other ferrous metals due to the chemical reaction producing iron carbide. Superhard materials often favor short covalent bond or high densities of valence electrons.[2] The former does good to resist plastic or elastic deformation, while the latter resists squeezing (i.e., with high bulk modulus). Applying this idea, two groups of materials are believed to be possible superhard candidates. One kind of superhard materials is the strong covalent-bonded solids, such as diamond, C-BN, C_3N_4,[5] BC_2N,[6] and B_6O.[7] The other is large, electron-rich transition metal boride, carbide, oxide and nitride, such as OsB_2,[1] WC, RuO_2,[8] OsN_2, IrN_2,[4] and PtN_2.[9] However, these materials generally require synthesis under conditions of extreme pressure and temperature, making them quite expensive. Once superhard materials are synthesized successfully with low cost, it will quickly yield practical benefits in industrial applications. Most recently, Chung *et al*[3] reported the arc-melting synthesis of rhenium diboride (ReB_2) at ambient pressure. ReB_2 shows very high bulk modulus (360 GPa) and the incompressibility along the c-axis which rivals that of diamond. Indeed, our study shows that ReB_2 is an ultra-incompressible material. Though the crystal structure of ReB_2[10] has been determined from power diffraction data four decades ago, few theoretical researches for ReB_2 are reported.[11−13] Further information is still demanded from the first-principles investigations for ReB_2.

In order to provide a fuller understanding of the properties of ReB_2, we investigate the structural and electronic properties of ReB_2 based on all-electron first-principles calculations. Firstly, we determine the optimized structure parameters of ReB_2 under local density approximation (LDA) exchange–correlation energy functional with or without spin–orbit (SO) interaction. Secondly, the compressibility of ReB_2 is

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investigated by plotting the curve about equation of state (EOS). We compare the compressibility of ReB_2 with that of OsB_2 and find that the former is lower than the latter. Finally, the relationship between the incompressibility and the electronic properties of ReB_2 is discussed.

2. Computational details

All our calculations are performed within density functional theory,[14] using full potential linearized augmented plane waves plus local orbitals (LAPW+LO)[15] method as implementation of the WIEN2k package to solve the scalar-relativistic Kohn–Sham equations.[16] In the LAPW+LO method, wave functions are expanded in spherical harmonics inside nonoverlapping atomic spheres of radius $R_{\rm MT}$ and in plane waves in the remaining space of the unit cell (the interstitial region). As the exchange–correlation energy functional, LDA is used in our calculations.[1)] The influence of spin-orbit coupling (SOC) on structural and electronic properties of ReB_2 is taken into account. The SOC is treated self-consistently via the second variational step scheme with relativistic $p_{1/2}$ local orbits included. We expand the basis function up to $R_{\rm MT}K_{\rm max} = 7.0$ ($K_{\rm max}$ is the maximum modulus for the reciprocal lattice vectors). The muffin-tin radii are chosen to be equal to 2.05 and 1.60 Bohr for Re and B, respectively. The maximum value for partial waves inside the atomic sphere is taken to be $l_{\rm max} = 10$. Fully relativistic approximation is used for core electrons, and scalar relativistic approximations are used for valence electrons of $5s5p4f5d6s$ for Re and $2s2p$ for B. Brillouin zone integrations are performed by using the modified special $\boldsymbol{k}$ points technique of Monkhorst and Pack and self-consistently obtained with 350 $\boldsymbol{k}$ points in the irreducible Brillouin zone.

3. Results and discussion

3.1. Structural properties

ReB_2 has a hexagonal lattice (space group $P6_3/mmc$, No.194) with the experimental lattice constants $a = 2.900 \pm 0.001$ and $c = 7.478 \pm 0.002$ Å (1 Å = 0.1 nm). There are two formula units per unit cell, in which two transition metal atoms occupy the $2c$ Wyckoff site (1/3, 2/3,1/4) and four boron atoms hold the $4f$ position (1/3, 2/3, z), where $z = 0.548 \pm 0.003$ Å.[10] In the ReB_2 structure, planar layers of rhenium atoms are separated by puckered layers of boron atoms. We optimize both lattice and internal coordinates to get a relaxed structure of ReB_2. Table 1 shows equilibrium structure parameters, bulk modulus and its derivative with respect to pressure at zero pressure in comparing with available experimental data for ReB_2. For comparison, we also present the results calculated from Perdew–Burke–Eruzerhof generalized gradient approximation (PBE–GGA) and Wu–Cohen GGA (WC–GGA).[17] It is found that all our structure parameters obtained by using different exchange–correlation functional, are very close to the experimental values with the deviations less than 1%, thus only LDA calculation results are discussed in the following. The bulk moduli and their pressure derivatives are obtained by fitting the total energy curves to the 3rd-order Birch Murnaghan EOS.[18] The calculated bulk modulus in the absence and in the presence of SOC are 377 GPa and 361 GPa, respectively. The latter is very close to the experimental result (360 GPa), showing that SOC can improve bulk modulus value obtained from LDA effectively.

To understand bulk volume compressibility of ReB_2, we compare the compressibility of ReB_2 and OsB_2 under pressure. The ultra-incompressibility of OsB_2 has been verified via experiment and first-principles calculations. The calculated volume compressibility as a function of pressure is shown in Fig.1(a),[2)] which exhibits that the compressibility of ReB_2 is lower than that of OsB_2. That is, ReB_2 is more difficult to be compressed than OsB_2. In addition, the dependence of volume compressibility on the different lattice directions (namely, c/a ratio) as a function of pressure for ReB_2 (Fig.1(b)) shows that the compressibility along c-axis is much lower than that along a-axis, which will result in high value of elastic constant C_{33} and a relatively lower value of elastic constant C_{11} and C_{22} (for ReB_2, C_{11} is equal to C_{22}). The calculated C_{11} and C_{33} are 685 GPa and 1088.3 GPa within LDA, respectively,[11] which verifies the validity of our viewpoint above. Such

1) We also optimize the structure parameter using Perdew–Burke–Eruzerhof general gradient approximation (PBE–GGA) and Wu–Cohen GGA.[17] Though WC–GGA give more accurate structure parameters than LDA, PBE-GGA and LDA+SO, there are little differences in calculated electronic properties under the different exchange–correlation functional.

2)Structure parameters and internal coordinates of OsB_2 were optimized within LDA+SO method. $a = 4.6713$ Å, $b = 2.8615$ Å, $c = 4.0440$ Å.

anisotropic results from a strong electronic repulsion along c-axis direction, which will be addressed later. On the other hand, it can also be understood by comparing the bulk modulus along a axis (B_a) with that along c axis (B_c).[19] Using the elastic constants obtained from the LDA calculation,[11] we find that the obtained B_a and B_c are 923.9 GPa and 1656.2 GPa, respectively, which again indicates much smaller compressibility along c axis than that along a axis. This anisotropy in the compressibility of the two different lattice directions has been confirmed by the high-pressure diffraction data.[3]

Table 1. Equilibrium lattice parameters, V_0 (Å^3), a (Å), c (Å), z, the B–B bond lengths d_1(Å), the shortest Re–B distance d_2 (Å), density ρ (g/cm^3), bulk modulus B_0 (GPa) and its derivative with respect to pressure at zero pressure B_0', density of states at Fermi level $N(E_F)$ (States/eV per unit cell), and electronic specific coefficient γ (mJ/mol·K^2) compared with available experimental data for ReB_2.

	LDA	LDA+SO	PBE–GGA	WC–GGA	Exp.[10]
V_0	53.121, 52.743*	53.753	55.090, 53.261*	54.047	54.464
a	2.876, 2.870*	2.887	2.911, 2.881*	2.897	2.900±0.001
c	7.416, 7.395*	7.444	7.507, 7.410*	7.469	7.478±0.002
z	0.5483	0.5483	0.548	0.5483	0.548±0.003
d_1	1.808	1.815	1.829	1.821	1.822
d_2	2.235	2.2434	2.264	2.251	2.255
	2.212	2.2201	2.237	2.228	2.228
ρ	12.995, 13.086*	12.831	12.531,12.959*	12.843	12.680±0.017
B_0	377, 377*	361	344, 362*	353	360
B_0'	4.023	4.330	4.182	4.513	4.000
$N(E_F)$	1.255	1.266	1.310	1.283	
γ	2.96	2.99	3.09	3.036	

* Ref.[11]

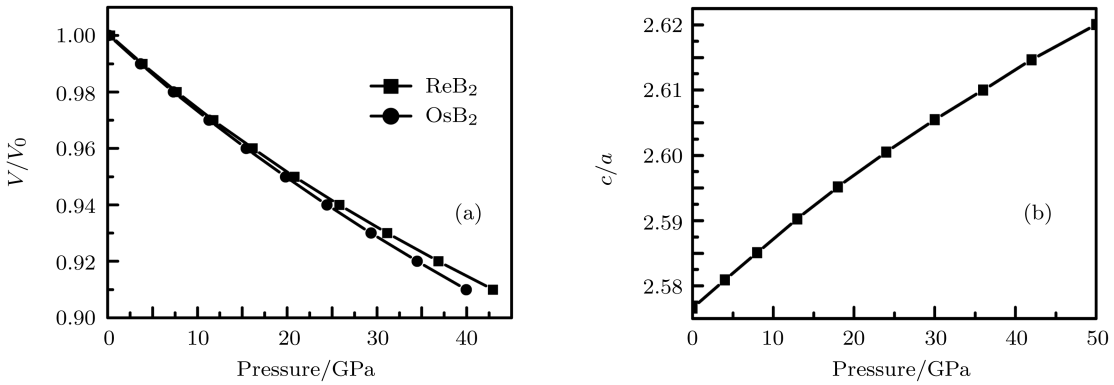


Fig.1. (a) The calculated volume-pressure data of ReB_2 and OsB_2. Pressure values are obtained by fitting the volume-energy curve to the 3rd-order Birch Murnaghan equation of states. V_0 is the quilibrium volume. (b) The calculated c/a ratios for ReB_2 as a function of pressure.

3.2. Electronic properties

Furthermore, to understand the correlation between the electronic properties and the mechanical properties, we present the electron density distribution, band energy and density of states (DOS) of ReB_2 both in the absence and in the presence of SOC in the equilibrium geometries.

As mentioned above, the bonding type takes responsibility for the hardness of materials. For resisting either plastic or elastic deformation, highly directional bonding is prior to highly ionic or metallic bonding. In order to

unravel the bonding properties of ReB_2, we plot the charge density distribution from the LDA+SO calculation in Fig.2. It is clearly seen that there is no strong bonding between Re–Re atoms as there is no accumulation of charges greater than the background charge density of the plane. It appears that the Re–Re bonding is predominantly metallic in ReB_2. From Fig.2(b), we note that charge highly accumulates between the Re–B atoms as well as between the B–B atoms. That is, a strong covalent bond exists between the B atoms, and a strong directional bonding exists between Re and neighboring B as well (i.e., Re–B and B–B bindings exhibit covalent characteristics). The covalent properties between Re and B are understood from the fact that there is almost equivalent electronegativity for Re and B atoms, which are 1.9 and 2.0 for Re and B, respectively. The planar layers of rhenium atoms are separated by puckered layers of boron atoms along the c-axis direction in the ReB_2 structure, which means that the atomic bonding in between layers is strong covalent, characteristic of Re–B and B–B. This implies that there is a greater electron density along c-direction than that in ab-plane, resulting in stronger electronic repulsions along c-axis than a-axis or b-axis. Thus, the compressibility along c-axis is much lower than that along a-axis, namely ab-plane anisotropy, as given in Fig.1(b).

Figures 3(a) and 3(b) present the band structures of ReB_2 in the absence and presence of SOC, respectively. The band splitting phenomenon due to SOC is observed at Γ, Σ, M, K, Λ and Δ near the Fermi level in ReB_2. It is worthwhile to note that the magnitude of the spin–orbital splitting is as high as 400 meV at Γ point. Both LDA and LDA+SO calculated band structures have main features in common excluding the band splitting resulted from SOC. The bands ranging from –14 eV to –6 eV are mainly B s-state with slight contributions from Re s-state and B p-state. The bandwidth of occupied Re d is about 9 eV. The bands between –9 eV and 15 eV are mainly Re d-state and B p-state. From band character analysis, it is confirmed that B $p_x(p_y)$ subband and Re $d_{x^2y^2}(d_{xy})$ and $d_{xz}(d_{yz})$ subbands cross the Fermi level which are rather dispersive in the whole Brillouin zone. The occupied Re d-state below Fermi level exists along Γ–M and Λ–Γ–A exceeding M–K–Λ directions. However, above the Fermilevel, the Re d-state mainly exists along Γ–M–K–Λ direction. The band structure shows that, contrary to the fact that most of the superhard materials are insulators (for example, PtN_2) or semiconductors,[20] ReB_2 has a clear metallic characteristic. This unusual metallicity is also observed in both OsB_2[21] and OsN_2.[22]

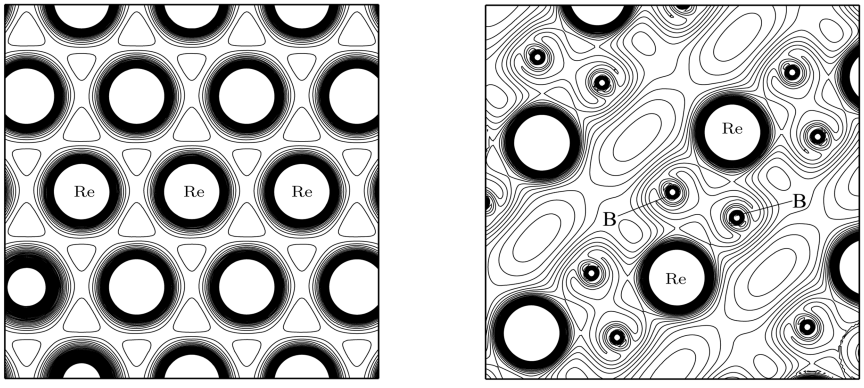


Fig.2. The valence electron density contour for ReB_2 obtained from LDA+SO. Charge density is in an increment of 0.01 e/a.u.^{3} from 0.01 e/a.u.^{3} to 0.4 e/a.u.^{3}. (a) (0001) plane; (b) $(11\bar{2}0)$ plane.

The partial and total DOS for ReB_2 with respect to the Fermi level are shown in Fig.4. The electronic DOS of ReB_2 plotted in Fig.4 shows several similarities to that of OsB_2.[21] The calculated DOS at Fermi level $N(E_F)$ and electronic specific coefficient γ are listed in Table 1. Dominant contributions to DOS at Fermi energy $N(E_F)$ come from Re-$d_{x^2y^2}(d_{xy})$,$d_{xz}(d_{yz})$ and B-$p_x(p_y)$. The large $N(E_F)$ value of ReB_2 unfolds its metallicity. Valence or conduction bands near Fermi level are mainly from the contribution of B-p and Re-d orbitals. The electronic structures of ReB_2 are governed by a strong hybridization between B-p and Re-d states, while with a rather small contribution from the Re-s, Re-p and B-s states as shown in Fig.4(b). The strong hybridisation between B-p and Re-d indicates strong covalent bonding of Re–B, which contributes to high bulk modulus.[23] On the other hand, the strong hybridisation between B-p and Re-d is consistent with the idea of a charge accumulation

of electron charge between the Re–B atoms noted in Fig.2. In addition, we also see a deep and wide valley near the Fermi level, which is named pseudogap. It is caused by the strong hybridisation of Re d orbital and B p orbital, as observed in OsB_2[24,25] and OsN_2.[26] In ReB_2, the width of valley is about 6 eV, indicating a strong covalent bonding of Re–B again.

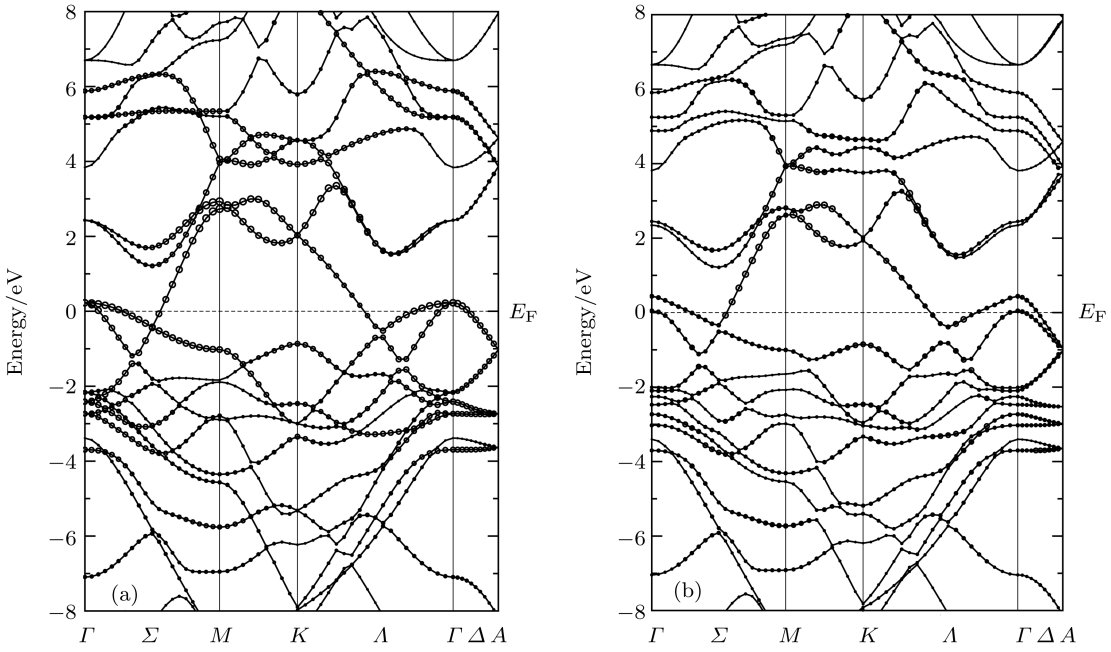


Fig.3. Band structure of ReB_2 obtained from (a) LDA and (b) LDA+SO. The Re d-states are characterized.

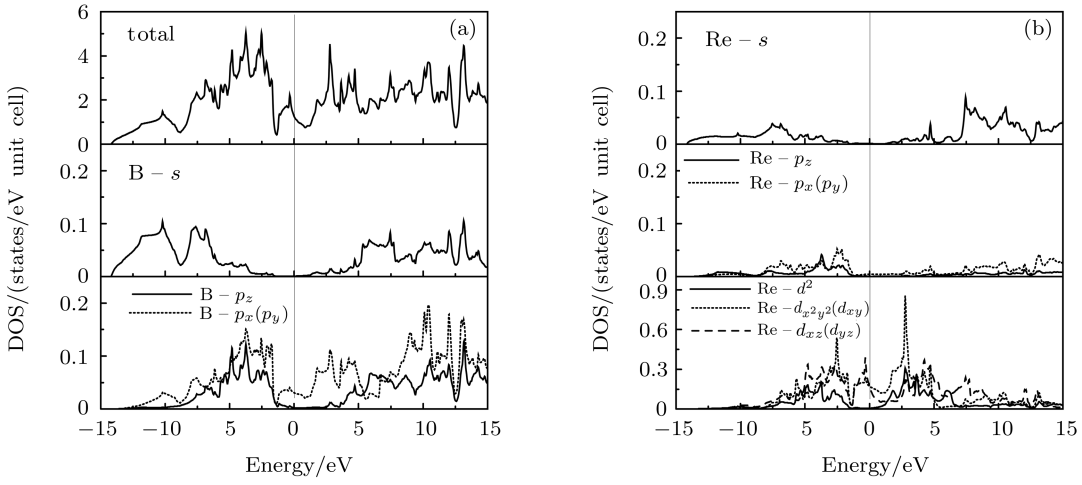


Fig.4. Total and partial density of states of ReB_2 obtained from LDA+SO calculations. Vertical dotted lines indicate the Fermi level.

4. Conclusion

We have performed the first-principles calculations on ReB_2 to understand its structural and electronic properties by using the highly accurate full-potential LAPW+LO method. The calculated equilibrium structural parameters and bulk modulus are in good agreement with experimental values. Spin–orbit coupling improves the relaxed geometry parameters and bulk modulus value obtained from LDA, making it more closer to the

experimental values. The ReB_2 shows metallicity and *ab*-plane anisotropy in compressibility. Furthermore, ReB_2 is confirmed to be an ultra-incompressible material in comparing its compressibility with that of OsB_2, that is, ReB_2 is even more difficult to be compressed than the ultra-incompressible OsB_2. The high bulk modulus is attributed to the strong covalent bonding between Re-*d* and B-*p* orbitals as well as the wider pseudogap near the Fermi level, which could be deduced from both electron charge density distribution and DOS. The good metallicity and ultra-incompressibility of ReB_2 suggest its potential application as pressure-proof conductors.

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