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Elastic anisotropy of OsB_2 and RuB_2 from first-principles study

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Abstract

The elastic anisotropy of the potential low compressible and hard materials OsB_2 and RuB_2 were studied by first-principles investigation within density functional theory. The structure, elastic constants, bulk modulus, shear modulus, Poisson's ratio and Debye temperature have been calculated within both local density approximation (LDA) and generalized gradient approximation (GGA). The results indicated that the calculated bulk modulus and shear modulus were in good agreement with the experimental and previous theoretical studies. The calculated elastic constants anisotropic factors and directional bulk modulus showed that OsB_2 and RuB_2 possess high elastic anisotropic.

Keywords: OsB_2 and RuB_2; Density functional theory; Elastic constants; Anisotropy

1. Introduction

Ultra-incompressible, superhard materials are of utmost importance due to their outstanding properties such as high elastic modulus and hardness, scratch resistance, surface durability as well as chemical stability. Therefore, intensive experimental and theoretical efforts have been focused on the synthesizing and designing new materials with compressibility and hardness comparable to diamond, which is known as the hardest and the least compressible material so far [1–5]. Recently, Cumberland et al. demonstrated that hardness may be enhanced by combining a small covalent bond-forming atom such as boron, carbon, nitrogen and/or oxygen into a soft transition metal with high valence electron density [3–5]. Applying this idea, the authors predicted that transition metal diborides such as OsB_2 and RuB_2 might be incompressible and hard materials. Both OsB_2 and RuB_2 form in an orthorhombic lattice (space group *Pmmn*, No. 59) with two formula units per unit cell, in which two transition metal atoms occupy the 2a Wychoff site and four B atoms hold the 4f positions [6,7] (Fig. 1). As an example, Cumberland et al. reported the synthesis, bulk modulus, and preliminary hardness testing of osmium diboride. The results indicated that OsB_2 was low compressible and hard compound with the bulk modulus in the range of 365–395 GPa and the compressibility along the *c*-direction even less than that of diamond [5]. In contrast to OsB_2, experimental data on the mechanical properties such as elastic constants or bulk modulus is not available for RuB_2. On the other hand, the theoretical calculations based on the density functional theory were employed to provide crucial information for understanding the physical properties, and suggested that the high bulk modulus and hardness are attributed to the covalent bonding between transition metal d states and boron p states [8–11].

It is known that superhard materials should preferably be isotropic, otherwise it would deform preferentially in a given direction [12]. That is to say, microcracks may be induced in materials owning to elastic anisotropy. Hence it is important to study elastic anisotropy for predicting new hard materials and finding mechanisms to improve their hardness. To our acknowledgement there is no any study on elastic anisotropy on the two compounds. Therefore, in this study, we focus our study on the calculation of elastic anisotropy from first-principles on both OsB_2 and RuB_2. In addition, we also reported the Debye temperature and Poisson's ratio. We hope our study could provide useful hint in designing superhard materials.

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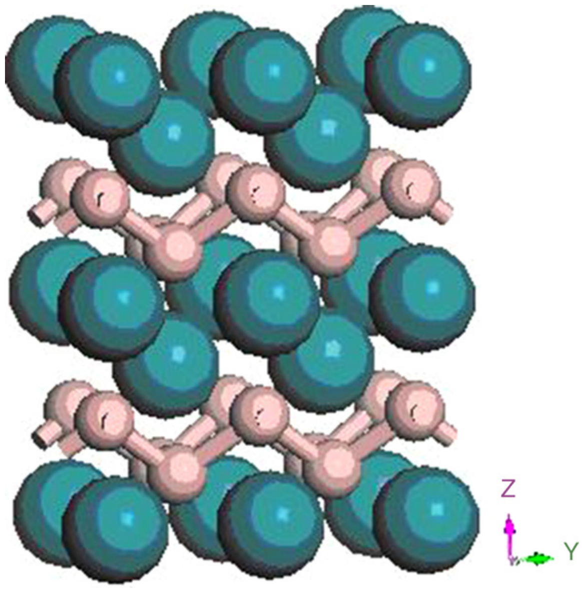

Fig. 1. Crystal structure of orthorhombic osmium (or ruthenium) diboride. The transition metal atoms are shown as big spheres and boron atoms as small spheres.

2. Computational method

The accurate calculation of elasticity is essential for understanding the macroscopic mechanical properties of solids because they are related to various fundamental solid-state properties and thermodynamic properties. In this paper, first-principles calculations are performed within CASTEP code [13] based on the density functional theory (DFT). The exchange and correlation functional was treated by both the local density approximation (LDA-CAPZ) [14] and the generalized gradient approximation (GGA-PBE) [15]. For both compounds, the Vanderbilt ultrasoft pseudo-potential (PP) was used with the cutoff energy of 400 eV and $5 \times 9 \times 6$ are generated using the Monkhorst-Pack scheme [16]. The Brodyden–Fletcher–Goldfarb–Shanno (BFGS) minimization scheme [17] was used in geometry optimization. The tolerances for geometry optimization were set as the difference in total energy being within 5×10^{-6} eV/atom, the maximum ionic Hellmann–Feynman force within 0.01 eV/Å, the maximum ionic displacement within 5×10^{-4} Å and the maximum stress within 0.02 GPa.

The elastic coefficients of single crystal are determined from a first-principles calculation by applying a set of given homogeneous deformation with a finite value and calculating the resulting stress with respect to optimizing the internal atomic freedoms, as implemented by Milman and Warren [18]. Three strain patterns brought out stresses related to all the nine independent elastic coefficients for the orthorhombic unit cell.

3. Results and discussion

The calculated lattice parameters, elastic constants and Debye temperature for OsB_2 and RuB_2, within both LDA and GGA are shown in Table 1, along with the available experimental and theoretical data for comparison. It is seen that the calculated lattice parameters a, b and c deviate from the corresponding experimental values within 2%, and within 3% for the calculated density, in excellent agreement with both experimental [6,7] and previous theoretical studies [8–11]. This demonstrated the reliability of the method. Meanwhile, it is also noted that the calculated lattice constants are larger at GGA than those at LDA, as is the usual case.

From Table 1, our calculated elastic constants for OsB_2 are in good agreement with the previous calculated values [8,10,11], but very different with the results reported by Ref. [9], especially the C_{44}. We believe that the root of the problem is the approximation which carried out in Ref. [9], where computed the elastic constants with atomic internal coordinates fixed. For RuB_2, on the other hand, since there are no either experimental or theoretical studies available on elastic constants, we hope our study could provide a useful guidance for future study. It can also be seen that LDA gives larger elastic constants than GGA from Table 1. This might be due to the smaller lattice parameters predicted in LDA than in GGA. The calculated results of OsB_2 showed that the elastic constants possess the trend $C_{11} \approx C_{22} < C_{33}$, indicating the anisotropy of the elasticity. The implication of this trend is that the bonding between nearest neighbors along the $\{0\,0\,1\}$ planes are stronger than that along the $\{1\,0\,0\}$ and $\{0\,1\,0\}$ planes, which agree with the experimental observation that the different compressibility was observed along different directions, and the compressibility along the c axis is the smallest [5]. For RuB_2, similar trend can be observed as OsB_2 which can be seen from Table 1. Therefore, we could conclude from the elastic constants that both OsB_2 and RuB_2 are elastic anisotropic. This will be confirmed by the following calculation.Since the size of single crystals of OsB_2 and RuB_2 are not large enough, the measurement of the elastic stiffness constants from experiment is impossible. However, according to the Voight–Reuss–Hill approximations [19], we could calculate the bulk modulus, and shear modulus for the polycrystalline aggregate, which may be determined on the polycrystalline samples. In addition, the Young's modulus E_H and the Poisson's ratio υ_H are obtained by use of the following equations:

$$E_H = \frac{9B_H G_H}{3B_H + G_H}, \qquad \upsilon_H = \frac{3B_H - 2G_H}{6B_H + 2G_H},$$

where the subscript H represents the Hill approximation. The calculated bulk modulus, shear modulus, Young's modulus and Poisson's ratio for OsB_2 and RuB_2 are listed in Table 2. The calculated bulk modulus of OsB_2 is 339 GPa and 317 GPa within LDA and GGA levels, respectively. These values are somewhat smaller than the experimental values 365–395 GPa [5], and previous theoretical values 364 GPa [9], 364.87 GPa [11], but close to theoretical value 332 GPa at LDA [8] and 307 GPa at GGA [8]. The calculated bulk modulus of RuB_2 is 319 GPa and 293 GPa within LDA and GGA, which is also smaller than previous theoretical value 334.77 GPa [11], in particular at GGA level. The values of calculated shear modulus for OsB_2 and RuB_2 shown in Table 2 suggested the more pronounced directional bonding between the transition metal and boron atoms due to the addi-

Table 1
Calculated lattice parameters a, b, c (Å), equilibrium volume V (Å^3), elastic constants C_{ij} (GPa) and Debye temperature T_D (K) of OsB_2 and RuB_2

	V	a	b	c	C_{11}	C_{22}	C_{33}	C_{44}	C_{55}	C_{66}	C_{12}	C_{13}	C_{23}	ρ	T_D
OsB_2															
LDA	53.06	4.629	2.837	4.039	596	597	843	79	228	219	188	202	130	13.26	601
GGA	54.08	4.652	2.859	4.066	570	568	786	78	220	212	174	189	118	13.01	591
Experimental[a]	54.83	4.684	2.872	4.076										12.83	
Theoretical		4.636[b]	2.842	4.044	585	588	827	61	225	217	180	195	124	13.19	
		4.664[c]	2.867	4.074	546	553	763	64	209	207	166	184	113	12.90	
		4.6433[d]	2.8467	4.4032	628.9	627.8	923.2	185.5	313.5	218.6	194.7	235.0	126.8		
		4.6581[e]	2.8700	4.0560	608.5	590.3	855.7	175.1	292.6	205.9	198.3	220.9	129.9		
					597.2[f]	584.5	833.8	80.2	214.5	209.2	188.7	217.5	164.0		
	53.57[g]	4.6444	2.8505	4.0464	597.0	581.2	825.0	70.1	212.0	201.3	198.1	206.1	142.6		
	55.78[h]	4.7049	2.8946	4.0955											
	53.646[i]	4.648	2.846	4.047											
RuB_2															
LDA	51.80	4.596	2.821	3.996	577	513	784	104	236	191	195	172	133	7.86	786
GGA	53.08	4.624	2.847	4.031	540	484	719	116	225	183	174	154	120	7.68	780
Experimental[a]	53.85	4.644	2.867	4.045											
Theoretical	52.563[i]	4.610	2.837	4.009											

Comparison has been made with both experiments and previous theoretical studies.
[a] Refs. [6,7].
[b] Ref. [8], theoretical study by LDA and PP (pseudo-potential) method.
[c] Ref. [8], theoretical study by GGA and PP method.
[d] Ref. [9], theoretical study by LDA and APW (augmented plane wave) + lo (local orbitals) method. The atomic internal coordinates are unrelaxed (fixed).
[e] Ref. [9], theoretical study by LDA + SO (spin–orbit coupling) and APW + lo method. The atomic internal coordinates are unrelaxed (fixed).
[f] Ref. [9], theoretical study by LDA and PP method. The atomic internal coordinates are relaxed.
[g] Ref. [10], theoretical study by LDA and PAW (projector augmented wave) method.
[h] Ref. [10], theoretical study by GGA and PAW method.
[i] Ref. [11], theoretical study by LDA and PP method.

tional covalent bond-forming atoms. The directional nature of the bond yields a low Poisson's ratio and will create the barrier to the nucleation and motion of dislocations and thus increases the shear strength and the hardness [12].

The Debye temperature is a fundamental parameter of a material which is linked to many physical properties, such as specific heat, elastic constants and melting point [19]. It can be obtained from the average sound velocity by use of the

Table 2
Shear modulus G_H, bulk modulus B_H, Young modulus E_H (in GPa), and Poisson's ratio υ_H of OsB_2 and RuB_2

	G_R	G_V	G_H	B_R	B_V	B_H	E_H	υ_H
OsB_2								
LDA	167	206	187	335	342	339	474	0.267
GGA	162	190	180	315	320	317	454	0.261
Experimental						365–395[a]		
Theoretical			174[b]			332[b]	444	0.277
			168[c]			307[c]	426	0.269
						365[d]		
						364[e]		
						336.1[f]		
						303.45[g]		
						364.87[h]		
RuB_2								
LDA	176	198	187	313	319	316	468	0.253
GGA	177	191	184	288	293	290	455	0.238
Theoretical						334.77[h]		

Comparison has been made with both experiments and previous theoretical studies.
[a] Ref. [5].
[b] Ref. [8], theoretical study by LDA and PP method.
[c] Ref. [8], theoretical study by GGA and PP method.
[d] Ref. [9], theoretical study by LSDA and APW + lo method.
[e] Ref. [9], theoretical study by LSDA + SO and APW + lo method.
[f] Ref. [10], theoretical study by LDA and PAW method.
[g] Ref. [10], theoretical study by GGA and PAW method.
[h] Ref. [11], theoretical study by LDA and PP method.

following equation:

$$T_\mathrm{D} = \frac{h}{k}\left[\frac{3n}{4\pi}\left(\frac{N_\mathrm{A}\rho}{M}\right)\right]^{1/3} \upsilon_\mathrm{m}$$

Here h is the Plank's constant; k the Boltzmann's constant; N_A the Avogadro's number; ρ the density; M the molecular weight; n is the number of atoms in the molecule. The average wave velocity υ_m is approximately estimated by the equation:

$$\upsilon_\mathrm{m} = \left[\frac{1}{3}\left(\frac{2}{\upsilon_\mathrm{t}^3} + \frac{1}{\upsilon_\mathrm{l}^3}\right)\right]^{-1/3}$$

where υ_l and υ_t are longitudinal and transverse elastic wave velocity of the polycrystalline materials, respectively and can be obtained by use of polycrystalline shear modulus and bulk modulus from Navier's equation [20]. Our results indicated that T_D is higher for RuB_2 than for OsB_2 owing to the small density of the former. For both compounds, GGA values are slightly smaller than those obtained from the LDA.

Elasticity describes the response of a crystal under external strain and provides key information about the bonding characteristic between adjacent atomic planes and the anisotropic character of the solid [19]. The shear anisotropic factors provide a measure of the degree of anisotropy in the bonding between atoms in different planes. The shear anisotropic factor is defined as

$$A_1 = \frac{4C_{44}}{C_{11} + C_{33} - 2C_{13}}$$

for the $\{1\,0\,0\}$ shear planes between $\langle 0\,1\,1\rangle$ and $\langle 0\,1\,0\rangle$ directions, for the $\{0\,1\,0\}$ shear planes between $\langle 1\,0\,1\rangle$ and $\langle 0\,0\,1\rangle$ directions it is

$$A_2 = \frac{4C_{55}}{C_{22} + C_{33} - 2C_{23}}$$

and similarly, for the $\{0\,0\,1\}$ shear planes between $\langle 1\,1\,0\rangle$ and $\langle 0\,1\,0\rangle$ directions it is

$$A_3 = \frac{4C_{66}}{C_{11} + C_{22} - 2C_{12}}$$

For an isotropic crystal the factors must be one, while the deviation from one is a measure of the degree of the elastic anisotropy. Furthermore, since the two compounds are orthorhombic, not cubic, the shear anisotropic factors are not sufficient to describe the elastic anisotropy. Therefore, the anisotropy of the linear bulk modulus should also be considered. The anisotropy of the bulk modulus along the a axis and c axis with respect to b axis can be estimated by use of the following equations:

$$A_{B_a} = \frac{B_a}{B_b}, \qquad A_{B_c} = \frac{B_c}{B_b}$$

Note that a value of one indicates elastic isotropy and any departure from one represents elastic anisotropy. Where B_a, B_b and B_c are the bulk moduli along different crystal axes, defined as

$$B_i = i\frac{\mathrm{d}P}{\mathrm{d}i}, \quad i = a, b \text{ and } c.$$

Table 3
Anisotropic factors A_1, A_2, A_3, A_{B_b}, A_{B_c}, A_G (%) and A_B (%), and directional bulk modulus B_a, B_b, B_c (in GPa) of OsB_2 and RuB_2

	OsB_2		RuB_2	
	LDA	GGA	LDA	GGA
A_1	0.3053	0.3190	0.4090	0.4879
A_2	0.7729	0.7871	0.9156	0.9346
A_3	1.0722	1.0734	1.0914	1.0828
A_{B_b}	1.123	1.139	1.298	1.269
A_{B_c}	1.568	1.529	1.637	1.577
A_G	10.45	7.95	5.88	3.80
A_B	1.03	0.78	0.95	0.86
B_a	951.9	909.1	966.7	884.7
B_b	847.2	797.9	744.4	697.2
B_c	1328.9	1220.1	1218.5	1099.7

In addition, the percentage elastic anisotropy for bulk modulus A_B and shear modulus A_G in polycrystalline materials can also be used as follows:

$$A_B = \frac{B_\mathrm{V} - B_\mathrm{R}}{B_\mathrm{V} + B_\mathrm{R}}, \qquad A_G = \frac{G_\mathrm{V} - G_\mathrm{R}}{G_\mathrm{V} + G_\mathrm{R}}$$

where B and G denote the bulk and shear modulus, and the subscripts V and R represent the Voigt and Reuss approximations. The implication of the definition is that a value of zero corresponds to elastic isotropy and a value of 100% identifies the largest elastic anisotropy.

The calculated results were listed in Table 3, along with the directional bulk moduli. It is seen that OsB_2 and RuB_2 are elastic anisotropic. The shear and bulk modulus anisotropy is higher at LDA level than those at GGA level. Moreover, it is interesting to note that these two compounds have the highest directional bulk modulus along the c axis and the lowest one along the b axis, indicating that the compressibility along the c axis is the smallest, while along the b axis is the largest. This agrees well with the experimental observation for OsB_2 [5]. The variations in elastic constants and the directional bulk moduli can also be understood in terms of the crystal structure. In the a and b axis, the boron and the transition metal atoms are offset from each other, therefore, the electrostatic repulsion did not push each other directly, and then could not maximize incompressibility. In contrast, along the c axis, the boron and the transition metal atoms are almost directly aligned, leading to highly directional repulsive electronic interactions, and then the least compressibility [5]. In addition, we also noticed that the percentage bulk modulus anisotropy is smaller than the percentage shear modulus anisotropy for both two compounds, suggesting that they are slightly anisotropic in compressibility [8].

4. Conclusions

Based on the first-principles calculations, we investigated the structural and elastic properties of the potential low compressible and hard materials OsB_2 and RuB_2. Our calculated bulk modulus and shear modulus are in agreement with the experimental and other theoretical values. The calculated elastic anisotropic factors and directional bulk moduli indicated that OsB_2 and RuB_2 have high elastic anisotropic. Moreover, the anisotropy can be understood from atomic arrangements along the different axis in the orthorhombic structure. In addition, we predicted that RuB_2 is less anisotropic in compressibility than in shear, similar to OsB_2.

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