Theoretical calculations of hardness and metallicity for multibond hexagonal 5d transition metal diborides with ReB_2 structure

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(Received 25 April 2017; revised manuscript received 26 June 2017; published online 10 September 2017)

The hardness, electronic, and elastic properties of 5d transition metal diborides with ReB_2 structure are studied theoretically by using the first principles calculations. The calculated results are in good agreement with the previous experimental and theoretical results. Empirical formulas for estimating the hardness and partial number of effective free electrons for each bond in multibond compounds with metallicity are presented. Based on the formulas, IrB_2 has the largest hardness of 21.8 GPa, followed by OsB_2 (21.0 GPa) and ReB_2 (19.7 GPa), indicating that they are good candidates as hard materials.

Keywords: hardness, metallicity, multibond, effective free electrons

PACS: 62.20.Qp, 71.15.Mb, 71.20.Be, 81.05.Zx **DOI:** 10.1088/1674-1056/26/10/106202

1. Introduction

Owing to the high melting points, hardness, and conductivity,[1–9] transition metal (TM) borides are good candidates for hard materials. Recent synthesis of hexagonal ReB_2 in bulk quantities via arc-melting under ambient pressure[1] has ignited great interest in this class of ultraincompressible transition metal diboride. The phase transition of new synthesized OsB_2 from orthorhombic structure to hexagonal structure at 10.8 GPa, obtained by first principles, indicates that hexagonal OsB_2 is more stable.[2–4] However, the 5d transition metal diborides with hexagonal ReB_2 structure have not yet been investigated experimentally except ReB_2.

In this work, we systematically calculate the hardness, elastic, and electronic properties of 5d transition metal diborides with hexagonal ReB_2 structure by using first principles based on density functional theory (DFT). The hardness is calculated by the semiempirical hardness model[10] and the position of pseudogap is determined by density of states (DOS).[11] The 5d transition metal diborides with hexagonal ReB_2 structure possess two types of bonds, i.e., TM–B and B–B, the difficulty in calculating hardness comes from the partial number of effective free electrons for each bond On the basis of the correlation between TM–B and B–B bonds, we propose a theoretical approach to calculating hardness with metallic multibond compounds for the first time to our knowledge. We hope our studies will be helpful in theoretically calculating the hardness of metallic multibond compounds for searching new hard or superhard materials.

2. Method of calculations

All calculations are performed by using CASTEP (Cambridge Serial Total Energy Package) code.[12] We employ Vanderbilt ultrasoft pseudopotential[13] to describe the electron–ion interactions, and the generalized gradient approximation (GGA) of Perdew–Burke–Ernzerhof (PBE)[14] as the exchange and correlation functional. The set of Monkhorst–Pack mesh of $12\times12\times6$ is used for all the diboride. The 500 eV is selected as the cutoff energy for each plane wave basis. The total energy and k points are 5.0×10^{-6} eV/atom and $12\times12\times6$, respectively. Each of the 5d transition metal diborides possesses the ReB_2 structure as shown in Fig. 1. The space group is $P6_3/mmc$ (No. 194). Atomic positions and lattice parameters are optimized simultaneously.

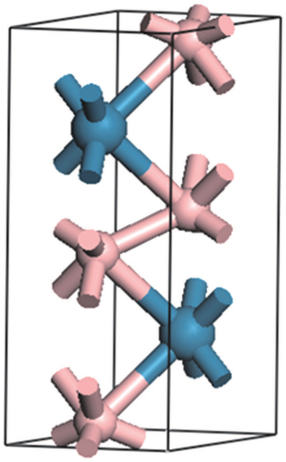


Fig. 1. (color online) Crystal structure for 5d transition metal diborides with ReB_2 structure 5d transition metal and boron atoms are shown as larger and smaller spheres, respectively.

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In the ReB_2 structure, each TM atom is coordinated by six boron atoms while each boron atom by three TM atoms and three boron atoms. TM atoms occupy the $2c$ Wckoff site (1/3, 2/3, 1/4), and the boron atoms reside at $4f$ site (1/3, 2/3, u), $u = 0.548$.

3. Results and discussion

3.1. Lattice parameters and elastic properties of 5d transition metal diborides

The calculated equilibrium lattice parameters a_0, c_0, and elastic constants C_{ij} of 5d transition metal diborides with hexagonal ReB_2 structure are shown in Table 1. The values of bulk modulus B, shear modulus G, Young's modulus E, and Poisson's ratio v are calculated in terms of the five independent elastic constants of C_{11}, C_{12}, C_{13}, C_{33}, and C_{44}, which are also shown in Table 1. The mechanical stability criteria are $C_{44} > 0$, $C_{11} > |C_{12}|$, $(C_{11}+2C_{12})C_{33} > 2C_{13}^2$.

For hexagonal phase,[15] the Voigt bulk modulus B_V and Reuss bulk modulus B_R are calculated from the following formulas in terms of the elastic constants:

$$B_V = [2(C_{11}+C_{12})+4C_{13}+C_{33}]/9, \quad (1)$$

$$B_R = C^2/M. \quad (2)$$

The Voigt shear modulus G_V and the Reuss shear modulus G_R are

$$G_V = (M+12C_{44}+12C_{66})/30, \quad (3)$$

$$G_R = 5C^2C_{44}C_{66}/2[3B_VC_{44}C_{66}+C^2(C_{44}+C_{66})], \quad (4)$$

where

$$M = C_{11}+C_{12}+2C_{33}-4C_{13}, \quad (5)$$

$$C^2 = (C_{11}+C_{12})C_{33}-2C_{13}^2, \quad (6)$$

$$C_{66} = (C_{11}-C_{12})/2. \quad (7)$$

The mechanical stability criteria are given by $C_{44} > 0$, $C_{11} > |C_{12}|$, $(C_{11}+2C_{12})C_{33} > 2C_{13}^2$.

Hill[16] proved that the Voigt and Reuss equations represent upper and lower limits of the true polycrystalline constants, respectively. Hence, the bulk modulus and shear modulus of hexagonal crystal can be approximated by

$$B = (B_V+B_R)/2, \quad (8)$$

$$G = (G_R+G_V)/2. \quad (9)$$

Young's modulus E and Poisson's ratio v are obtained by the following formulas:

$$E = 9BG/(3B+G), \quad (10)$$

$$v = (3B-2G)/2(3B+G). \quad (11)$$

It can be seen from Table 1 that the calculated equilibrium lattice parameters and elastic properties for TaB_2, ReB_2, OsB_2, and IrB_2 compare favorably with the previous theoretical values.[4,9,17–20] For the only experimentally synthesized 5d transition metal diborides, ReB_2, the calculated theoretical lattice parameters, $a_0 = 2.908$ Å, $c_0 = 7.490$ Å, and bulk modulus, $B = 341$ GPa, are in good agreement with the available experimental values,[1] $a_0 = 2.900$ Å, $c_0 = 7.478$ Å, $B = 360$ GPa. The calculated elastic constants as shown in Table 1 indicate that all 5d transition metal diborides are mechanically stable except HfB_2 and TaB_2. Among the mechanically stable diborides, ReB_2 has the largest bulk modulus (341 GPa), shear modulus (271 GPa), Young modulus (643 GPa), followed by WB_2, which has the smallest Poisson's ratio (0.164).

Table 1. Calculated values of equilibrium lattice parameters a_0 (Å), c_0 (Å), elastic constants C_{ij} (GPa), bulk modulus B (GPa), shear modulus G (GPa), Young's modulus E (GPa), and Poisson's ratio v for 5d transition metal diborides with ReB_2 structure.

		a_0	c_0	C_{11}	C_{12}	C_{13}	C_{33}	C_{44}	B	G	E	v
HfB_2		3.084	8.535	194	246	87	469	69	187	–	–	–
TaB_2		3.021	8.153	143	408	118	600	125	239	–	–	–
	Theor.	2.993[a]	8.081[a]	–	–	–	–	–	245[a]	–	–	–
WB_2		2.927	7.743	601	156	95	938	276	311	269	626	0.164
ReB_2		2.908	7.490	633	173	118	1034	263	341	271	643	0.186
	Expt.	2.900[b]	7.478[b]	–	–	–	–	–	360[b]	–	–	–
	Theor.	2.872[c]	7.405[c]	716[c]	151[c]	133[c]	1108[c]	290[c]	359[c]	310[c]	725[c]	0.17[c]
		2.880[d]	7.420[d]	675[d]	147[d]	115[d]	1081[d]	278[d]	347.7[d]	295.4[d]	690.6[d]	0.17[d]
		2.8809[e]	7.4096[e]	667.9[e]	136.7[e]	147.4[e]	1062.7[e]	273.2[e]	354.5[e]	289.4[e]	682.5[e]	0.1791[e]
				643[f]	159[f]	129[f]	1035[f]	263[f]	344[f]	304[f]	642[f]	0.21[f]
OsB_2		2.930	7.330	465	171	227	869	211	323	187	469	0.258
	Theor.	2.941[g]	7.338[g]	461[g]	177[g]	236[g]	873[g]	209[g]	326[g]	207[g]	513[g]	0.24[g]
IrB_2		3.092	6.999	364	202	236	748	126	296	113	302	0.330
	Theor.	3.072[a]	7.074[a]	315[a]	197[a]	254[a]	695[a]	126[a]	280[a]	109[a]	289[a]	0.33[a]
PtB_2		3.103	7.258	354	150	191	560	24	251	62	172	0.386

[a]Ref. [9]; [b]Ref. [1]; [c]Ref. [17]; [d]Ref. [18]; [e]Ref. [19]; [f]Ref. [20]; [g]Ref. [4].

3.2. Electronic structure analysis of 5d transition metal diborides

The calculated total and partial densities of states (TDOSs and PDOSs) of 5d transition metal diborides at zero pressure are shown in Fig. 2, where the vertical line is the Fermi level (E_F). A strong hybridization between TM-5d and B-2p orbitals results in covalent bonding. The metallic behaviors for 5d transition metal diborides are indicated by the finite TDOSs at the Fermi level, namely $N(E_F)$. It is found that the electrons from both TM-5d and B-2p orbitals contribute to the DOSs at the Fermi level. The DOSs at the Fermi level for HfB_2 and TaB_2 are 4.631 electrons/eV and 4.988 electrons/eV, respectively, which are much larger than those for other 5d transition metal diborides.

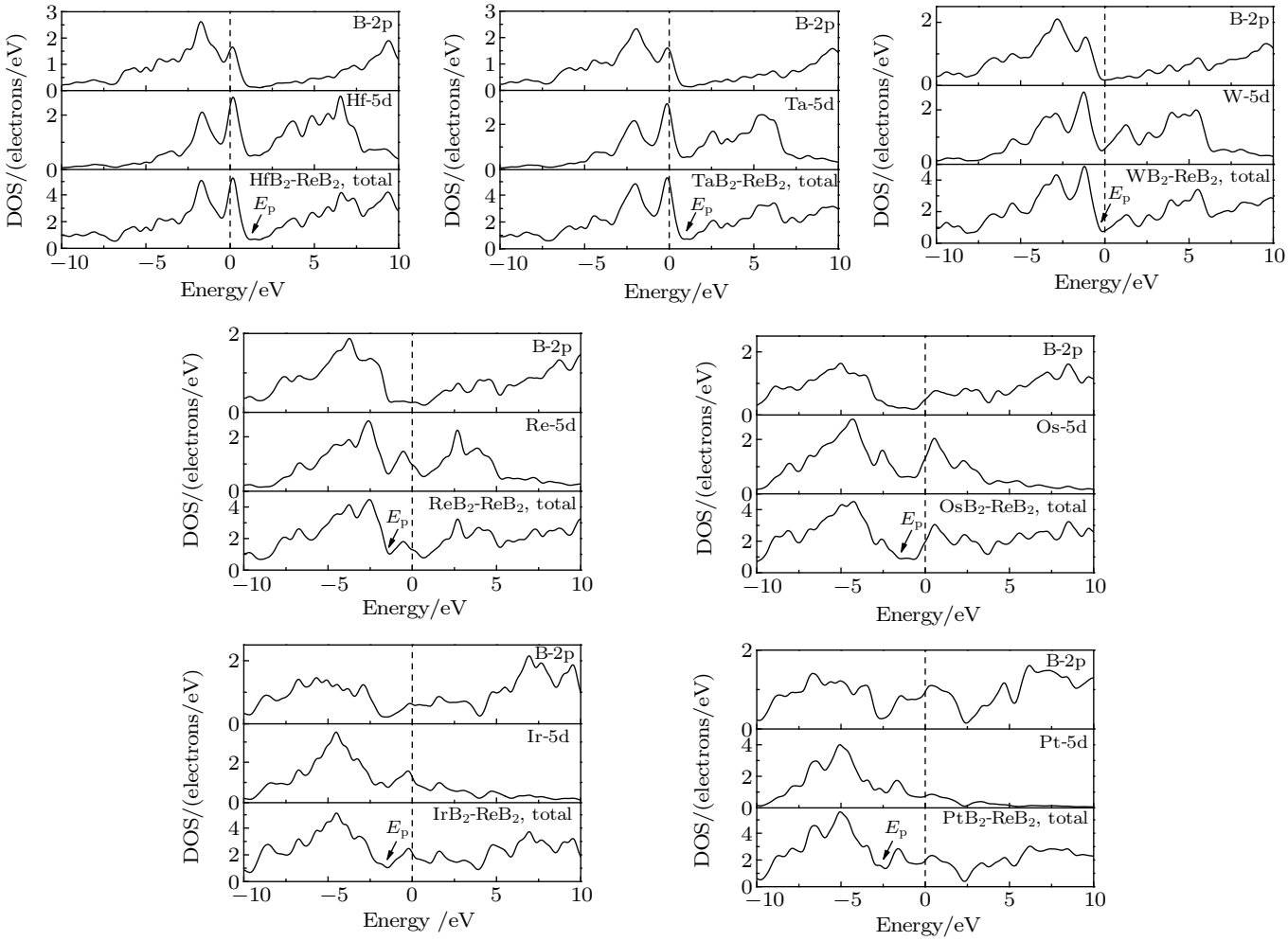


Fig. 2. Total and partial densities of states for 5d transition metal diborides with ReB_2 structure. Vertical dotted line at zero indicates Fermi energy level. The position of E_p is indicated by an arrow.

The position of pseudogap (E_p) is determined by the PDOS of B-2p.[11] The structural stability is related to the position of E_F and the pseudogap.[21–25] For HfB_2 and TaB_2, the Fermi level falls below the pseudogap, indicating that not all the bonding states are filled. As the atomic number increases, all the bonding states are just filled for WB_2. For ReB_2, OsB_2, IrB_2, and PtB_2, the Fermi level falls above the pseudogap, which suggests that all the bonding states and partial antibonding states are filled. On the basis of the band filling theory,[22,23] the cohesion (or stability) will be enhanced or reduced by filling bonding or antibonding/nonbonding states. Thus, HfB_2 and TaB_2 require some extra electrons to reach maximum stability, while ReB_2, OsB_2, IrB_2, and PtB_2 can improve the stability by extracting electrons. The nearly saturated bonding states and just unoccupied antibonding/nonbonding states[26] for WB_2 result in larger bulk modulus, shear modulus and the smallest Poisson's ratio.

The charge density distributions in $(11\bar{2}0)$ plane for WB_2 is shown in Fig. 3 in order to have an insight into the bonding behavior for 5d transition metal diborides. The electron density around W atoms is much larger than that near B atoms, indicating that W has a higher valence electron density. The charge density between W and B atoms indicates a strong covalent effect, resulting in favorable elastic properties. In addition, the covalent bonding between B and B atoms is much stronger than that of W–B, which will enhance the hardness for WB_2.

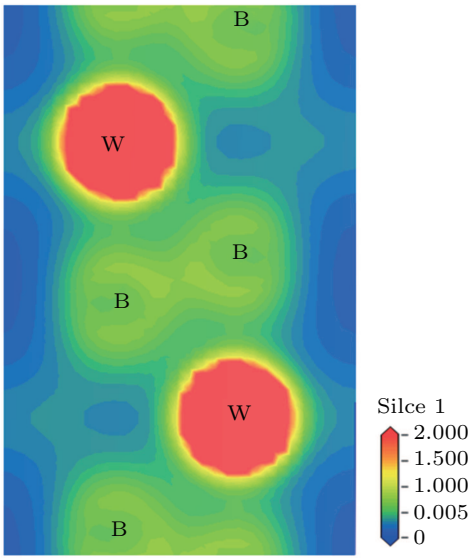


Fig. 3. (color online) Charge density distribution in $(11\bar{2}0)$ plane for WB_2 with ReB_2 structure.

3.3. Hardness calculations of 5d transition metal diborides

In general, the hardness values of μ-type bond for complex multibond compounds are calculated according to the following formulas proposed by Gao:[27]

$$H^{\mu}_{\text{vcalc.}}\,(\text{GPa}) = 740 P^{\mu} (v^{\mu}_{\text{b}})^{-5/3}, \tag{12}$$

$$v^{\mu}_{\text{b}} = (d^{\mu})^3 / \sum_{\nu} [(d^{\nu})^3 N^{\nu}_{\text{b}}], \tag{13}$$

where $H^{\mu}_{\text{vcalc.}}$ is the calculated Vickers hardness of μ-type bond, P^{μ} is the Mulliken overlap population of μ-type bond, v^{μ}_{b} is the bond volume of μ-type bond, d^{μ} is the bond length of the μ-type bond, and N^{ν}_{b} is the bond number of ν-type bond per unit volume.

Since the electrons occupying the levels above E_{p} become delocalized and not directly related to hardness, a correction to formula (12) should be considered for crystals with partial metallic bonding as shown below

$$H^{\mu}_{\text{vcalc.}}\,(\text{GPa}) = 740 \left(P^{\mu} - P'^{\mu}\right) (v^{\mu}_{\text{b}})^{-5/3}, \tag{14}$$

where P'^{μ} is the metallic population of μ-type bond.

The formulas proposed by Gou *et al.*[10] only give a method of calculating the metallic population for single bond compounds with metallic bonding by using the total number of effective free electrons defined as

$$n_{\text{free}} = \int_{E_{\text{p}}}^{E_{\text{F}}} N(E)\,\text{d}E, \tag{15}$$

$$P' = n_{\text{free}}/V, \tag{16}$$

where n_{free} is the total number of effective free electrons per unit volume, E_{F} is the Fermi level, E_{p} is the pseudogap, $N(E)$ is the density of state, P' is the metallic Mulliken population, and V is the volume of cell.

But for multibond compounds with metallicity, it is difficult to determine the partial number of effective free electrons for each bond. Segall *et al.*[28] found the correlations of overlap population with bond strength, so for multibond compounds with metallicity, the partial number of effective free electrons for each bond can be calculated by the total and partial Mulliken overlap population. The calculation formulas are as follows:

$$n^{\mu}_{\text{free}} = N^{\mu}_{\text{b}} P^{\mu} n_{\text{free}} / \sum_{\nu} (P^{\nu} N^{\nu}_{\text{b}}), \tag{17}$$

$$P'^{\mu} = n^{\mu}_{\text{free}}/V, \tag{18}$$

$$f^{\mu}_{\text{m}} = P'^{\mu}/P^{\mu}, \tag{19}$$

where n^{μ}_{free} is the partial number of effective free electrons of μ-type bond, N^{μ}_{b} is the number of μ-type bonds per unit volume, N^{ν}_{b} is the bond number of ν-type bonds per unit volume, P^{ν} is the Mulliken overlap population of ν-type bond, and f^{μ}_{m} is the metallicity of μ-type bond.

For multibond compounds, the weakest bond will play a determinative role in the hardness of multibond material.[27] In other words, if there are differences in strength among different bonds, the bonds will start to break from a softer bond. The hardness of 5d transition metal diborides are shown in Table 2. The hardness calculated from B–B bond is much larger than that from TM–B bond, so the smaller hardness, that is the hardness of TM–B bond, will be taken as the hardness of 5d transition metal diborides.

As shown in Table 2, Ir–B bond possesses the largest Mulliken overlap population, indicating the strongest covalency. So IrB_2 has the largest hardness (21.8 GPa), which is slightly smaller than the corresponding theoretical value (26.65 GPa) calculated by Zhao and Wang,[9] which maybe because the metallicity is considered in our calculations. Among all 5d transition metal diborides, only experimental hardness values from 16.9 GPa to 48.0 GPa are obtained for ReB_2. The microhardness of ReB_2 measured by Chung *et al.*[1] are 30.1 ± 1.3 GPa and 48.0 ± 5.6 GPa under applied loads of 4.9 N and 0.49 N, respectively, while lower hardness values of 20.7 GPa and 31.1 GPa are obtained by Locci *et al.*[29] under the same loads. This may be due to the different synthesized methods while Chung *et al.*[1] took advantage of a casting technique and Locci *et al.*[29] obtained bulk ReB_2 through sintering. It is currently in dispute over the hardness of ReB_2. The measured hardness usually increases with load decreasing. The noticed inverse relationship of load to hardness results from the well-known indentation size effect (ISE).[29] The ISE makes the hardness results larger under smaller loads, and this scenario is just the opposite under larger loads. That is to say, the smaller loads applied to ReB_2 by Locci *et al.*[29] and Chung *et al.*[1,30] will result in larger hardness results. Dubrovinskaia

et al.[31] also suggested that the load which is used to measure the hardness of ReB_2 is not in the asymptotic-hardness region. Gao F M and Gao L H[32] suggested that a comparative load should be chosen to test the accurate Vickers hardness. The load is taken approximately as $9.8H_v^{cal}/H_v^{dia}$, where H_v^{cal} is the calculated hardness of compoud and H_v^{dia} is the Vickers hardness of diamond under 9.8-N load, about 96 GPa. So we should choose larger load while measuring compound with larger hardness to avoid the ISE. Qin *et al.*[33] adopted larger loads, 2.94 N, 4.9 N, 9.8 N, 29.4 N, and 49 N, and the hardness of ReB_2 are 18.8 ± 2 GPa, 18.4 ± 1 GPa, 18 ± 1.2 GPa, 17.2 ± 0.8 GPa, 16.9 ± 0.6 GPa, respectively, in agreement with our calculations (19.7 GPa), which implies that our calculated results are reliable.

Table 2. Calculated values of bond distance d^μ (Å), Mulliken overlap population P^μ, bond volume v_b^μ (Å^3), partial number of effective free electrons n_{free}^μ, metallic population P'^μ, metallicity f_m^μ, and hardness $H_{vcalc.}^\mu$ (GPa) of TM–B and B–B bonds for 5d transition metal diborides with ReB_2 structure.

		d^μ	P^μ	v_b^μ	n_{free}^μ	P'^μ	f_m^μ	$H_{vcalc.}^\mu$	H_v
HfB_2	Hf–B	2.594	0.173	4.962	1.047	0.015	0.086	8.1	8.1
	B–B	1.848	0.790	1.792	2.385	0.034	0.043	211.5	
TaB_2	Ta–B	2.478	0.243	4.468	0.804	0.012	0.051	14.1	14.1
	B–B	1.831	0.710	1.803	1.173	0.018	0.026	191.7	
WB_2	W–B	2.342	0.220	3.898	0.029	0.001	0.002	16.8	16.8
	B–B	1.802	0.690	1.776	0.046	0.001	0.001	195.9	
ReB_2	Re–B	2.262	0.243	3.621	0.853	0.016	0.064	19.7	19.7, $30.1 \pm 1.3 \sim 48.0 \pm 5.6$[a], 20.7 $\sim$ 31.1[b],
	B–B	1.824	0.647	1.897	1.133	0.021	0.032	159.3	37.0 ± 1.2[c], $16.9 \pm 0.6 \sim 18.8 \pm 2$[d]
OsB_2	Os–B	2.229	0.243	3.525	0.654	0.012	0.049	21.0	21.0
	B–B	1.855	0.617	2.031	0.829	0.015	0.025	136.6	
IrB_2	Ir–B	2.219	0.267	3.560	1.289	0.022	0.083	21.8	21.8 26.65[e]
	B–B	1.983	0.577	2.539	1.394	0.024	0.042	86.6	
PtB_2	Pt–B	2.322	0.183	3.940	1.634	0.027	0.147	11.8	11.8
	B–B	1.914	0.703	2.206	3.134	0.052	0.074	128.9	

[a]Ref. [1]; [b]Ref. [29]; [c]Ref. [30]; [d]Ref. [33]; [e]Ref. [9].

Thus, the hardness values of 5d transition metal diborides with ReB_2 structure are all smaller than 40 GPa, indicating that they are not superhard materials. However, besides instable HfB_2 and TaB_2, the mechanical properties and hardness of 5d transition metal diborides with ReB_2 structure are both remarkable, meaning that they are good candidates for hard materials.

4. Conclusions

The hardness, elastic, and electronic properties of 5d transition metal diborides with hexagonal ReB_2 structure are calculated by using first principles based on density functional theory. The calculated equilibrium lattice parameters and elastic properties for TaB_2, ReB_2, OsB_2, and IrB_2 compare favorably with the previous theoretical and experimental values. The partial number of effective free electrons for each bond of multibond compounds with metallicity given for the first time in this paper is used to calculate the theoretical hardness of 5d transition metal diborides. The results indicate thatall5d transition metal diborides with ReB_2 structure are not superhard materials but good candidates for hard materials. We hope our models of hardness calculations play an important role in searching for new hard or superhard materials.

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