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Structural Stability and Elastic and Electronic Properties of Rhenium Borides: First Principle Investigations

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The structural stability and elastic and electronic properties of rhenium borides with different boron concentration are calculated systemically by means of first principle total energy calculations. The total energy calculations reveal that the WC-type structure is more energetically favorable for ReB and that the Re_2P-type structure is more preferred for Re_2B. The formation enthalpy of these borides have been studied by the solid synthesis routes. The calculated elastic properties indicate that Re_2B_3, ReB, and Re_2B phases are also potential hard materials. Although valence-electron density was often employed to evaluate elastic properties of materials, our calculations indicate that the bulk elastic properties of these borides are not direct correlation with their valence-electron density. The analysis of electronic structure, charge density distribution, and Mulliken overlap population provides further understanding of the elastic and superconductivity properties of these borides.

1. Introduction

Rhenium borides have attracted considerable attention due to their superior mechanical and superconductivity properties.[1−6] Among them, the structural, mechanical, and electronic properties of ReB_2 have been frequently studied both experimentally and theoretically.[1,7−11] Furthermore, the superconductivity of Re_3B, Re_7B_3, and Re_2B phases have also been reported, and their superconductivity transition temperature (Tc) is 4.8, 3.3, and 2.8 K, respectively.[2−4] However, the structure of Re_2B has not been determined in the experiment, and the structural and physical properties of other rhenium borides, such as ReB, Re_2B_5, Re_3B_7, and ReB_3 (see ref 12, Table 1), are still far from being clear. Systemic studies on the structural stability and elastic and electronic properties of rhenium borides with different boron concentration have not been carried out. In this work, by means of first principle total energy calculations, we present the deep studies on the structural stability, elastic properties of Re_3B, Re_7B_3, Re_2B, ReB, Re_2B_3, Re_3B_7, Re_2B_5, and ReB_3. Generally speaking, the bulk modulus and shear modulus show the same trends. However, our calculations indicate the trends of the bulk modulus and shear modulus of the calculated rhenium borides are opposite: The bulk modulus of these borides gradually decreases with the increase of boron concentration (from Re_7B_3 to ReB_2). The shear modulus G value increases with the enhancement of boron concentration from Re_7B_3 to ReB_2. And also the physical and superconductivity properties of these borides are further understood via the calculations in the electronic structure, charge density distribution, and Mulliken overlap population.

2. Crystal Structure and Computational Method

Structures. In the present study, the structures of Re_3B, Re_7B_3, ReB_2, and ReB_3 are presented by the experimentally determined orthorhombic (space group *Cmcm*) and hexagonal (space group

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$P6_3mc$) phases.[13] For the other borides, such as Re_2B, ReB, Re_2B_3, Re_3B_7, and Re_2B_5, no experimentally structural parameters are found up to now, we thus select some possible structures. The structures of Re_2P (space group *Pbnm*), Fe_2B (space group *I4/mcm*), W_2B (space group *P6mmm*), and W_2C (space group *Pnnm*) have been considered for Re_2B phase. For the crystal structure of ReB, we possess the four possible structures: WC (space group *P6m*2), NiAs (space group $P6_3/mmc$), FeB (space group *Pnma*), CrB (space group *Cmcm*), Wurtzite (space group $P6_3mc$), NaCl (space group $Fm\bar{3}m$), CsCl (space group $Pm\bar{3}m$), and ZnS (space group $F4\bar{3}m$). For the compound of Re_2B_3, the hexagonal Os_2B_3-type (space group $P6_3/mmc$) and anti-Ta_3B_2-type (space group *P4/mbm*) are considered.[13] Furthermore, the hexagonal anti-Re_7B_3-type (space group $P6_3/mmc$) is chosen for Re_3B_7. W_2B_5-type phases with space group (space group $P6_3/mmc$) and Mo_2B_5-type phases with space group (space group $R\bar{3}m$) are adopted for Re_2B_5 in the present calculation.[9] Moreover, for comparison, rhenium (Re) is also calculated.

Method. The geometry optimization and electronic properties were calculated using the CASTEP code[14] based on the density functional theory within the generalized gradient approximation (GGA-PBE).[15] The exchange and correlation functional was treated by norm-conserving pseudopotential. An energy cutoff of 440 eV was performed in the convergence calculations, and Brillouin zone integration was performed using the special *k*-point Monkhorst-Pack sampling scheme. (The detailed information is given in Table 2),[16] and finite displacement methods[17] are applied for the theoretical phonon calculation.

3. Results and Discussion

Structural Features. The equilibrium lattice constants of rhenium borides with different boron concentration were obtained by performing total-energy calculations as shown in Table 1. It can be seen that the calculated lattice parameters of Re_3B, *a*, *b*, and *c*, are in excellent agreement with the existing experimental data,[1−3,5−11,13,18] with a difference of about 0.017, 0.087, and 0.058 Å, respectively. In this structure, each B atom locates at the center of triangular prism of Re atom (see Figure 1a),[13,19] and the shortest distances of Re−B in Re_3B, 2.20 Å, is smaller than the sum of bonding radii, 2.16 Å, of Re (r=1.28 Å) and B ($r = 0.88$ Å) atoms,[20] suggesting the strong bonding feature. For Re_7B_3(see Figure 1b), each B atom is at the center of trigonal pyramid of Re atom[13,19] with Re−B between 2.182 and 2.645 Å. The Re−Re bond is separated range upward from 2.781 Å. The discrepancies in the lattice constants (*a* and *c*) of Re_7B_3 are less than 0.049 and 0.106 Å, respectively. Furthermore, for the ReB_2 phase, the close-packed Re layers alternate with puckered triangle-mesh B layers along [001] (see Figure 1f).[13,19] The calculated lattice constants of ReB_2 ($a = 2.894$ and $c = 7.416$ Å) are very close to the experimental values ($a = 2.900$ and $c = 7.479$ Å).[1] These results suggest that the present calculations are reasonable. Moreover, we also increase the cutoff energy and the number of *k*-points to 550 eV and 10 × 10 × 10 for all the studied borides; the total energy of these borides changes less than 1% per atom (see Table 2), indicating the convergence of present calculations. Furthermore for the structure of Re_2B phase, the Re_2P-type structure is more preferred than the Fe_2B, W_2B, and Fe_2C-type structures (see Table 3). The Re_2P-type Re_2B consist of BRe_7 polyhedra (see Figure 1c). The interatomic distances of Re−B vary from 2.202 to 2.301 Å, and the Re−B−Re angles are between 61.27 and 87.23 degree. For ReB phase, the calculated total energy of ReB in these different structures indicates that the phase with WC-type structure is more energetically stable than the other structures shown in Table 4, which is similar with the previous studied compound of OsB.[21] The WC-type ReB is built by the infinite columns of base-linked BRe_6 trigonal prisms share edges to form a 3D-framework. (see Figure 1d),[13,19] and the interatomic distance of Re−B in ReB, 2.212 Å, is slightly larger than the sum of bonding radii, 2.16 Å, of Re and B atoms. Furthermore, the results of Re_2B_3 phase indicate that the Os_2B_3-type structure has lower energy than that of the anti-Ta_3B_2 type structure. This Os_2B_3-type Re_2B_3 phase consists of the infinite slabs of BRu_6 trigonal prisms and puckered hexagon-mesh B layers alternate along [001] (see Figure 1e).[13,19] Finally, for Re_2B_5 phase, the W_2B_5-type structure is more stable in energy than that of Mo_2B_5-type phase (see Figure 1h). In the present work, we have calculated the more energetically stable structures for Re_2B, ReB, Re_2B_3, and Re_2B_5 in detail. The proposed structures of Re_3B_7 and ReB_3 are also shown in Figure 1g and i.

Formation Enthalpy Considerations. To explore the possible synthesis routes in the experiment, we also calculate the formation enthalpy of these borides. The previous experiments suggest that rhenium borides could be synthesized by the solid reaction of rhenium and boron.[1,2,5] We thus calculated the formation enthalpy by the following equations, and the results were also summarized in Table 1: $\Delta H = E_{\text{total}}(Re_xB_y) - (xE_{\text{total}}(Re) + yE_{\text{total}}(B))$. The negative values of the formation enthalpies indicate that they are thermodynamically stable to be experimentally synthesized.[22] From that, we notice that the values of formation enthalpies are all negative from Re_3B to ReB_2 phases, which explain these borides have been experimentally observed.[1−5] Among these borides, the Re_7B_3 phase has a relatively lower formation enthalpy than the other boride phases, which suggesting that the Re_7B_3 phase can be easily obtained under ambient condition in the Re−B system. Whereas the phases

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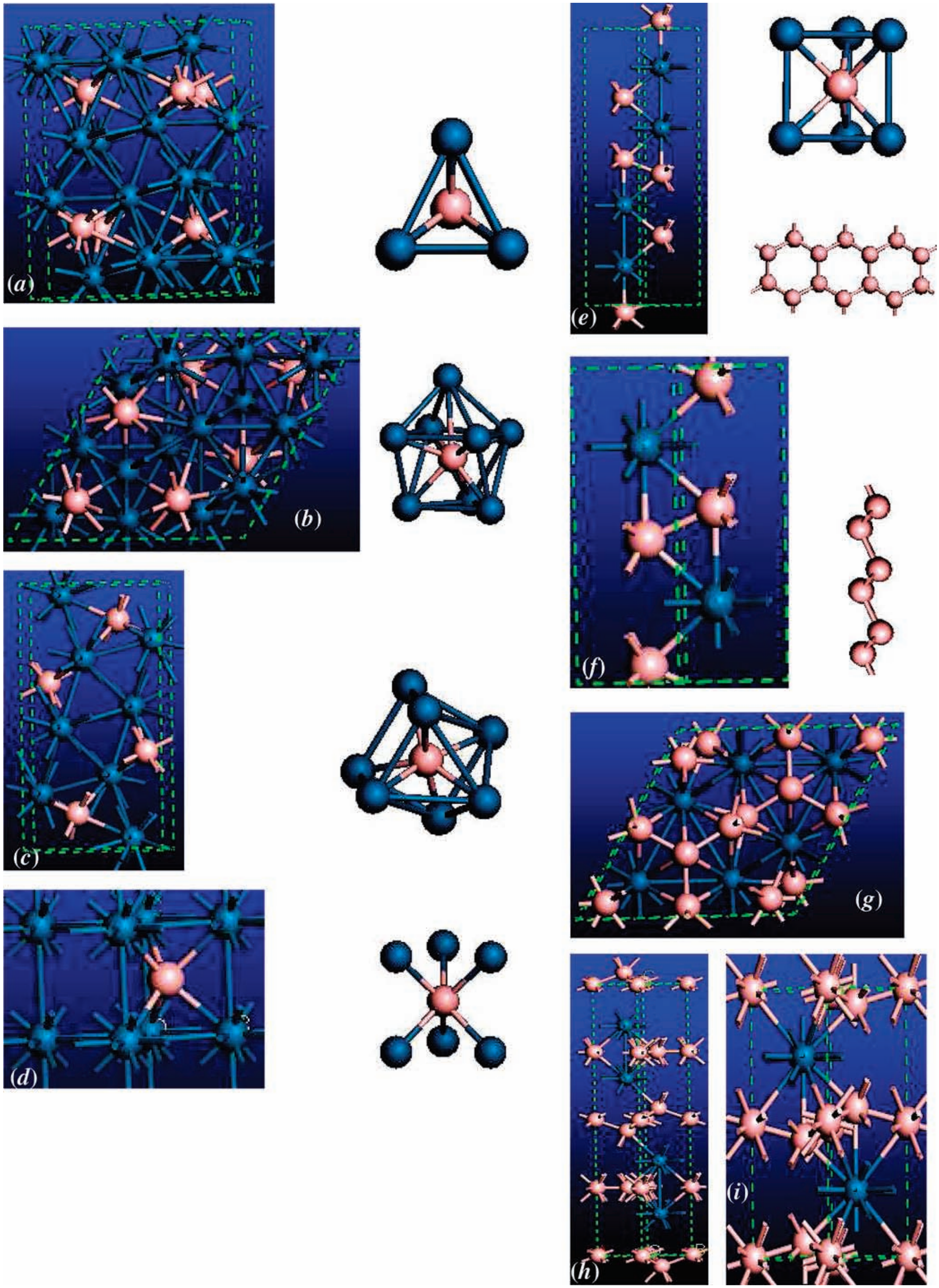

Figure 1. Crystal structure of rhenium borides: (a) Re_3B, (b) Re_7B_3, (c) Re_2B, (d) ReB, (e) Re_2B_3, (f) ReB_2, (g) Re_3B_7, (h) Re_2B_5, and (i) ReB_3.

Table 1. Calculated Lattice Parameters, *a* (Å), *b* (Å), *c* (Å), Formation Enthalpy, Δ*H* (eV), Bulk Modulus *B* (GPa), Shear Modulus *G* (GPa), Young's Modulus *E* (GPa), and Poisson's Ratio (*ν*) of Rhenium and Rhenium Borides and Compared with Available Experimental Data

		a	*b*	*c*	Δ*H*	*B*	*G*	*E*	*ν*
Re	expt.[11]	2.761		4.458		372[16]			
		2.760		4.433		380	177	460	0.2984
Re_3B	expt.[2]	2.896	9.317	7.270					
		2.881	9.304	7.328	−0.80	379			
Re_7B_3	expt.[11]	7.540		4.772					
	expt.[2]	7.516		4.890					
		7.491		4.878	−2.31	378	160	420	0.3145
Re_2B		9.750	5.154	2.799	−0.51	367	216	542	0.2540
ReB		2.875		2.925	−0.62	359	249	607	0.2185
Re_2B_3		2.887		13.258	−1.96	351	264	633	0.1993
ReB_2	expt.[1]	2.900		7.479		360			
		2.894		7.416	−1.34	348	288	677	0.1757
Re_3B_7		7.357		7.756	2.66	279			
Re_2B_5		3.072		14.126	3.80	321			
ReB_3		3.141		7.586	3.08	297			

Table 2. Parameters ($E_{\text{cut-off}}$ and *k* point) of the Geometry Optimization and the Difference of Total Energy, Δ*E* (eV/atom) for Rhenium Borides

phase	E_{cutoff} and *k* point	E_{cutoff} and *k* point	Δ*E* (eV/atom)
Re_3B	440 eV, 9 × 3 × 3	550 eV, 10 × 10 × 10	0.82%
Re_7B_3	440 eV, 4 × 4 × 6	550 eV, 10 × 10 × 10	0.54%
Re_2B	440 eV, 3 × 5 × 9	550 eV, 10 × 10 × 10	0.49%
ReB	440 eV, 10 × 10 × 10	550 eV, 10 × 10 × 10	0.63%
Re_2B_3	440 eV, 10 × 10 × 2	550 eV, 10 × 10 × 10	0.91%
ReB_2	440 eV, 10 × 10 × 4	550 eV, 10 × 10 × 10	0.40%
Re_3B_7	440 eV, 4 × 4 × 4	550 eV, 10 × 10 × 10	0.07%
Re_2B_5	440 eV, 9 × 9 × 2	550 eV, 10 × 10 × 10	0.02%
ReB_3	440 eV, 9 × 9 × 4	550 eV, 10 × 10 × 10	0.39%

Table 3. Calculated Total Energy of ReB in the Different Structures

phase	type	space group	energy (eV/fu)
ReB	WC	P6*m*2	−382.6100
	NiAs	$P6_3/mmc$	−382.4523
	FeB	*Pnma*	−382.1946
	CrB	*Cmcm*	−382.1732
	Wurtzite	$P6_3mc$	−381.8735
	NaCl	$Fm\bar{3}m$	−381.5583
	CsCl	$Pm\bar{3}m$	−381.3302
	ZnS	F4$\bar{3}$*m*	−380.2810

Table 4. Calculated Total Energy of Re_2B in the Different Structures

phase	type	space group	energy (eV/fu)
	Re_2P	*Pbnm*	−686.8098
Re_2B	Fe_2B	*I4/mcm*	−686.7824
	Fe_2C	*Pnnm*	−686.2400
	W_2B	*P6/mmm*	−682.2233

of Re_3B_7, Re_2B_5, and ReB_3 have larger positive formation enthalpies, which may imply that these phases will be prone to decompose in the course of synthesis. It is impossible to stabilize these high borides using this synthesis routes.

Elastic Properties. The complete sets of zero-pressure single crystal elastic constants are calculated to obtain the elastic properties of rhenium borides. The elastic stability is first checked by the whole set of elastic stiffness constants c_{ij} that satisfies the Born−Huang criterion.[23] Our results indicate that the phases of Re_3B, Re_3B_7, and Re_2B_5 are elastically unstable under ambient condition. A nonstoichiometric sample for Re_3B may be obtained in the experiments.[2−5] Furthermore, the calculated bulk modulus (*B*), shear modulus (*G*), Young's modulus (*E*), and Poisson's ratio (*ν*) of both elastically and thermodynamically stable rhenium borides were calculated according to the Voight−Reuss−Hill (VRH) approximations[24] as also listed in Table 1. Our calculated elastic moduli of ReB_2 are in satisfactory agreement with the available experimental and theoretical results.[5−11] In addition, we notice that the bulk modulus of Re_7B_3 (378 GPa) is slightly smaller than that of the parent metal Re (380 GPa),[18] which is also a low compressible material. Moreover, the bulk modulus of these borides gradually decreases with the increase of boron concentration (from Re_7B_3 to ReB_2) compared with that of the parent Re metal. Furthermore, the *G* value is of gradual increase with the enhancement of boron concentration from Re_7B_3 to ReB_2, until the *G* modulus reaches at the maximum value, 288 GPa, for ReB_2. And the *G* values of Re_2B, ReB, and Re_2B_3 are 216, 249, and 264 GPa, respectively. In addition, besides ReB_2, ReB, and Re_2B_3 also have lower Poisson's ratio. The largest *G* value and the low Poisson's ratio of Re_2B, ReB, Re_2B_3, and ReB_2 indicate the strong directional bonding, which may suggest that they are also potential hard materials.[25,26] At the same time, we also calculate the temperature

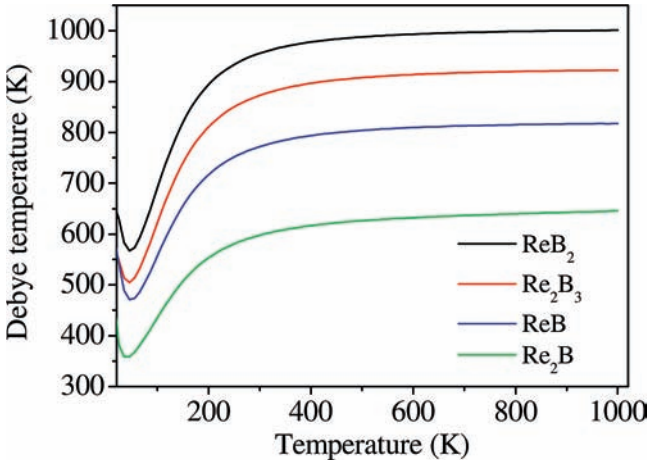

Figure 2. Temperature dependence of Debye stiffness of Re_2B, ReB, Re_2B_3, and ReB_2.

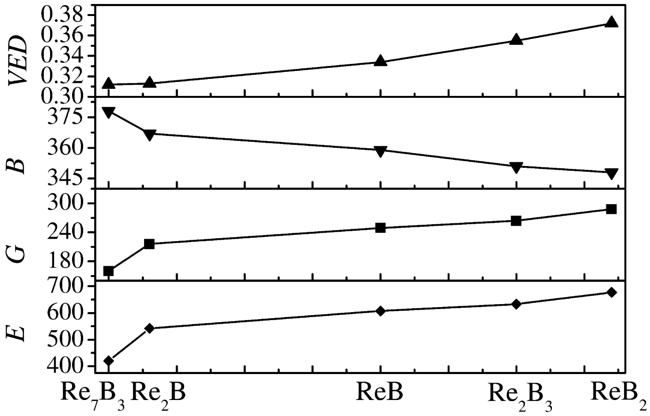

Figure 3. Elastic properties (*B*, *G*, *E*) and valence-electron density (VED)of rhenium borides.

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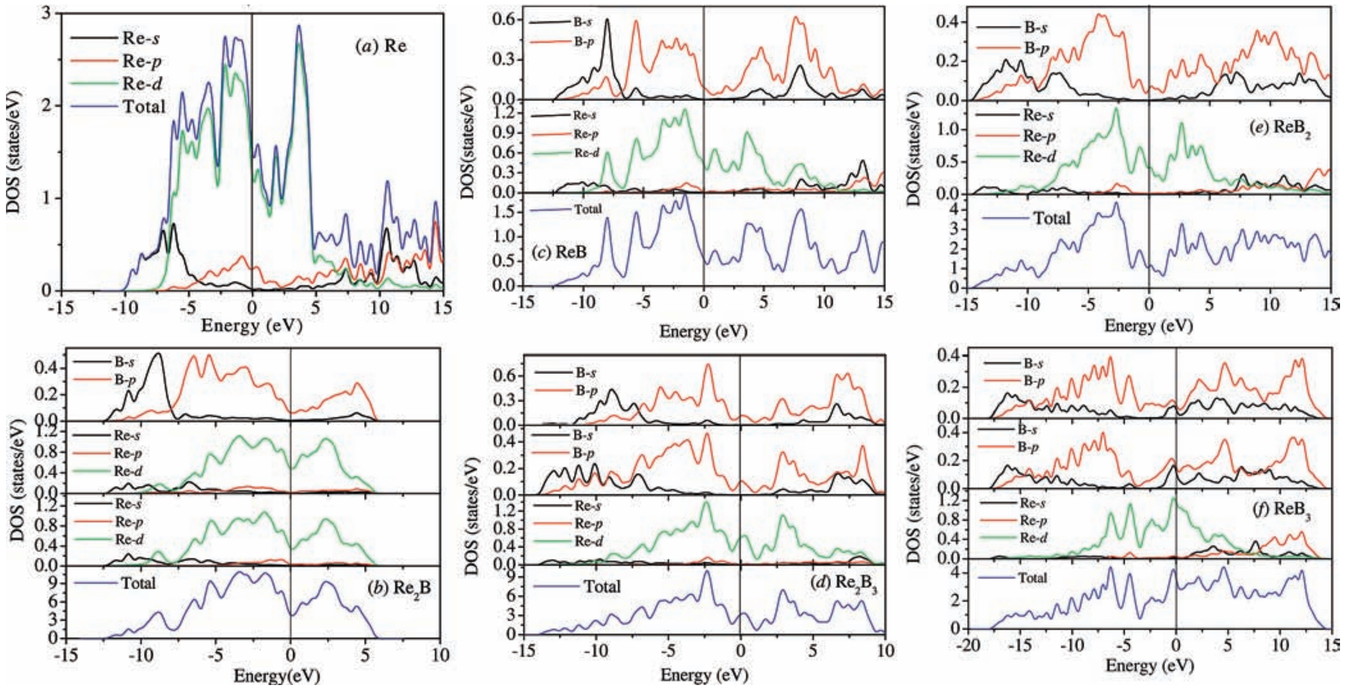

Figure 4. Total (black line) and partial (green line, Re-d state; Red line, B-p state) densities of states (DOSs) of (a) Re, (b) Re_2B, (c) ReB, (d) Re_2B_3, (e) ReB_2, and (f) ReB_3.

dependence of Debye stiffness[27] of Re_2B, ReB, Re_2B_3, and ReB_2 by means of theoretical phonon density of states displayed in Figure 2. It can be seen that the Debye temperature of ReB_2 within the range of studied temperature is greater than that of the other borides but much smaller than that of *c*-BN.[27] The present results indicate that the ReB_2 phase is a stiffest solid in the Re−B system but much softer than that of *c*-BN.[27]

On the basis of the correlation between bulk modulus and valence electron densities,[1,28,29] it is expected that the bulk elastic properties of these rhenium borides may be possible correlation with their valence-electron density (VED). We thus calculated VED of these borides shown in Figure 3. The calculated VED of Re, 0.479 electrons/Å^3, is in excellent agreement with the experimental data, 0.476 electrons/Å^3.[1] From Figure 3, the VED increases from Re_7B_3 to ReB_2 phase, but the *B* value decreases increasingly, which is opposite to the change of metal from Re to Os (the bulk modulus increase from Re (360 GPa) to Os (395 GPa) with the increase of valence-electron density from 0.476 electrons/Å^3 in Re to 0.572 electrons/Å^3 in Os).[1,18] While the general trend of *G* and *E* in these borides is the same as that of VED. It thus can be concluded that the valence-electron density is impossibly direct correlation with the bulk modulus within the Re−B system.

Bonding Properties. The electronic structure is crucial to understand the origin of elastic and physical properties of these borides; the total and partial densities of states (DOSs) of Re, Re_2B, ReB, Re_2B_3, ReB_2, and ReB_3 are calculated at zero pressure as shown in Figures 2−5(a−f), where the vertical line is the Fermi level (E_F). From that we see that DOS spectra of all these borides cross at $E_{F,}$ showing the metallic behavior. The lowest energy of the DOS spectra is formed by the chiefly B-2s states. In the vicinity of the Fermi level the contribution of DOS is mainly composed of Re-5d and B-2p states, and more importantly, the hybridizations of Re-5d and B-2p states are much deeper in energy from the E_F, indicating the potential covalent bonding character in these borides.[30−32] For Re_3B and Re_7B_3, the DOS spectrum of Re is preserved because of the addition of lower boron concentration (not shown here), which explain the higher value of bulk modulus. Furthermore, we notice that the contribution to the Fermi level of B-2p increases with further addition of boron concentration (from Re_2B to ReB_2), suggesting the increasing hybridization between Re-5d and B-2p states, and the ReB_2 phase has the lowest value of $N(E_F)$ in all the studied borides, indicating the relatively strong covalent bonding behavior in the ReB_2. Finally, for ReB_3, in addition to the contribution of Re-5d and B-2p states, the B-2s states have a relatively significant contribution at the Fermi level compared with the other borides, which is quite different with that of the other borides. To further comprehend the bonding mechanism of these borides, we have displayed the charge density distribution in different planes (Figure 5a−f). From Figure 5a, we observe that the parent metal Re has a metallic bonding behavior because of the uniform distribution of charge density. The addition of boron results in an increase of the charge density and forms

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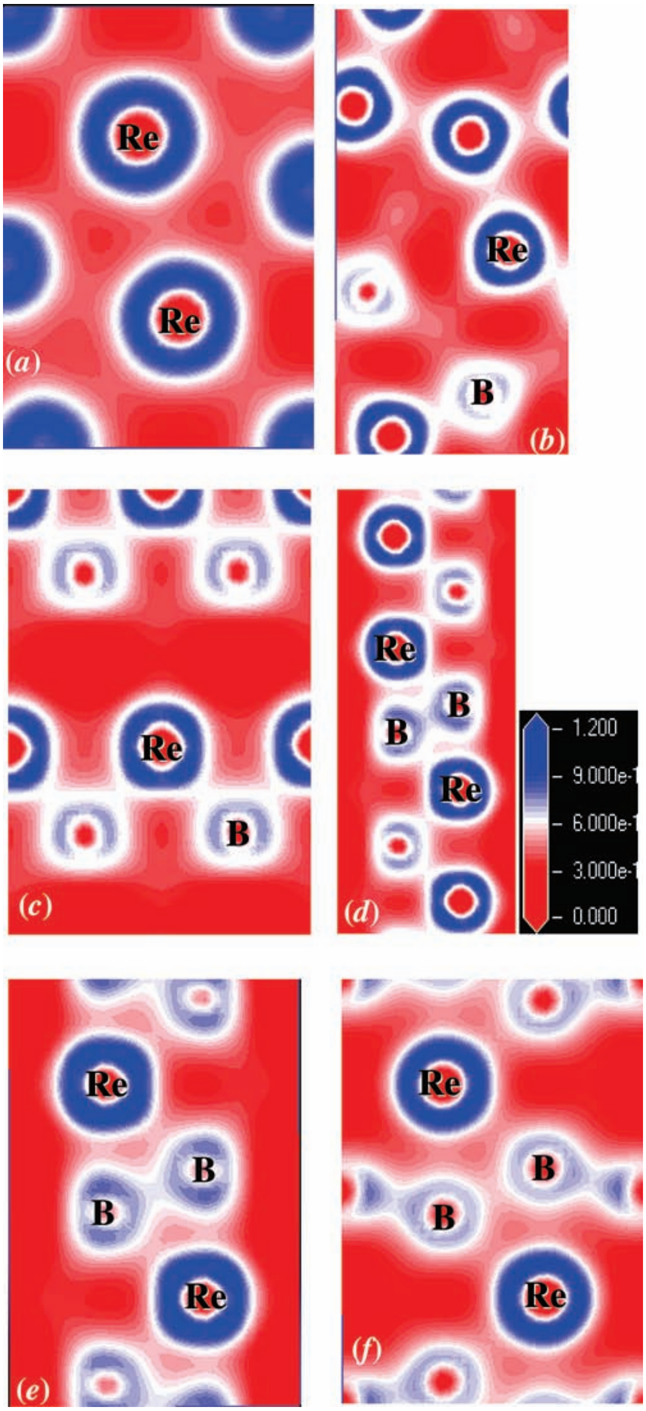

Figure 5. Charge denstiy distribution in different planes for rhenium (a) and rhenium borides (b) Re_2B, (c) ReB, (d) Re_2B_3, (e) ReB_2, and (f) ReB_3.

Table 5. Calculated Partial and Total Density of States at the Fermi Level (PN(E_F) and TN(E_F), States/eV cell), Specific Heat Coefficients (γ, mJ mol^{-1} K^{-2}), and Electron-Phonon Coupling Constant (λ) of Rhenium Borides and Compared with Available Experimental Data

	PN(E_F)						
	Re-5d	B-2p	B-2s	TN(E_F)	γ_{theor}	γ_{exptl}[2]	λ
Re_3B	1.929	0.093	0.010	2.159	5.08	6.3	0.24
Re_7B_3	4.434	0.255	0.009	4.840	11.39		
Re_2B	0.845	0.063	0.004	0.977	2.30		
ReB	0.430	0.094	0.003	0.551	1.30		
Re_2B_3	1.227	0.325	0.005	1.597	3.76		
ReB_2	0.409	0.117	0.002	0.544	1.28		

the finite covalent bonds in the Re_2B (see Figure 5b), which is in agreement with the DOS results. Further increasing the boron concentrations up to ReB (Figure 5c), the directional bonding is quite strong between Re and B atoms, which is also conformed by the calculated average Mulliken overlap population (MOP) of Re−B bond (0.58 in Re_2B and 1.93 in ReB). For Re_2B_3, there exist strong directional bonding not only between Re and B atoms but also between B and B atoms (Figure 5d). Moreover, the calculated MOP of B−B bond in Re_2B_3 is 2.21, but the MOP of Re−B bond in Re_2B_3 (0.55) is smaller than that of the calculated value in ReB (1.93), which may suggest the decreasing covalent bonding character of Re−B bond in Re_2B_3. When the boron concentrations increased to ReB_2 (see Figure 5e), the zigzag network formed by the Re−B and B−B bonds strength the covalent bonding to further increase the hardness of ReB_2.[6−11] This distinctly structural arrangement between Re_2B_3 and ReB_2 phases explains the difference of elastic moduli between these phases, although the calculated MOP of both Re−B and B−B bond in ReB_2 is similar with that of Re_2B_3 (see Figure 1e−f). For ReB_3 phase, there is also a strong directional bonding in B−B atom (Figure 5f). However, the calculated MOP of B−B bond in ReB_3 (1.59) is much smaller than that in ReB_2, and the MOP of all the B−Re bonds is negative value, indicating the antibonding behavior of all the Re−B bonds in ReB_3. This may explain the previous studied instability of ReB_3. Furthermore, the calculated partial and total DOS (P*N* (E_F) and T*N* (E_F) at the E_F of these borides are shown in Table 5 to study the experimentally found superconducting in these borides. From that we notice that a larger value of density of states appears at Fermi level for Re_3B and Re_7B_3, which may explain the relatively high superconductivity temperature (*Tc*) in these compounds,[2−5] and we also find that the dominating contributions to the T*N* (E_F) derive from Re-5d states (larger than 75%), whereas the contributions of the B 2p states gradually increase from 4.3% in Re_7B_3 to 21.5% in ReB_2. It is known that the B-2p band contribution to the DOS at the Fermi level is important to the superconductivity in MgB_2.[33] It is expected that the ReB_2 phase may be a high *Tc* superconductor, while the previous studies indicate that ReB_2 phase had *Tc* less than 1 K and even no superconductivity signature. This noticeable difference in *Tc* between MgB_2 and ReB_2 may suggest the different superconductivity mechanism. Recently, the results of Lue et al.[5] explain that the Re_3B and Re_7B_3 phases are *s*-wave superconductor by means of the ^{11}B nuclear magnetic resonance spectroscopy. The calculated B-2*s* Fermi-level densities of states of these borides are also shown in Table 5. From that we found that B-2s is important for the superconductivity signature although the contribution to the Fermi-level densities of states is negligible. Moreover, according to the free electron model, we also calculate the specific heat coefficients γ ($\gamma_{theor.}=(\pi^2/3)N(E_F)k_B^2$)[18] listed in Table 5. From these values, we can simple calculate the electron−phonon coupling constant λ ($\gamma_{expt.} = \gamma_{theor.}(1 + \lambda)$) of these borides. The calculated λ of Re_3B, 0.24, is much

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smaller that of MgB_2 ($\lambda = 2$),[34] indicating that these borides are the weak coupling compounds.[16] Therefore, the analysis of the electronic structure is important for the understanding of the mechanical and physical properties of rhenium borides, which also suggests that the Re−B system can be tailored by controlling the boron concentration during the materials design and synthesis in future.

4. Conclusion

To conclude, using first principle calculations, the lattice parameters, structural stability, bulk and shear moduli, Young's modulus, Poisson's ratio and valence electron densities, and Debye stiffness of rhenium borides with different boron concentration have been calculated. The crystal structures of Re_2B and ReB have been predicted. Moreover, the calculations show that Re_7B_3, Re_2B, ReB, and Re_2B_3 and ReB_2 phases are both thermodynamically and elastically stable, and the calculations of bulk modulus of these stable phases reveal that they are potential low compressible materials. Besides ReB_2, the larger shear moduli and lower Poisson's ratio of Re_2B, ReB, and Re_2B_3 indicate that they are also potential hard materials. In addition, the studies indicate that the bulk elastic properties of these stable borides are not direct correlation with their valence-electron density. The analysis of electronic structure, charge density distribution, and Mulliken overlap population is necessary to further explain the elastic and superconductivity properties.

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