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First-principles calculations on crystal structure and physical properties of rhenium dicarbide

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ABSTRACT

Structural stability, elastic behavior, hardness, and chemical bonding of ideal stoichiometric rhenium dicarbide (ReC₂) in the ReB₂, ReSi₂, Hex-I, Hex-II, and Tet-I structures have been systematically studied using first-principles calculations. The results suggest that all these structures are mechanically stable and ultra-incompressible characterized by large bulk moduli. Formation enthalpy calculations demonstrated that they are metastable under ambient conditions, and the relative stability of the examined candidates decreases in the following sequence: Hex-I > Hex-II > ReB₂ > Tet-I > ReSi₂. The hardness calculations showed that these structures are all hard materials, among which the Hex-I exhibits the largest Vickers hardness of 32.2 GPa, exceeding the hardness of α -SiO₂ (30.6 GPa) and β -Si₃N₄ (30.3 GPa). Density of states and electronic localization function analysis revealed that the strong C–C and C–Re covalent bonds are major driving forces for their high bulk and shear moduli as well as small Poisson's ratio.

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1. Introduction

Designing and searching for ultra-incompressible and superhard materials is always of great scientific interest due to its variety of industrial applications. The introduction of light and covalent-bondforming elements into the transition metal (TM) lattices is expected to have profound influences on their chemical, mechanical, and electronic properties [1–3]. Based on this prospect, recent design of new intrinsically potential superhard materials ($H_v \ge 40$ GPa) has concentrated on light element (B, C, N, and O) TM compounds with high elastic moduli, in particular the 5d TM compounds [4–11]. A primary example and among the first synthesized materials following this principle is OsB_2 [4], which was expected to be an ultraincompressible hard material. However, further high-pressure X-ray diffraction, scratch test, and micro-hardness measurements show that OsB₂ is a hard material [12–13]. Later, Li et al. proposed two different orthorhombic *Pmn2*₁ structure for OsN and OsC with high bulk modulus (351 and 355 GPa), respectively, energetically much superior to the previously proposed WC-type structure [14-15]. Moreover, the crystal structures and related physical properties of other osmium borides, carbides, and nitrides have been extensively studied [16–19]. Another more promising material, ReB₂, has been synthesized at ambient pressure and was proposed to be superhard with claimed hardness of 36.4-48 GPa, though extensive debate exists [2,5,20–21]. In order to hunt for new potential superhard rhenium-based materials, researches start to look closely at other light elements surrounding B in the periodic table. Experimentally, novel rhenium nitrides (Re₂N and Re₃N) recently synthesized by Friedrich et al. [22] have stimulated great interest because of their ultra-incompressibility with bulk moduli of about 400 GPa. This value is comparable to that of superhard *c*-BN (around 400 GPa) and higher than that of ReB₂ (334–371 GPa). A hexagonal Re₂C has been synthesized recently by Juarez-Arellano et al. [23] under high pressure and high temperature and it has large bulk modulus of about 400 GPa. Theoretically, Du et al. [24] proposed a new potential superhard tetragonal P4/mmm structure for ReN₂ with theoretical hardness of 46.3 GPa. Chen et al. [25] computationally designed ReC in the WC and NiAs structures with very high bulk and shear moduli may be the hardest binary metal carbides so far discovered. Compared to the potential superhard ReB₂, Re₂C, ReN₂, and ReC, the experimental and theoretical investigations on ReC₂ are rarely studied. Therefore, the study on the structural stability, mechanical property, electronic density of states (DOS), and chemical bonding is motivated for this exciting compound.

In the present work, we have employed the first-principles calculations to explore the structural stabilities and related physical properties of ReC_2 based on the known structures of light element TM compounds. It is known that the synthesized ReB_2 [5] and

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Fig. 1. (Color online) Crystal structures of ReC₂ for ReB₂-type (a), ReSi₂-type (b), Hex-I (c), Hex-II (d), and Tet-I (e). The large and small spheres represent Re and C atoms, respectively.

ReSi₂ [26] adopts the hexagonal (space group: P6₃/mmc, Fig. 1a) and tetragonal (space group: I4/mmm, Fig. 1b) structure, respectively. In addition, two hexagonal structures of P-6m2 (hereafter denoted as Hex-I, Fig. 1c) and P6₃/mmc (hereafter denoted as Hex-II, Fig. 1d) proposed by Wang et al. [9] for WN₂ have also been reported as possible stable phases for OsC₂ [27]. The superhard tetragonal P4/mmm phase (hereafter denoted as Tet-I, Fig. 1e) of ReN₂ mentioned above is also fascinating and competitive [24]. Therefore, these five possible structures, namely, ReB₂, ReSi₂, Hex-I, Hex-II, and Tet-I are chosen for ReC_2 in this work. Moreover, these candidates represent the most typical variants of coordination numbers (CNs) of Re atom in their crystal structures: ReSi₂-type (CNs=10), ReB₂type (CNs=8), Tet-I (CNs=8), Hex-I (CNs=6), and Hex-II (CNs=6). The calculated results indicate that all these structures are mechanically stable and exhibit excellent mechanical properties. We hope our results can stimulate further experimental research to synthesize these ultra-incompressible and potential superhard compounds.

2. Computational details

Ab initio structural relaxations and electronic calculations were carried out using density functional theory within the Perdew–Burke–Ernzerhof exchange-correlation as implemented in the VASP code [28–30]. The all-electron projector augmented wave

method [31] was adopted with $2s^22p^2$ and $4p^65d^56s^2$ treated as valence electrons for C and Re, respectively. The energy cutoff 520 eV and appropriate Monkhorst–Pack *k* meshes [32] were chosen to ensure that total energy calculations are well converged to better than 1 meV/atom. The phonon calculations were carried out by using a supercell approach as implemented in the PHONOPY code [33]. Single crystal elastic constants were determined from evaluation of stress tensor generated small strain and bulk modulus, shear modulus, Young's modulus, and Poisson's ratio were thus estimated by using the Voigt–Reuss–Hill approximation [34]. The theoretical Vickers hardness was estimated by using Šimůnek model [20].

3. Results and discussion

The crystal structures of ReC_2 within five considered structures are shown in Fig. 1. The typical feature of the ReB_2 and ReSi_2 structure is the Re polyhedrons, being centered by C atoms, are connected by edges along *c* axis. In the other three structures, different rhenium-carbon polyhedrons are linked by C–C bonding along *c* axis, forming an intriguing C–Re–C sandwiches stacking order, and one might expect their excellent mechanical properties. Table 1 lists the calculated lattice constants, equilibrium volumes, bulk moduli, and their pressure derivatives of five structures.

Table 1

Calculated equilibrium lattice constants a_0 (Å), c_0 (Å), equilibrium volume V_0 (Å³/f.u.), EOS fitted bulk modulus B_0 (GPa), its pressure derivative B_0' , and formation enthalpy ΔH_f (eV/atom) for ReC₂ in the ReB₂, ReSi₂, Hex-I, Hex-II, and Tet-I structures, respectively.

Structure	<i>a</i> ₀	<i>C</i> ₀	Vo	B ₀	Bo	$\Delta H_{\rm f}$
ReB ₂	2.583	10.06	29.055	301	4.662	0.722
ReSi ₂	2.786	6.728	26.108	352	4.695	1.420
Hex-I	2.880	4.067	29.205	336	4.536	0.377
Hex-II	2.876	8.237	29.492	323	4.255	0.597
Tet-I	2.691	3.842	27.823	363	4.517	0.807



Fig. 2. The dependences of the calculated total energy on the f.u. volume of ReC_2 in different structures.



Fig. 3. (Color online) Phonon dispersion curves of Hex-I at 0 GPa.

The bulk moduli and their pressure derivatives are obtained by fitting pressures and cell volumes with the third-order Birch–Murnaghan equation of state (EOS) [35]. From this table, it can be seen that two tetragonal structures (ReSi₂ and Tec-I) have smaller volumes than those of the other three hexagonal structures that may result in the higher bulk moduli. Moreover, Fig. 2 presents the dependences of the calculated total energy on the f.u. volume for these five candidates. Clearly, the Hex-I structure is the most energetically favorable phase, whereas the ReSi₂ is the most unfavorable phase with the largest equilibrium volume. The relative stability of the examined ReC₂ polymorphs decreases in the following sequence: Hex-I > Hex-II > ReB₂ > Tet-I > ReSi₂, while on the contrary it grows with reduction of CNs of Re atom.

It is important to explore the thermodynamic stability of ReC₂ in these structures for further experimental synthesis. The thermodynamic stability at ambient pressure with respect to decomposition is quantified in terms of the formation enthalpy, using $\Delta H_f = H_{(\text{ReC}_2)} - H_{(\text{Re})} - 2H_{(\text{C})}$. The ΔH_f is the formation enthalpy, the hexagonal Re (space group: P6₃/mmc) and diamond C are chosen as the reference phases. The calculated $\Delta H_{\rm f}$ per atom of these phases are listed in Table 1, and the results indicated that they are all metastable at ambient conditions. Therefore, high temperatures are needed to synthesize them in actual experiment. It should be noted that the much high formation enthalpy of ReSi2 phase, comparing to those of the others, is unfavorable to its stable. On the contrary, the Hex-I structure has the lowest formation enthalpy among these structures, suggesting that it is most likely to be synthesized. Accordingly, the dynamical stability of Hex-I structure was carefully checked by the phonon calculations. As shown in Fig. 3, no imaginary phonon frequency was detected in the whole Brillouin zone, indicating the dynamical stability of the Hex-I structure at ambient pressure.

The complete set of zero pressure elastic constants for five structures were calculated by strain-stress method [36-37] in order to check their mechanical stability, as shown in Table 2. The key criterion for mechanical stability of a crystal is that strain energy must be positive. This means in a tetragonal crystal that the elastic constants should satisfy the following inequalities [38]: $C_{11} > 0$, $C_{33} > 0$, $C_{44} > 0$, $C_{66} > 0$, $(C_{11} - C_{12}) > 0$, $(C_{11}+C_{33}-2C_{13}) > 0$, and $2(C_{11}+C_{12})+C_{33}+4C_{13} > 0$; while for a hexagonal crystal: $C_{33} > 0$, $C_{44} > 0$, $C_{12} > 0$, $C_{11} > |C_{12}|, (C_{11} + 2C_{12})$ $C_{33} > 2C_{13}^2$. According to the above criteria, it is clear that ReC₂ within all these structures are mechanically stable at ambient condition. It also can be seen that these five phases possess much large C_{11} and C_{33} , manifesting that their *a*-axis and *c*-axis directions are extremely stiff. Based on the calculated elastic constants, the bulk modulus (B) and shear modulus (G) are calculated by the Voigt-Reuss-Hill approximation in Table 2. The Young's modulus E and Poisson's ratio v are obtained from the equations of E =9BG/(3B+G) and v = (3B-2G)/(6B+2G). Strikingly, the calculated bulk moduli agree well with those directly obtained from the fitting of the third-order Birch-Murnaghan equation of state (EOS), which further demonstrates the reliability of our calculations. The calculated bulk moduli of ReSi2 and Tex-I structures are 357 GPa and 363 GPa, which are rival with that (around 400 GPa) of c-BN, indicating their ultra-incompressible nature. Compared

Table 2

Calculated elastic constants C_{ii}, bulk modulus B, shear modulus G, Young's modulus E, and hardness H in unit of GPa of ReC₂. Also shown are Poisson's ratio v and G/B ratio.

Structure	<i>C</i> ₁₁	<i>C</i> ₁₂	C ₁₃	C ₃₃	C ₄₄	C ₆₆	В	G	Ε	G/B	ν	Н
ReB ₂	908	243	80	400	76	324	303	175	440	0.576	0.258	26.7
ReSi ₂	826	50	153	880	62	269	357	172	445	0.482	0.292	22.8
Hex-I	565	173	206	906	179	196	346	204	510	0.587	0.255	32.2
Hex-II	521	163	230	837	212	179	335	201	503	0.600	0.250	31.8
Tet-I	752	168	168	748	204	242	363	244	597	0.671	0.225	23.2

to bulk modulus, the shear modulus of a material quantifies its resistance to the shear deformation, which is a better indicator of potential hardness. For the calculated shear modulus, Tex-I possesses the largest value of 244 GPa among the considered structures, followed by Hex-I (204 GPa) and Hex-II (201 GPa). However, the relative lower shear moduli of ReB₂ and ReSi₂ structures are mainly due to their smaller C_{44} , which relates to the monoclinic shear distortion in the (100) plane [39]. The relative directionality of the bonding in the material also has an important effect on its hardness and can be determined by the G/Bratio. The obtained values of *G*/*B* ratio for these structures are in range from 0.482 to 0.671, which are close to those of OsB_2 (0.5). PtN_2 (0.61), IrN_2 (0.66), and OsN_2 (0.72), suggesting the strong direct bonding between the C and Re atoms. All these excellent mechanical properties strongly suggest that these candidates are ultra-incompressible and potential superhard materials.

In view of the high bulk and shear moduli of these structures, the hardness calculations are of great interest. According to the Šimůnek model, the hardness of the idea single crystal is proportional to the bond strength and to their number in the unit cell. More specifically, the hardness of crystals having different bond strengths is given by the following expressions [20]:

$$H = (C/\Omega)n \left[\prod_{i,j=1}^{n} (N_{ij}S_{ij})\right]^{1/n} e^{-\sigma f_e},$$

$$f_e = 1 - \left[k \left(\prod_{i=1}^{k} e_i\right)^{i/k} / \sum_{i=1}^{k} e_i\right]^2,$$

and

$$S_{ij} = \sqrt{e_i e_j} / (n_i n_j d_{ij}),$$

where N_{ii} is the number or multiplicity of the binary system, S_{ii} is the strength of the individual bond between atoms i and j; the reference energy e_i is defined as $e_i = Z_i / r_i$, Z_i is the number of valence electrons and r_i is the radius of the sphere (centered at atom *i*) in which Z_i electrons are contained; n_i and n_j are coordination numbers of atoms *i* and *j*, respectively; d_{ij} is the interatomic distance, k corresponds to the number of different atoms in the system. In the present work, the values C=1450. σ =2.8, and the atomic radio r_i of elements from Kittel's text book [40] are used. The estimated values of hardness by this method are shown in Table 2, and the Hex-I phase has the largest hardness (32.2 GPa) among the considered structures. Similar to the trend in structure stability, the values of the estimated hardness of these polymorphs also grow with reduction of CNs of Re atom. It is interesting to note that the Tex-I has the largest bulk modulus (363 GPa) and shear modulus (244 GPa) but possesses a smaller hardness. This suggests that there is on clear connection between hardness and elastic moduli.

To illustrate the mechanical properties of these five structures of ReC_2 on a fundamental level, their total and site projected electronic densities of states (DOS) were calculated at ambient pressure, as shown in Fig. 4. The obtained DOS curves show large similarities in these structures as follows. All these phases exhibit metallic behavior by evidence of the finite electronic DOS at the Fermi level (E_F). From the partial DOS, it reveals that the peaks below -10 eV are mainly attributed to C-2s and 2p states with a



Fig. 4. (Color online) Total and partial densities of states of ReB₂-type (a), ReSi₂-type (b), Hex-I (c), Hex-II (d), Tet-I (e) at ambient pressure. The vertical dashed line denotes the Fermi level at zero.



Fig. 5. (Color online) Contours of ELF of Hex-I structure on the (100) plane (a) and that of Hex-II structure on the (001) plane (b), respectively.

small contribution from Re-5*d*. The states from -10 to 0 eV mainly originate from Re-5*d* and C-2*p* orbitals. Moreover, the partial DOS profiles for both Re-5*d* and C-2*p* are very similar in the range of -10 to 0 eV, reflecting the strong orbital hybridization between these two orbitals. This fact also shows that a strong covalent interaction between the Re and C atom. The typical feature of the total DOS is the presence of the so-called pseudogap, which is considered as the borderline between the bonding and antibonding states. It can be seen that the calculated Fermi energy is located above the pseudogap (except ReB₂ and Hex-I) that indicating the whole bonding states and partial antibonding states have been filled by Re-5*d* and C-2*p* orbitals. In addition, the contribution to E_F is mainly due to Re-5*d* orbital which is the principal cause for metallicity in these candidates.

In order to quantitatively identify the chemical bonding features of ReC₂ in these structures, we have calculated the Electronic Localization Function (ELF) [41-42], which is a measure of the probability of finding an electron near another electron with the same spin related to the Pauli Exclusion Principle [43]. The ELF is represented as a contour plot in real space, where different contours correspond to numerical values ranging from 0.0 to 1.0. The upper limit ELF=1 corresponding to perfect localization and the value ELF=0.5 corresponding to electron-gas-like pair probability. High ELF values show that at the examined position the electrons are more localized than in a uniform electron gas of the same density. In view of the similar chemical bonding of ReC₂ within these structures described above, here only the ELF results of Hex-I and Hex-II structures are presented. For the (100) plane of Hex-I structure in Fig. 5a, we note strong C-C covalent bonds with nearly identical C-C covalent "point attractors" at ELF=0.85. There are also Re-C covalent bonds manifested at ELF=0.55, although not as strong as C-C bonds. Similarly, for the Hex-II structure in Fig. 5b, the contours of the ELF domains on the (001)plane show nearly identical features as those in Hex-I structure: the strong Re-C covalent bonding.

4. Conclusion

In summary, we have presented a complete theoretical analysis of the structural, electronic, elastic, and chemical bonding properties of ReC₂ within five considered structures using firstprinciples calculations. All positive eigenvalues of the elastic constant matrix confirm that they are mechanically stable. The calculated elastic moduli and hardness demonstrated that these structures are ultra-incompressible and hard materials. Particularly, the bulk moduli of Tet-I and ReSi₂ structures are close to that of *c*-BN. The most energetically stable phase, Hex-I, which is dynamically stable and possesses the largest hardness (32.2 GPa) at ambient condition, and the experimental work is thus strongly recommended. The evidence of strong covalent bonding of C–C and Re–C, which play an important role to form an ultraincompressible material, is manifested by the partial DOS and ELF analysis. We expect that our calculations will stimulate extensive experimental efforts toward the synthesis of these novel materials.

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