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First principles calculation of electronic structure, chemical bonding and elastic properties of ultra-incompressible Re_2P

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Abstract: The electronic structures, chemical bonding and elastic properties of the Co_2P-type structure phase ultra-incompressible Re_2P (orthorhombic phase) were investigated by density-functional theory (DFT) within generalized gradient approximation (GGA). The calculated energy band structures show that the orthorhombic structure phase Re_2P is metallic material. The density of state (DOS) and the partial density of state (PDOS) calculations show that the DOS near the Fermi level is mainly from the Re-5d state. Population analysis suggests that the chemical bonding in Re_2P has predominantly covalent character with mixed covalent−ionic character. Basic physical properties, such as lattice constant, bulk modulus, shear modulus, and elastic constants C_{ij}, were calculated. The elastic modulus and Poisson ratio were also predicted. The results show that the Co_2P-type structure phase Re_2P is mechanically stable and behaves in a brittle manner.

Key words: Re_2P; first principles; electronic structures; chemical bonding; elastic properties

1 Introduction

The searching for new superhard and ultra-incompressible materials with prominent physical and chemical properties is one of the most attractive research fields [1−6]. Transition-metal (TM) borides, carbides and nitrides are of great interest and importance for their unique properties, such as good chemical stability, high strength, high hardness, high ultra-incompressibility, high melting point, low electrical resistivity and high thermal conductivity [7−13]. These properties are ascribed to the directional bonding in covalent networks of atoms coordinated by a small number of ligands with short interatomic distances, which consist of atoms with low *Z* elements, such as Be, B, C, N, O, Al, Si, or P.

However, there are few reports on the physical properties of hardness and incompressibility of materials with slightly heavier low *Z* elements (e.g., Si, P or S) in detail because the values for hardness and incompressibility are thought to be lower than the expected ones compared with the incorporation of B or N [14]. Recently, in situ high-pressure experiments and theoretical calculations have classified Co_2P-type structures phase Re_2P into the ultra-incompressible materials with a bulk modulus of above 300 GPa [14]. Despite the experimental and theoretical researches on Re_2P, few is known regarding the relationship of their chemical bonding and mechanical properties. Motivated by these observations, in this work, a systematic first principles study on the electronic structure, chemical bonding and elastic properties of the orthorhombic phase Re_2P.

2 Calculation details

The first principles calculations described here are based on DFT using a plan-wave expansion of the wave function [15,16]. The exchange correlation energy is calculated by the GGA with the Perdew−Burke−Ernzerhof (PBE) functionality [17]. The ionic cores are represented by ultra-soft pseudopotentials for Re and P

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atoms. The Re $5s^25p^65d^56s^2$ electrons and P $3s^23p^3$ electrons are explicitly treated as valence electrons. The Monkhorst and Pack scheme of k-point sampling is used for integration over the first Brillouin zone [18]. The cutoff energy is chose to be 500 eV, and the Brillouin-zone sampling k-point set mesh parameters are 6×8×3. The set of parameters assure the total energy convergence of 5.0×10^{-6} eV/atom, the maximum force of 0.01 eV/Å, the maximum stress of 0.02 GPa and the maximum displacement of 5.0×10^{-4} Å.

3 Results and discussion

3.1 Geometry and structure properties

The crystal structure of the Co_2P-type structure phase Re_2P belongs to the space group *Pnma* (No. 62, *Z*=4), which puckers Re−Re and Re−P strands in the [100] direction, straightens Re−Re−P stacking in the [001] direction and linear strands of Re and P atoms in the [010] direction as depicted in Fig. 1. There are inequivalent atomic positions: Re 1 at 4c site (0.8426, 1/4, 0.0744), Re 2 at 4c site (0.8462, 1/4, 0.7828), and P at 4c site (0.356, 1/4, 0.1425) [14]. The experimental lattice parameters are *a*=5.5464 Å, *b*= 2.9421 Å and *c*=10.0483 Å.

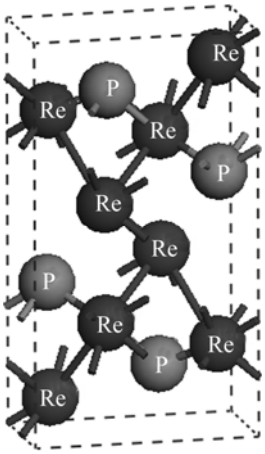

Fig. 1 Crystal structure of Re_2P

At the first stage, the full structural optimization of this phase is performed both over the lattice parameters and the atomic positions including the internal coordinate. The calculated optimization lattice parameters *a*, *b*, *c*, *V* and atomic coordinates compared with available experimental data [14] for Re_2P are summarized in Table 1, which shows that the calculated values by GGA are in agreement with the available experimental and theoretic data.

3.2 Electronic and chemical bonding

The calculated energy band structure of Re_2P along with the high-symmetry points of the Brillouin-zone by GGA shows that the energy band curves pass through Fermi energy (E_F) level (Fig. 2(a)), indicating that Re_2P is metallic compound. The total densities of states (TDOS) and partial densities of states (PDOS) for Re_2P are plotted in Fig. 2(b). The DOS at the Fermi level (E_F) locates at the bottom of a valley and originates mainly from the Re-5d electrons.

The Mulliken bond population is useful for evaluating the bonding character in a material. A high value of the bond population indicates a covalent bond, and a low value indicates an ionic bond. Positive and negative values indicate bonding and anti-bonding states, respectively [19,20]. The Mulliken atomic population of Re_2P reported in Table 2 shows a significant charge transfer between Re and P, indicating the ionic character of Re and P. The bond population reported in Table 3 shows the strong covalent character of $P—Re_2^{II}$. The chemical bonding in Re_2P has predominantly covalent character with mixed covalent- ionic character.

3.3 Elastic properties

Elastic properties are very important for materials because they provide information on interatomic potentials and relate to various fundamental solid state phenomena such as interatomic bonding, equations of state, phonon spectra as well as specific heat, thermal expansion, and Debye temperature [21,22].

Elastic constants are defined by means of a Taylor expansion of the total energy, namely, the derivative of the energy as a function of a lattice strain [15,16]. The orthorhombic phase Re_2P crystal has nine independent single crystal elastic constants, C_{11}, C_{22}, C_{33}, C_{44}, C_{55}, C_{66}, C_{12}, C_{13} and C_{23} [23]. The C_{ij} value calculated by GGA are presented in Table 4. For the orthorhombic crystal, its mechanical stability requires that its independent elastic constants should satisfy the Born's stability criteria [23]

Table 1 Calculated lattice parameters and atomic internal coordinate compared with available experimental and theoretic (PDF-PBESOL) data [14] for Re_2P

Method	*a*/nm	*b*/nm	*c*/nm	V/nm^3	x_P	z_P	$x_{Re1/Re2}$	$z_{Re1/Re2}$
Experiment	0.55464	0. 29421	1.00483	0.16397	0.356	0.1425	0.8426/0.8462	0.0744/0.7828
PBESOL	0.55203	0.29215	0.99916	0.16115	0.4032	0.1016	0.8258/0.8539	0.0647/0.7862
GGA-USP	0. 55591	0.29501	1.01268	0.16607	0.4026	0.1015	0.8248/0.8524	0.0643/0.7870

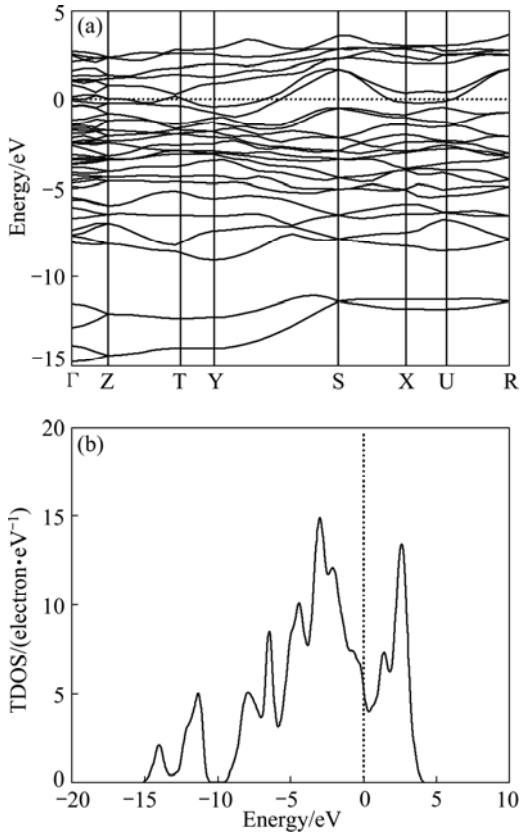

Fig. 2 Band structure calculated by GGA of Re_2P along some high-symmetry lines in Brillouin zone (a) and TDOS of Re_2P (b) (zero of energy is at Fermi level)

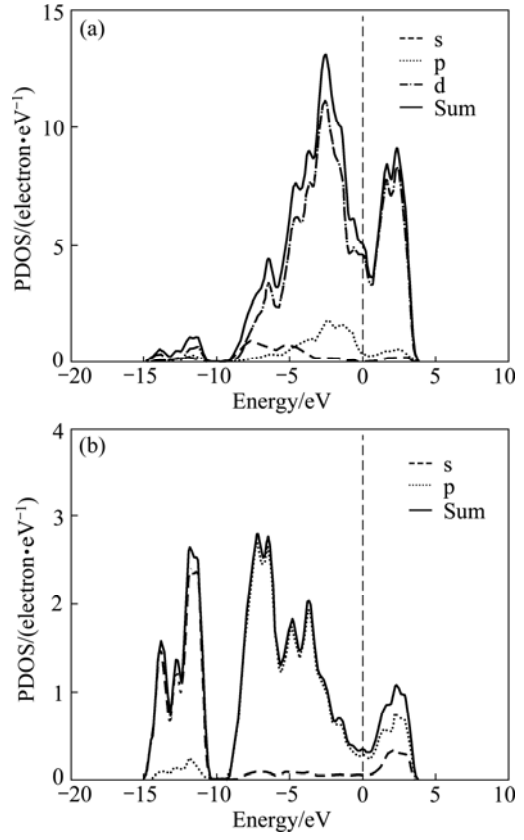

Fig. 3 PDOS of Re (a) and P (b) of Re_2P calculated by GGA

Table 2 Mulliken atomic population of Re_2P calculated by GGA-USP

Species	s	p	d	Total	Charge/e
P	1.48	3.14	0.00	4.62	0.38
Re1	2.57	6.86	5.73	15.16	−0.16
Re2	2.57	6.87	5.78	15.22	−0.22

Table 3 Mulliken bond population of Re_2P calculated by GGA-USP

Bond	Population	Length/nm	Bond	Population	Length/nm
P—Re_2^{II}	1.04	0.233606	Re_1—Re_2^{II}	−0.08	0.276790
P—Re_1	0.20	0.237747	Re_1—Re_1^{II}	−0.83	0.276892
P—Re_1^{II}	0.43	0.256823	Re_1—Re_2	−0.91	0.281251
P—Re_2^{I}	0.17	0.274963	Re_1—Re_2^{I}	−0.05	0.286899
P—P^{II}	-0.08	0.275293	Re_2—Re_2^{I}	−1.35	0.287893

Symmetric code I: $-x$+0.5, $-y$, z+0.5; II: $-x$,y +0.5, $-z$; III: x+0.5, y, $-z$+0.5.

$$C_{ii}>0, i=1-6,$$
$$C_{11}+C_{22}-2C_{12}>0,$$
$$C_{22}+C_{33}-2C_{23}>0,$$
$$C_{11}+C_{33}-2C_{13}>0,$$
$$C_{11}+C_{22}+C_{33}+2(C_{12}+C_{13}+C_{23})>0,$$
$$(C_{12}+C_{13}+C_{23})/3<B_0<(C_{11}+C_{22}+C_{33})/3,$$
$$B_0=(C_{11}+C_{22}+C_{33}+2C_{12}+2C_{13}+2C_{23})/9 \quad (1)$$

From Table 4, it can be seen that these criteria are all satisfied, indicating that Re_2P is mechanically stable. The single crystal bulk modulus B is about 294.42 GPa, which is very close to the experimental result [14]. The polycrystal bulk modulus B and shear modulus G are estimated by the Voigt−Reuss−Hill approach in the following forms [23−25]:

$$B_H=(B_R+B_V)/2,\quad G_H=(G_R+G_V)/2 \quad (2)$$

Elastic modulus E and Poisson ratio v are estimated as follows:

$$E=9BG/(3B+G),$$
$$v=(3B-E)/6B=(3B-2G)/(6B+2G) \quad (3)$$

All the calculated results are presented in Table 5. It can be seen that the value of B_H/G_H ratio for Re_2P is 1.62, which is smaller than the critical value (1.75) separating ductile and brittle materials [23−28], indicating that Re_2P behaves in a brittle manner.

It is known that the value of the Poisson ratio (v) is the minimal for covalent materials (v=0.1), and increases for ionic systems [29]. In our case, the calculated Poisson ratio is 0.2426, which means a sizable ionic contribution in intra-bonding.

The elastic anisotropy in compressibility (A_B) and shear (A_G) using the model in Ref. [30] for polycrystalline materials is

Table 4 Calculated single crystal elastic constants C_{ij}, bulk modulus B and compressibility coefficient β of Re_2P

Method	C_{11}	C_{22}	C_{33}	C_{44}	C_{55}	C_{66}	C_{12}	C_{13}	C_{23}	B/GPa	β
Experiment										304	
PBESOL										323	
GGA-USP	638.44	474.62	485.61	205.36	196.53	174.20	196.56	187.11	169.92	294.42	0.0034

Table 5 Calculated polycrystalline elastic constants, elastic modulus E, Poisson ratio v and B_H/G_H of Re_2P by GGA-USP

B_V/GPa	B_R/GPa	B_H/GPa	G_V/GPa	G_R/GPa	G_H/GPa	B_H/G_H	E/GPa	v
300.65	294.42	297.53	184.89	182.23	183.56	1.62	459.49	0.2426

$$A_B = (B_V - B_R)/(B_V + B_R)$$
$$A_G = (G_V - G_R)/(G_V + G_R) \quad (4)$$

A value of zero represents elastic isotropy and a value of 1 is the largest possible anisotropy. The calculated polycrystalline elastic anisotropy in bulk modulus A_B is 0.01047 and shear modulus A_G is 0.00725. Both the A_B and A_G are very small. The small anisotropy may minimize cracking propagation during sample preparing and using.

4 Conclusions

1) The GGA calculated structural parameters of the orthorhombic phase Re_2P are in agreement with the available experimental and theoretic data.

2) The electronic band structures and DOS present that Re_2P is a metallic material. The DOS and the PDOS calculations show that the DOS near the Fermi level is mainly from the Re-5d state.

3) The chemical bonding analysis shows that Re_2P is mainly covalent character with mixed covalent-ionic character. The hard and the ultra-incompressible characteristic of Re_2P is ascribed to the mixed covalent-ionic chemical bonding.

4) The elastic constants were calculated and the bulks and shear modulus, elastic modulus, Poisson ratio were derived. All results show that Re_2P is mechanically stable and behaves in a brittle manner.

5) The calculated polycrystalline elastic anisotropy in bulk modulus and anisotropy in shear modulus show that orthorhombic phase Re_2P is less anisotropy.

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极端不可压缩 Re_2P 的电子结构、化学键及弹性性质的第一性原理研究

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摘 要：利用基于密度泛函理论(DFT)的广义梯度近似(GGA)，研究 Co_2P 类型结构的极端不可压缩 Re_2P 的电子结构、化学键和弹性性质。能带结构显示 Re_2P 为金属性材料；态密度和分态密度的计算结果表明，费米能级附近的态密度主要来自 Re-5d 态；布居分析表明 Re_2P 中的化学键具有以共价性为主的混合离子−共价特征。计算得到 Re_2P 的晶格参数、体模量、剪切模量和单晶的弹性常数，由此导出弹性模量和泊松比。结果表明，Re_2P 是力学稳定的，且具有一定的脆性。

关键词：Re_2P；第一性原理；电子结构；化学键；弹性性质

(Edited by Hua YANG)