1. Introduction

Among the platinum group metals, Rh has the smaller density and better oxidation resistance with a high melting temperature, ensuring it as a promising candidate for industry applications such as developing refractory superalloys. During the past decades, Rh-based alloys have received great research interest due to these properties among all the metals, e.g. high melting temperature, the highest corrosion resistance and high strength. Meanwhile, Hf is used extensively as an alloying element in transition metal-based superalloys, which are designed to withstand high temperatures and pressures. Hf is a useful addition to transition metals, in which it can form the second phase to improve a material’s strength under extreme conditions. The investigations on Hf–Rh systems should be of critical importance, which has attracted attention with respect to the superalloys, the occurrence of superconductivity, the amorphization behavior and the electrocatalytic hydrogen production ability of Hf–Rh alloys.

The Hf–Rh phase diagram was studied by Waterstrat et al., and suggested the existence four types of binary compounds, i.e., Hf$_2$Rh, HfRh, Hf$_3$Rh$_5$ and HfRh$_3$. Lately, Eremenko et al. reassessed this diagram, and reported seven intermediated phases in this system, including Hf$_2$Rh, HfRh (with three types of polymorphs), Hf$_3$Rh$_4$, Hf$_3$Rh$_5$ and HfRh$_3$. Based on published results, Okamoto et al. has reviewed the Hf–Rh phase diagram, and determined the crystal structure of several binary Hf–Rh compounds. Hf$_2$Rh and Hf$_3$Rh$_5$ should form peritectically at 1723 K and 2168 K and have Ti$_3$Ni- and Ge$_3$Rh$_5$-type structures, respectively. Besides, HfRh$_3$ has a cubic L1$_2$ type structure, and can melt congruently at 2278 K at the stoichiometric composition. In addition, the equiatomic HfRh phase has a more complex situation. Initially, the high temperature δ (B2) HfRh phase is confirmed, and should melt congruently at 2453 K at the stoichiometric composition. Secondly, the δ’ (L1$_0$) HfRh phase is proposed to be stable at medium temperature from ~873 K to 973 K. Still, there is a low temperature δ” HfRh phase existing below ~873 K without informing of the crystal structure. The similar situation has also occurred in Hf$_2$Rh$_4$, which should form peritectically at 1718 K and lack of structure information.

Although the Hf–Rh system has been studied for a long time, it is believed that the systematically theoretical study on Hf–Rh system discussing and revealing the crystal structure to
unknown HfRh and Hf$_x$Rh$_y$ phases has been eluded. Also, the experimental studies are also limited. The reliable information, such as formation enthalpies, and elastic properties (i.e., elastic constant, and bulk/shear/Young’s modulus) are lacking. Intensive studies are also required to clarify the phase and mechanical stability and the properties of the binary compounds. Therefore, a comprehensive investigation of the ground-state phase stability, elastic and electronic properties of Hf–Rh compounds using first-principles calculations based on the density functional theory (DFT) has been performed in this work. In Section 2, the computational strategies are presented in detail. The calculated results are discussed and compared with the available experimental and theoretical results in Section 3. Finally, the conclusions are summarized in Section 4.

2. Computational methods

All theoretical calculations were carried out by a first-principles plane-wave pseudopotential method based on DFT through the CASTEP package$^{27}$ in the current work. The ultrasoft pseudo-potential was used to model the ion–electron interaction.$^{18}$ The generalized gradient approximation (GGA) with the Perdew–Burke–Ernzerhof (PBE) exchange–correlation functional was utilized.$^{19–21}$ The states of Hf5d$^6$6s$^2$ and Rh4d$^5$5s$^1$ were taken as the basis set in the calculations. The kinetic cutoff energy for plane waves was settled at 400 eV. The special points sampling integration over the Brillouin zone was employed by using the Monkhorst–Pack method$^{22}$ with determined $k$-point separation of 0.02 Å$^{-1}$ in three lattice directions for each structure. The Pulay scheme of density mixing was applied for the evaluation of energy and stress.$^{23,24}$ The optimization of atom coordinates and lattice constants were made by minimization of the total energy. The Broyden–Fletcher–Goldfarb–Shanno (BFGS) minimization scheme was used in the geometry optimization.$^{25}$

The tolerances of the geometry optimization were set as follows: the difference of the total energy within 0.001 eV per cell, maximum ionic force within 100 eV Å$^{-1}$, maximum ionic displacement with 100 Å, and maximum stress within 100 GPa. The calculation of total energy and electronic structure were followed by cell optimization with SCF tolerance of $1.0 \times 10^{-4}$ eV per cell. The total energies and the density of states (DOS) under the optimized structures were calculated by means of the corrected tetrahedron Böchl method.$^{26}$

From the view of thermodynamics, the formation enthalpy ($H_f$) is defined as the total energy difference between the compound and its constituents in proportion to the composition. The formation enthalpy ($H_f$) is calculated by the following equation:

$$H_f = \frac{1}{a + b} \left( E_{\text{total}} - aE_{\text{Hf}}^{\text{solid}} - bE_{\text{Rh}}^{\text{solid}} \right) \quad (1)$$

where $E_{\text{total}}$ is the total energy of the unit cell, $a$ (or $b$) is the atom number of Hf (or Rh) in a unit cell, and $E_{\text{Hf}}^{\text{solid}}$ (or $E_{\text{Rh}}^{\text{solid}}$) is the energy per Hf (or Rh) element in the solid state of the crystal structure. During the calculation for $E_{\text{Hf}}^{\text{solid}}$ and $E_{\text{Rh}}^{\text{solid}}$, Hf and Rh are HCP and FCC structure, respectively. The formation enthalpy ($H_f$) is used to evaluate the thermodynamic stability of the compound. The lower $H_f$ value represents the better thermodynamic stability.

3. Results and discussion

3.1 Crystal structure and stability

Based on the former studies, five chemical compositional Hf$_x$Rh$_y$ compounds (i.e., Hf$_2$Rh, HfRh, Hf$_3$Rh$_4$, Hf$_5$Rh$_3$, and HfRh$_3$) are adopted. The Ti$_2$Ni-type Hf$_2$Rh, Ge$_3$Rh$_2$-type Hf$_5$Rh$_3$, and L1$_2$HfRh$_3$ are used in accordance with the experimental observations. The optimized lattice constants for these compounds are listed in Table 1, along with published lattice constants for comparison from experimental (Ti$_2$Ni-type Hf$_2$Rh$^{27}$, Ge$_3$Rh$_2$-type Hf$_5$Rh$_3$,$^{28}$ L1$_2$HfRh$_3$ (ref. 29)) and theoretical (Ti$_2$Ni-type Hf$_2$Rh$^9$ and L1$_2$HfRh$_3$ (ref. 4, 5 and 30)) results at the ground state. For these three compounds, the differences between the optimized and experimental lattice constants are small accordingly. Thus, the reliability of our calculation method and the chosen parameters have been confirmed, which also assure the credibility of subsequent results.

For HfRh, Ramam et al.$^{14}$ reported the L1$_0$HfRh was stable at lower temperature, and B2 HfRh was observed at higher temperatures experimentally. Waterstrat et al.$^{16}$ confirmed the existence of B2 HfRh, and also reported the occurrence of "tetragonally distorted" B2 phase (Hf$_4$Rh$_{34}$, a = 3.268 Å, c = 3.150 Å; Hf$_5$Rh$_{35}$, a = 3.12 Å, c = 3.418 Å). Such phase was ascribed to the L1$_0$HfRh in the Hf–Rh phase diagram generalized by Okamoto.$^{16}$ In addition, Waterstrat et al.$^{16}$ also considered the possible formation of Hf$_2$Rh phase in the ZrIr-type$^{12}$ and/or NbRu-type (Hf$_2$Rh$_{58}$; a = 4.392 Å, b = 4.306 Å, c = 3.470 Å (ref. 12)) crystal structures.

About the ZrIr-type structure, an earlier X-ray diffraction (XRD) study suggested the ZrIr-type compound may have either B27 or B33 structure.$^{31}$ In disagreement with this analysis, Semenova et al.$^{32}$ identified the structure as a monoclinic TiNi (B19$^\prime$)-type. However, Waterstrat et al.$^{33}$ considered that the ZrIr-type compound should be a new orthorhombic structure that was resembling to the DyGe$_3$ structure. Stalick et al.$^{34}$ agreed this idea and determined the crystal structure of orthorhombic ZrIr compound using powder neutron diffraction data. Through first-principles calculations, Chen et al.$^{35}$ theoretically computed the structural properties of ZrIr compound with the B19$^\prime$, B27, B33 and ZrIr-type (from ref. 34) structures, and found the calculated lattice constants of ZrIr-type phase were in good agreement with the available experimental results. Therefore, the crystal information of the original ZrIr-type phase is adopted from ref. 34.

Regarding the NbRu-type structure, it is suggested to be an orthorhombic structure.$^{36–41}$ However, its crystal structure has ever reached consensus yet. For example, Mitari et al.$^{39}$ studied the crystal structure of NbRu-type IrTi using XRD analysis experimentally and refined the structure with ab initio calculation theoretically. They proposed that the NbRu-type structure has space group $Cmcm$ (65), and the atomic positions: Nb (1) 0.0 0.5 0.0, (2) 0.5 0.0 0.0; Ru (1) 0.0 0.0 0.5, (2) 0.5 0.5 0.5. Shao et al.$^{40}$ discussed the structural, thermodynamic and elastic
properties of NbRu, and found the Pnma (62)/B27 NbRu structure was both thermodynamically and mechanically stable at the ground state. As a result, both Cmmm (65) and Pnma (62) structures are used for structural optimization in this work. The obtained equilibrium lattice constants for Cmmm (65) HfRh and Pnma (62) HfRh are shown in Table 1. Clearly, the Cmmm (65) HfRh is more approaching to the experimentally reported NbRu-type HfRh (Hf$_{54}$Rh$_{35}$; $a$ = 4.392 Å, $b$ = 4.306 Å, $c$ = 3.470 Å (ref. 12)), indicating that Cmmm (65) NbRu structure is more probable.

Resultantly, the HfRh is theoretically inclined to form the crystal structure in the following sequence of ZrIr-type > L1$_0$ > B2 > B27 > B33 > B19 > B11 structures based on the $H_f$ values. Our results show good accordance with the experimental observations. For instance, Okamoto et al. generalized Hf–Rh phase diagram based on the available experimental data, and concluded there were three phases for equiatomic HfRh, including the high temperature $\delta$ (B2) phase, medium temperature $\delta'$ (L1$_0$) phase, and low temperature unknown $\delta''$ phase. Basically, the lower temperature phase at the ground state should possess the more negative $H_f$ value.$^{42,43}$ Therefore, the $H_f$ values for HfRh phases are in the order of $\delta''$ > L1$_0$ > B2 structures. Theoretically, Xing et al.$^{44}$ suggested the thermodynamic stability of HfRh was in the order of B33 > L1$_0$ > B2 > B19 structure. However, the B33 structure phase has ever reported for HfRh. Similarly, Levy et al.$^{44}$ considered the Pnma (B27) HfRh should be more stable than the B2 type, where they did not provide lattice constants for evaluation. Nevertheless, we have proved Pnma (B27) HfRh is less possible to form as the NbRu-type structure (Table 1). Conclusively, it is suggested that the unknown $\delta''$ phase at low temperature should be ZrIr-type, which also corresponds to Waterstrat’s work,$^{19}$ and the HfRh phases are able to crystallize in the order of ZrIr-type > L1$_0$ > B2 structures.

For Hf$_4$Rh$_{14}$, the Pu$_3$Pd$_4$, Ta$_3$B$_4$, Ti$_3$Cu$_4$, C$_2$Al$_4$, Co$_3$S$_4$, Th$_3$P$_4$-type structure are considered. Co$_3$S$_4$ and Th$_3$P$_4$-type Hf$_4$Rh$_{14}$ are unlikely to more due to their positive $H_f$ values. The Pu$_3$Pd$_4$-type Hf$_4$Rh$_{14}$ should be the favored crystal structure with the most negative $H_f$ value. This is similar to Zr$_3$Rh$_{14}$ which also possesses the Pu$_3$Pd$_4$-type structure.$^{45}$
Fig. 1 exhibits the convex hull plot of the formation enthalpies of binary Hf–Rh compounds calculated at the ground state, along with the theoretical values from Levy’s work,44 Miedema’s model,36 Koteski’s work46 and Xing’s work,39 and experimental values from Guo’s work49 and Gachon’s work.51 For Hf2Rh, our calculated value is $-0.6538$ eV per atom, agreeing well with the experimental value of $-0.6934 \pm -0.0156$ eV per atom (ref. 51) and theoretical value of $-0.64$ eV per atom.44 About HfRh, our calculated value is $-0.791$ eV per atom, which is in good accordance with the theoretical value of $-0.762$ eV per atom (ref. 44) and $-0.891$ eV per atom.39 All these values are a bit larger than the experimental value of $-0.6603 \pm -0.0125$,31 although this experimental value is based on the phase $\text{Rh}_{0.79}\text{Hf}_{0.21}$. In addition, the enthalpies of formation for other six Hf–Rh phases fall on a common straight line, implying that the concentrations ranges for different compounds are quite narrow. Comparably, the convex hull plot of Miedema’s model shows the lowest point of $H_f$ values at the HfRh phase. However, the convex hull plots of this theoretical work, Levy’s theoretical work44 and Gachon’s experimental work49 have complied well with each other, and exhibited the similar contours, where the Hf3Rh5 compound has the most negative $H_f$ value, signifying it is the most stable phase among binary Hf–Rh compounds.

### 3.2 Mechanical properties

To investigate the mechanical stability and elastic properties, the single-crystal elastic constants of the binary Hf–Rh phases, as well as pure Hf and Rh, are calculated by the stress–strain method at their optimized structures. To calculate the elastic constant ($C_{ij}$), a deformed cell is introduced. The elastic strain energy is presented as following:44

$$U = \frac{\Delta E}{V_0} = \frac{1}{2} \sum_i \sum_j C_{ij} \varepsilon_i \varepsilon_j \quad (2)$$

where $\Delta E$ is the energy difference; $V_0$ is the volume of unit cell; $C_{ij}$ ($i, j = 1, 2, 3, 4, 5$ and $6$) is the elastic constant; $\varepsilon_i$ and $\varepsilon_j$ are the applied strains.

Using the stress–strain methods, the single-crystal elastic constants for seven Hf–Rh binary intermetallics and pure Hf and Rh metals have been derived and summarized in Table 2, in comparison with the available experimental and theoretical values. For pure Hf and Rh metals, our calculated elastic constants are in good agreement with experimental and theoretical values. It has thus indicated the calculation method adopted in the work is effective to predict the elastic properties of metallic compounds. For HfRh, the derived elastic constants are in good agreement with the available theoretical values.4 However, the experimental and theoretical elastic constants for other six Hf–Rh compounds are not available to the best of our

<table>
<thead>
<tr>
<th>Compound</th>
<th>$C_{11}$</th>
<th>$C_{22}$</th>
<th>$C_{33}$</th>
<th>$C_{44}$</th>
<th>$C_{55}$</th>
<th>$C_{66}$</th>
<th>$C_{12}$</th>
<th>$C_{13}$</th>
<th>$C_{23}$</th>
<th>$C_{14}$</th>
<th>$C_{15}$</th>
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<td>205.2</td>
<td>56.4</td>
<td>82.7</td>
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<td>197.0</td>
<td>55.7</td>
<td>77.0</td>
<td>66.0</td>
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<td>Hf$_2$Rh</td>
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<tr>
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<td>243.7</td>
<td>277.9</td>
<td>85.7</td>
<td>92.5</td>
<td>60.6</td>
<td>135.5</td>
<td>161.1</td>
<td>132.4</td>
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<td>69.1</td>
<td>165.7</td>
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<td>304.6</td>
<td>301.2</td>
<td>96.1</td>
<td>85.1</td>
<td>47.6</td>
<td>116.2</td>
<td>149.8</td>
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<td>Hf$\text{Rh}_4$</td>
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<td>144.3</td>
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<tr>
<td>Rh</td>
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<td>171.7</td>
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<td>172.0</td>
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<tr>
<td>Ref. 4 (theo. values)</td>
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<td>171.0</td>
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knowledge. Therefore, our calculated elastic constants for Hf₂Rh, ZrIr-HfRh₃, L₁₀-HfRh₃, B₂-HfRh₃, Hf₅Rh₄, and Hf₃Rh₅ compounds should provide useful data for comparison in future experimental and theoretical studies.

In order to evaluate the phase stability of the compound, the mechanical stability is analyzed in combination of the elastic constant and Born’s stability criteria.⁵⁷ For a stable crystalline structure, the elastic constant should satisfy the Born’s criteria to prove its mechanical stability. In terms of seven binary Hf–Rh intermetallics considered in this work, Hf₂Rh, B₂-HfRh₃, and HfRh₃ are ascribed to the cubic structure, ZrIr-HfRh and Hf₃Rh₅ have the orthorhombic structure, and Hf₅Rh₄ and L₁₀-HfRh₃ possess the trigonal and tetragonal structure, respectively.

For the cubic crystal, there are three independent elastic constants. The mechanical stability criteria are provided in the following equation:⁶⁸⁻⁶⁹

\[
C_{11} > 0; \ C_{44} > 0; \ C_{11} > |C_{12}|; \ C_{11} + 2C_{12} > 0
\]  (3)

In Table 2, the elastic constants of the cubic Hf₂Rh, B₂-HfRh₃, and HfRh₃ crystals can satisfy the above criteria accordingly, confirming their mechanically stability.

Regarding the orthorhombic phase, it has nine independent elastic constants, and the restrictions of mechanical stability for are presented the following equation:

\[
C_{11} > 0; \ C_{22} > 0; \ C_{33} > 0; \ C_{44} > 0; \ C_{55} > 0; \ C_{66} > 0; \ C_{11} + C_{22} + C_{33} + 2(C_{12} + C_{13} + C_{23}) > 0; \ C_{11} + C_{22} - 2C_{12} > 0; \ C_{11} + C_{33} - 2C_{13} > 0; \ C_{22} + C_{33} - 2C_{23} > 0
\]  (4)

It is seen that the elastic constants for ZrIr-HfRh and Hf₃Rh₅ can both meet the restrictions of mechanical stability, implying both compounds are mechanically stable.

About the trigonal Hf₃Rh₄ phase with seven independent elastic constants, the mechanical stability criteria are included in the following formula:⁴⁴

\[
C_{11} > 0; \ C_{33} > 0; \ C_{44} > 0; \ C_{11} > |C_{12}|; \ (C_{11} + C_{12})C_{33} - 2C_{13}^2 > 0; \ (C_{11} - C_{12})C_{44} - 2C_{14}^2 > 0
\]  (5)

Clearly, all the elastic constants of Hf₃Rh₄ exhibited in Table 2 can satisfy Born’s criteria for mechanical stability.

For the tetragonal crystal, the stability criteria are shown in the following formula:⁴¹

\[
C_{11} > 0; \ C_{33} > 0; \ C_{44} > 0; \ C_{66} > 0; \ C_{11} - C_{12} > 0; \ C_{11} + C_{33} - 2C_{13} > 0; \ 2(C_{11} + C_{12}) + C_{33} + 4C_{13} > 0
\]  (6)

Through the validation of the formula (6), the L₁₀-HfRh₃ phase has six independent elastic constants to ensure its mechanical stability.

Conclusively, the seven Hf–Rh intermetallics considered, i.e., Hf₂Rh, ZrIr-HfRh₃, L₁₀-HfRh₃, B₂-HfRh₃, Hf₅Rh₄, Hf₅Rh₃, and HfRh₃, are all suggested mechanically stable.

The elastic constants C₁₁, and C₃₃ should characterize the x direction and z direction resistances to linear compression, respectively.⁶⁸⁻⁶⁹ In Table 2, the ZrIr-HfRh and Hf₅Rh₄ have larger C₃₃ values, indicating their higher incompressibility under the z direction uniaxial stress. In Hf₅Rh₃, it is more compressible along z direction than that along x direction due to the larger C₁₁ value. In the case of C₄₄, it is interpreted as the resistance to monoclinic shear in the (100) plane, and is the critical parameter relating to the shear modulus.⁶⁸⁻⁶⁹ In Table 2, the largest C₄₄ for HfRh₃ has suggested that HfRh₃ has the strongest resistance to shear in the (100) plane, while Hf₅Rh₃ has the smallest C₄₄ to show the weakest resistance to shear in the (100) plane.

Based on the single-crystal elastic constant, three types of algorithms corresponding to different bounds are adopted to estimate elastic properties of polycrystalline materials. In detail, the Voigt/Reuss method is the larger/smaller value of the actual effective modules on the assumption of uniform strain/stress imposed on the polycrystalline structure. For the cubic structure, the upper and the lower bounds for the bulk (B) and shear (G) modulus related to Voigt and Reuss methods are exhibited in the formula (7-1) to (7-3):⁶⁹

\[
B_v = B_R = \frac{1}{3}(C_{11} + 2C_{12}) \quad (7-1)
\]

\[
G_v = \frac{1}{5}(C_{11} - C_{12} + 3C_{44}) \quad (7-2)
\]

\[
G_R = \frac{5(C_{11} - C_{12})C_{44}}{4C_{44} + 3(C_{11} - C_{12})} \quad (7-3)
\]

Furthermore, the equations used to compute the upper and the lower bounds for the bulk and shear modulus with orthorhombic, trigonal and tetragonal structures can be referred to the ref. 60, 61 and 42, accordingly.

In addition, the arithmetic average of Voigt and Reuss bounds is termed as the Voigt–Reuss–Hill (VRH) method.⁶⁸ Using the VRH averaging method, the bulk modulus (B) and shear modulus (G) are calculated in the eqn (8):

\[
B = \frac{1}{2}(B_R + B_v) \quad (8-1)
\]

\[
G = \frac{1}{2}(G_R + G_v) \quad (8-2)
\]

Young’s modulus (E) and Poisson’s ratio (ν) are also major elasticity related parameters, which can be calculated using the following formula:

\[
E = \frac{9BG}{3B + G} \quad (9-1)
\]

\[
\nu = \frac{3B - 2G}{2(3B + G)} \quad (9-2)
\]

The calculated polycrystalline bulk modulus, shear modulus, Young’s modulus, Poisson’s ratio and B/G values for seven Hf–Rh compounds and pure Hf/Rh metals using VRH methods are calculated and tabulated in Table 3. For pure Hf and Rh metals, the obtained elastic properties are in good agreement with the
published experimental\textsuperscript{55,56} and theoretical\textsuperscript{4} values, validating the precision of the predicted elastic properties of metallic materials.

The bulk modulus is a measure of resistance to volume change under external pressures. From Table 3, it is observed that the HfRh3 has the strongest resistance to volume change by applied pressure, while Hf2Rh owns the smallest. In addition, the bulk modulus has also been deemed as the measure of the average bond strength of atoms, and Hf2Rh should be the weakest one. In addition, the B2- and L10-HfRh phases have the similar bulk moduli, and both are a bit larger than the ZrIr-HfRh (Table 3). For Hf2Rh, B2-HfRh and HfRh3, the calculated bulk moduli are in good agreement with those theoretical values for Hf2Rh (Cavor’s work\textsuperscript{69}), B2-HfRh (Nova-kovic’s work\textsuperscript{70}), and HfRh3 (Chen’s\textsuperscript{4} and Surucu’s\textsuperscript{5} work), accordingly. Notably, the theoretical bulk modulus for HfRh3 reported by Rajagopalan\textsuperscript{71} is much larger than other available values, which requires further scrutinizing.

When ZrIr-type HfRh is considered, the relationship between bulk modulus and atomic concentration of Rh has been exhibited in Fig. 2. It is seen that the bulk moduli of Hf–Rh compounds are linearly rising with the increasing Rh atomic concentration (at%), and the fitting line is $y = 117.96 + 1.357x$ with $R^2 = 0.9961$. It is noteworthy that the $R^2$ is quite small to assure the precision of the fitted relationship.

The shear modulus is a measure of resistance to reversible deformations over the shear stress. In Table 3, the HfRh3 has the strongest resistance to reversible deformations over the shear stress, and Hf2Rh possesses the smallest among Hf–Rh compounds. Furthermore, the B2- and L10-HfRh phases have the similar shear moduli, and both are smaller than the ZrIr-HfRh (Table 3). Regarding the Young’s modulus, it represents the stiffness of materials. Overall, HfRh3 owns the largest, and Hf2Rh3 has the smallest Young’ modulus among the Hf–Rh compounds (Table 3). It means HfRh3 and Hf2Rh3 are the most and least stiffest phases among binary Hf–Rh intermetallics, respectively. Besides, the ZrIr-HfRh has the larger Young’s modulus than both B2- and L10-HfRh phases (Table 3). Generally, the calculated shear and Young’s moduli are both in well compliance with those theoretical values for HfRh3 (Chen’s\textsuperscript{4} and Surucu’s\textsuperscript{5} works).

The obtained shear modulus and Young’s modulus are depicted as a function of Rh atomic concentration in Fig. 3a and b, respectively. Since there is not explicit relationship shown in each figure, the connecting lines are only used as the guide for observation in both figures. However, the variations of shear modulus (Fig. 3a) and Young’s modulus (Fig. 3b) have exhibited the similar tendencies with increasing Rh concentration, if the ZrIr-HfRh is selected. Therefore, the relationship between shear modulus ($G$) and Young’s modulus ($E$) has been constructed, as shown in Fig. 3c, showing that $E$ has linearly increased with the growing $G$. The linear relation can be formulated as $E = 13.523 + 2.443G$. Clearly, the $R^2$ of the fitted line is 0.9989, which implies good relationship between these two factors.

Poisson’s ratio ($v$) is used to quantify the stability of the crystal against shear deformation, which usually ranges from $-1$ to 0.5.\textsuperscript{72-73} The larger Poisson ratio signifies the better plasticity in materials. The Poisson’s ratio for ductile materials is larger than 0.26, while the value of brittle materials is less than 0.26.\textsuperscript{74} For binary Hf–Rh intermetallics, they are all ductile materials (Table 3). The hardest HfRh3 phase has the Poisson’s ratio of 0.282, while the comparatively softest compound of Hf2Rh3 owns a higher Poisson’s ratio of 0.405. Poisson’s ratio also provides useful information about the characteristic of bonding forces in solids.\textsuperscript{75-76} The lower and upper limits for central force solids are 0.25 and 0.5, respectively. In this work, the Poisson’s ratio for binary Hf–Rh compounds are larger than the lower limit 0.25, indicating that the interatomic forces in these intermetallics are all central forces.

The ratio of shear modulus to bulk modulus ($B/G$) has been proposed to estimate brittle or ductile behavior of materials.\textsuperscript{77} A

![Graph showing the calculated bulk modulus (B) versus atomic concentration of Rh for the binary Hf–Rh compounds.](image-url)

**Table 3** The polycrystalline bulk modulus ($B$), shear modulus ($G$), Young’s modulus ($E$), Poisson’s ratio ($v$), and $B/G$ ratio for binary Hf–Rh compounds and pure Hf/Rh metals deduced from the VRH method.

<table>
<thead>
<tr>
<th>Compound</th>
<th>B (GPa)</th>
<th>G (GPa)</th>
<th>E (GPa)</th>
<th>v</th>
<th>B/G</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hf</td>
<td>118.5</td>
<td>57.2</td>
<td>147.9</td>
<td>0.292</td>
<td>2.070</td>
</tr>
<tr>
<td>Ref. 55 (exp. values)</td>
<td>108.5</td>
<td>55.8</td>
<td>142.9</td>
<td>0.280</td>
<td>1.944</td>
</tr>
<tr>
<td>HfRh</td>
<td>165.4</td>
<td>57.5</td>
<td>154.5</td>
<td>0.344</td>
<td>2.877</td>
</tr>
<tr>
<td>Ref. 40 (theo. values)</td>
<td>148.7</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>HfRh (ZrIr)</td>
<td>183.8</td>
<td>70.5</td>
<td>187.5</td>
<td>0.330</td>
<td>2.609</td>
</tr>
<tr>
<td>HfRh (L10)</td>
<td>188.2</td>
<td>52.0</td>
<td>142.7</td>
<td>0.374</td>
<td>3.622</td>
</tr>
<tr>
<td>HfRh (B2)</td>
<td>188.8</td>
<td>52.3</td>
<td>143.7</td>
<td>0.373</td>
<td>3.61</td>
</tr>
<tr>
<td>Ref. 48 (theo. values)</td>
<td>173.0</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Hf2Rh</td>
<td>192.9</td>
<td>39.3</td>
<td>110.3</td>
<td>0.405</td>
<td>4.913</td>
</tr>
<tr>
<td>Hf2Rh3</td>
<td>200.3</td>
<td>76.2</td>
<td>202.8</td>
<td>0.331</td>
<td>2.629</td>
</tr>
<tr>
<td>Hf2Rh4</td>
<td>223.5</td>
<td>114.1</td>
<td>292.5</td>
<td>0.282</td>
<td>1.959</td>
</tr>
<tr>
<td>Ref. 4 (theo. values)</td>
<td>204.0</td>
<td>105.4</td>
<td>269.7</td>
<td>0.280</td>
<td>1.936</td>
</tr>
<tr>
<td>Ref. 5 (theo. values)</td>
<td>215.0</td>
<td>112.6</td>
<td>287.6</td>
<td>0.277</td>
<td>1.910</td>
</tr>
<tr>
<td>Ref. 70 (theo. values)</td>
<td>274.8</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Rh</td>
<td>254.0</td>
<td>141.2</td>
<td>357.5</td>
<td>0.265</td>
<td>1.798</td>
</tr>
<tr>
<td>Ref. 55 (exp. values)</td>
<td>267.0</td>
<td>149.4</td>
<td>377.8</td>
<td>0.264</td>
<td>1.787</td>
</tr>
<tr>
<td>Ref. 56 (exp. values)</td>
<td>270.0</td>
<td>149.4</td>
<td>378.4</td>
<td>0.266</td>
<td>1.807</td>
</tr>
<tr>
<td>Ref. 4 (theo. values)</td>
<td>243.3</td>
<td>141.7</td>
<td>356.0</td>
<td>0.256</td>
<td>1.717</td>
</tr>
</tbody>
</table>
higher $B/G$ ratio is associated with the better ductility, whereas a lower value corresponds to the naturally brittle behavior. The critical value which separates ductile from brittle material is 1.75. If $B/G > 1.75$, the material behaves in a ductile manner. Otherwise, the material behaves in a brittle manner. According to Table 3, all the binary Hf–Rh compounds are ascribed to

Fig. 3  The calculated (a) shear modulus ($G$) and (b) Young's modulus ($E$) versus Rh concentration (at%) for binary Hf–Rh compounds; (c) Young's modulus versus shear modulus for binary Hf–Rh intermetallics.

Fig. 4  The calculated (a) Poisson's ratio ($v$) and (b) $B/G$ ratio versus Rh concentration (at%) for binary Hf–Rh compounds; (c) Poisson's ratio versus $B/G$ ratio for binary Hf–Rh intermetallics.
ductile materials, which agrees well with the prediction from the Poisson’s ratio.

In the case that the ZrIr-HfRh is adopted, the variations of Poisson’s ratio and \( B/G \) ratio have exhibited similar trends with the increasing Rh concentration from Fig. 4a and b, respectively. The relationship between Poisson’s ratio and \( B/G \) ratio are shown in Fig. 4c. It has further confirmed the ductile essence of binary Hf–Rh compounds, and found the compound with a higher Poisson’s ratio owns a higher \( B/G \) ratio simultaneously.

3.3 Density of states

In this work, the calculated electronic structure is helpful to get an insight into the bonding characteristics of binary Hf–Rh compounds.
compounds, and to reveal the underlying mechanism of structural stability. In Fig. 5a–g, the theoretically calculated total and partial density of states (DOS) for the seven compounds in the Hf–Rh system, where the zero energy in each plotted figure corresponds to Fermi level ($E_F$). Based on the histogram curves, some common features can be identified in these compounds. For example, the peaks of the bonding state below Fermi level are mainly due to the hybridization between Rhd and Hfd electrons in the TDOS. While, the peaks of the antibonding state above Fermi level are mainly due to the corresponding Hfd electrons. The s electrons of Rh and Hf can make the dominant contributions at deep levels between $–8$ and $–3$ eV below the Fermi level. Additionally, the p electrons of Hf are effective around Fermi level in both bonding and antibonding states, and the p electrons of Rh are merely active. Similar featuring around Fermi level in both bonding and antibonding states, the number of bonding electrons per atom have the results of 5.6594, 6.4974, 6.8527, 7.122 and 6.2456 accordingly. Therefore, the sequence of structural stability should be Hf$_3$Rh$_5$ > Hf$_3$Rh$_4$ > ZrIr-HfRh > HfRh$_3$ > Hf$_2$Rh. This conclusion is in consistency with the conclusion drawn from formation enthalpies for five intermetallics, as shown in Fig. 1.

4. Conclusions

The phase stability, elastic and electronic properties of binary Hf–Rh compounds have been investigated using first-principles calculations. There are several conclusions are drawn as following:

(1) Based on the formation enthalpy analysis, the equiatomic HfRh phase should tend to crystallize in ZrIr-type structure, followed by L1$_0$, and then B2 at the ground state. Therefore, the lower temperature HfRh phase is suggested to be the ZrIr-type. This conclusion is in good agreement with the experimental reports in the literature. Besides, Hf$_2$Rh$_4$ is proposed to be Pu$_2$Pd$_4$-type for the first time.

(2) There are seven compounds (i.e., Hf$_2$Rh, ZrIr-HfRh, L1$_0$-HfRh, B2-HfRh, Hf$_3$Rh$_4$, Hf$_3$Rh$_5$, and HfRh$_3$) are considered. The optimized lattice constants show a good consistency with available results. Furthermore, Hf$_2$Rh$_4$ is the most stable with the lowest formation enthalpy among the binary Hf–Rh compounds.

(3) The calculated elastic constants for Hf$_2$Rh, ZrIr-HfRh, L1$_0$-HfRh, B2-HfRh, Hf$_3$Rh$_4$, and Hf$_3$Rh$_5$ can all satisfy the Born’s criteria, indicating their mechanical stabilities.

(4) The elastic modulus of the compound is calculated using the VRH method. When ZrIr-HfRh is considered, the bulk modulus ($B$) increases linearly with the growing Rh concentration. Besides, it is found Young’s modulus has linearly increased with the growing shear modulus, and the compound with a higher Poisson’s ratio owns a higher $B/G$ ratio simultaneously. Overall, the analysis made on the Poisson’s ratio and $B/G$ ratio have indicated that all the considered Hf–Rh compounds should be ductile.

(5) The number of bonding electrons for each compound has been derived from the DOS analysis. The results show the sequence of structural stability should be Hf$_2$Rh > Hf$_3$Rh$_4$ > ZrIr-HfRh > Hf$_3$Rh$_5$ > Hf$_2$Rh, which is in remarkable agreement with the thermodynamic analysis.

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References