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ABSTRACT

The structural, elastic, electronic and phonon properties of HfX (X = Rh, Ru and Tc) in the caesium-chloride phase have been investigated using the density functional theory within the generalized gradient approximation. The optimized lattice constant (a_0), bulk modulus (B) and the elastic constants (C_{ij}) are evaluated. The results are in a good agreement with the available experimental and theoretical data in the literature. Electronic band structures and densities of states have been derived for these compounds. The present band structure calculations indicate that the phases of caesium-chloride HfX (X = Rh, Ru and Tc) compounds are metals. Phonon dispersion curves and their corresponding total and projected density of states have been obtained using the direct method. The phonon spectra suggest that these compounds are dynamically stable in the caesium-chloride phase.

Introduction

Hafnium is widely used in the control rods and safety mechanisms of nuclear power plants due to its high neutron cross sections [1]. In addition, its high corrosion properties and biocompatibility makes it to be utilized in medical implants and other medical industry applications [2]. Despite the growing importance of Hf compounds, theoretical and experimental results of these compounds are very sparse. Some intermetallic compounds of Hafnium with transition metals such as Fe, Co, Pd, Pt, Ru, Rh etc. are used as hydrogen storage material [3]. However, there is a limited number of studies on Hf-TM compounds (TM = Pf, Pd, Fe, Co, Tc, Rh, Ru) with regards to their structure, electronic structure, cohesive energy, enthalpy, phase stability, structural stability and thermodynamic properties [2,5–11]. Levy et al. [2] studied the hafnium binary systems with metals, transition metals and alkali metals using *ab initio* calculations. Guo et al. [4,5] carried out experimental studies on the standard enthalpies of intermetallic compounds, including those of hafnium. Novaković et al. [6] studied the phase diagrams, cohesive energy, enthalpy of formation, structural and electronic properties of HfRh and HfRu compounds using the full-potential

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LAPW method. The standard enthalpies of formation of HfRh compound were determined experimentally at 1400 K by Topor and Kleppa [7]. The structural phase stabilities and enthalpies of formation of TM and TM_3 (T = Hf, Ti, Zr M = Ir, Os, Pd, Pt, Ru, Rh) were investigated using VASP code by Xing et al. [8]. Kryklya et al. [9] determined the structural and phase equilibria properties of HfRu and HfRh systems using X-ray diffraction (XRD), micro-structural analysis (MSA), differential thermal analysis (DTA) and electron microprobe analysis (EMPA). Although some of the structural features of HfX (X = Rh, Ru and Tc) compounds have been studied in terms of their theoretical and experimental aspects, the dynamic properties of these compounds have not been examined at sufficient levels. For instance, it is necessary to achieve full phonon dispersion curves in order to understand the lattice dynamics. Knowing the phonon spectrum is very important to determine material properties such as thermodynamic stability, phase transition and thermal transport, this work focuses on investigating the full phonon properties of HfX (X = Rh, Ru and Tc) compounds using the direct method.

Method

The first-principle calculations were done using the plane-wave pseudopotential density functional theory (DFT) via the MedeA-VASP package [12,13] with the projected augmented wave [14]. The generalized gradient approximation (GGA) of Perdew–Burke–Ernzerhof (PBE) [15] was chosen for exchange-correlation functional. An energy cut-off of 500 eV was found for the calculation of structural, elastic and phonon properties. The energy convergence criteria was set to 10^{-9} eV using the Normal (blocked Davidson) algorithm and reciprocal space projection operators. An $8 \times 8 \times 8$ Monkhorst-Pack [16] grid of k-point for HfX (X = Rh, Ru and Tc) compounds was carried out for the best convergence and relaxation zero strain. Fermi level was smeared by Methfessel-Paxton type [17] with a width of 0.225 eV. The elastic constants were computed using stress-strain approach [18], whereby the stress resulting from an applied strain was directly computed. The phonon spectra were obtained using the MedeA-Phonon in conjunction with MedeA-Vasp by the direct method. $3 \times 3 \times 3$ supercells containing 54 atoms for CsCl phase were used.

Results

HfX (X = Rh, Ru and Tc) compounds belong to Pm-3 m space group, with Hf and X atoms occupying the Wyckoff site of 1a (0, 0, 0) and 1b (1/2, 1/2, 1/2), respectively. The crystal structure of HfX (X = Rh, Ru and Tc) compounds are presented in Figure 1. The calculated equilibrium lattice parameter and bulk modulus for all the studied compounds are presented in Table 1 together with available experimental and theoretical results [4, 5, 7, 10, 11 and 21] for comparison. The calculated results for lattice constants are 1.073% for HfRh and 0.42% for HfRu, which are higher than the experimental values. The calculated bulk modulus for HfRh and HfRu are in good agreement with available theoretical data. The elastic constants are important parameters to define how a material behaves under stress. There are only three elastic constants of cubic crystals, namely C_{11}, C_{12} and C_{44}. The computed elastic constants for HfX (X = Rh, Ru and Tc) compounds are presented in Table 1. The mechanical stability conditions [19] of the cubic crystals are given as $C_{11} + C_{12} > 0$, $C_{44} > 0$, $C_{12} < B < C_{11}$ and $C_{11} - C_{12} > 0$. Therefore, it is clear that HfX (X = Rh, Ru and Tc)
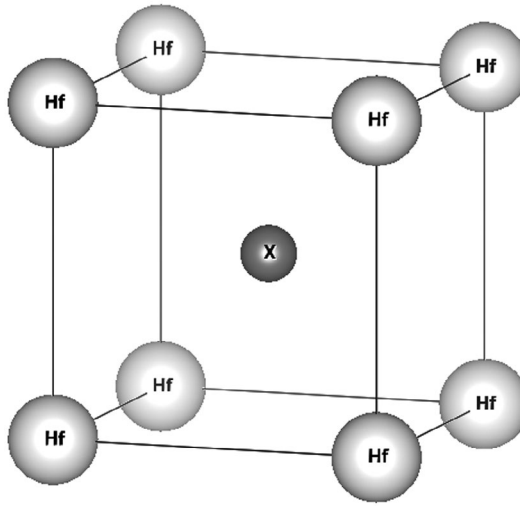
Figure 1. The crystal structure of HfX (X = Rh, Ru and Tc) compounds in the CsCl structure.

Table 1. Calculated lattice constant *a*, bulk modulus *B* (GPa), elastic constants C_{ij} (GPa) and shear modulus *G* (GPa), *B/G* for HfX (X = Rh, Ru and Tc) compounds, compared with the available experimental and theoretical data.

Compounds		*a*	*B*	C_{11}	C_{12}	C_{44}	*G*	*B/G*
HfRh	This work	3.262	180.142	204.050	168.188	58.828	36.616	4.919
	Exp. [11]	3.227						
	Ref. 4		173					
	Ref. 10	3.280						
HfRu	This work	3.239	197.694	368.617	112.233	82.547	98.530	2.006
	Exp. [11]	3.225						
	Ref. 5		206					
	Ref. 7	3.240						
	Ref. 24			355.84	127.21	84.37		
HfTc	This work	3.258	185.469	312.678	121.864	58.142	70.978	2.613
	Exp. [21]	3.256						

compounds are mechanically stable in B2 phase. There is no experimental or theoretical data found in literature to compare the elastic constants of these materials. The ductile and brittle properties of the material are determined with the value of B/G ratio (the critical value is 1.75) according to the Pugh criterion [20]. In the case of values smaller than 1.75, brittle properties are seen. Otherwise, the material behaves in a ductile manner. Since the B/G ratios of the HfX (X = Rh, Ru and Tc) compounds are larger than the critical value of 1.75, they have a ductile nature. The calculated electronic structure curves of HfX (X = Rh, Ru and Tc) compounds in the B2 phase are presented in Figure 2. These band calculations presented no energy gap at the Fermi level for these three compounds. Thus, the calculated electronic structure curves show that these materials have a metallic nature. The band calculations of HfRh and HfRu are in good agreement with the available theoretical result [7]. The overall electronic band profiles of HfX (X = Rh, Ru and Tc) compounds have the same trends with the previous work [22,23] which belongs to the same phase and space group. In order to understand the characteristics of electronic band states of HfX (X = Rh, Ru and Tc)
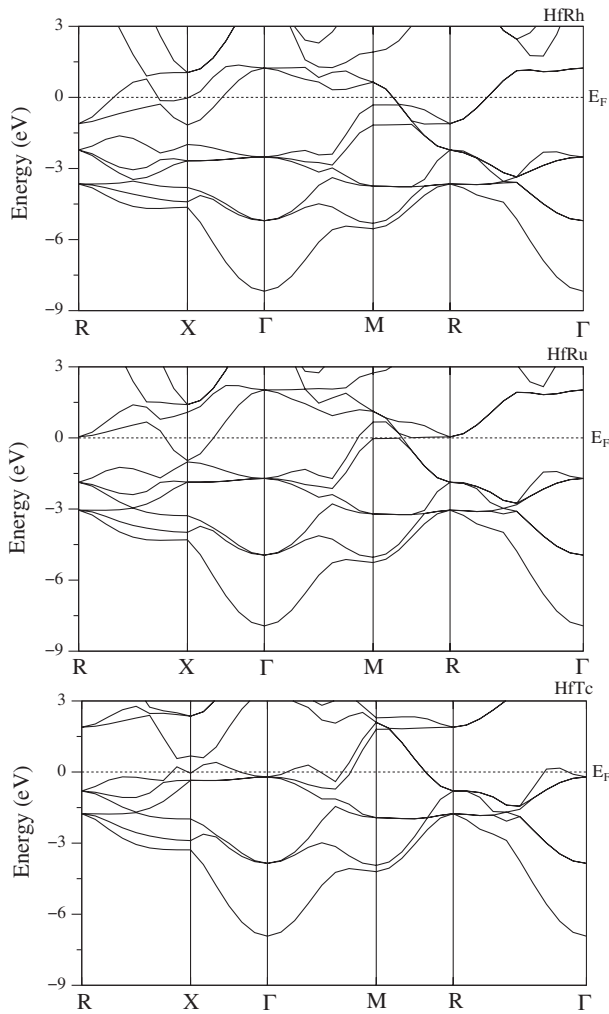
Figure 2. The calculated electronic band structure for HfRh, HfRu and HfTc compounds in the CsCl structure.

compounds, the total and the partial density of states (DOS) of these materials are found and illustrated in Figure 3. The scattered bands over the Fermi level for three compounds are due to Ru-d states (Rh-d and Tc-d) and Hf d-states. The electronic states below the Fermi level are mainly dominated by the Rh-d states for HfRh, the Ru-d states for HfRu and the Tc-d states for HfTc (see Figure 3). The density of states at the Fermi level $N(E_F)$ is dominated by the d-states of both atoms for HfRh and HfRu. However, the contribution of Tc d-states to $N(E_F)$ for HfTc is much larger than the corresponding contribution of Hf d-states. Traditionally, the stability in compounds is associated with low density of states (DOS) at the Fermi energy E_F [24]. For this purpose, we have calculated the density of states at the Fermi level $N(E_F)$. The value of this parameter is 1.483, 0.206 and 1.570 states/eV Cell for HfRh, HfRu and HfTc, respectively. We conclude that the HfRu has the lowest value of $N(E_F)$, this confirms that HfRu is the more stable compound. Also from Figure 3, one can notice that Hf d-states and Rh (Tc) d-states in HfX (X = Rh, Ru, Tc) compounds shift to
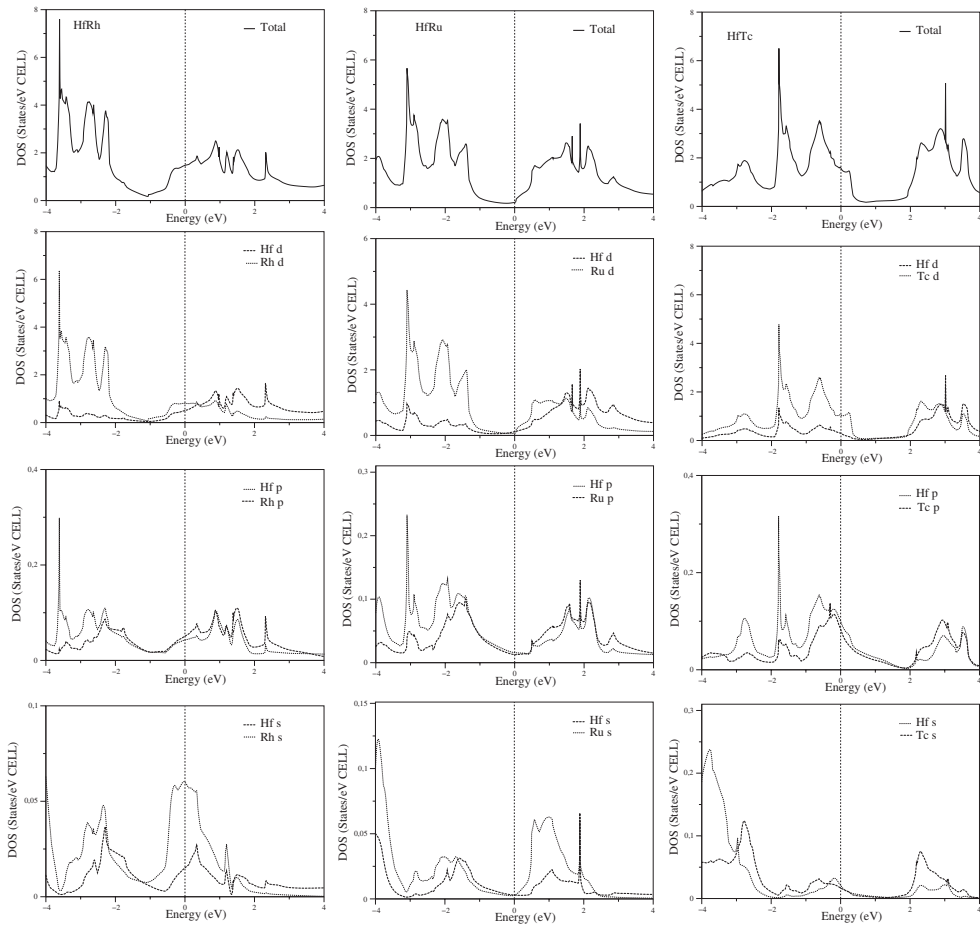
Figure 3. The calculated projected density of states for HfRh, HfRu and HfTc compounds in the CsCl structure.

higher energies in the following sequence from HfRu to HfRh and HfTc. The computed full Phonon dispersion curves, the total and the projected density of states of HfX (X = Rh, Ru and Tc) compounds in the B2 phase are shown in Figure 4. As for the B2 phase containing two atoms in the primitive cell, the phonon spectra demonstrates 6 phonon branches, three acoustic and three optical modes. For HfRu and HfTc, the Hf atoms vibrate in the lower frequency region while the Ru and Tc atoms vibrate in the upper frequency region since the Hf atoms are heavier than the Ru and Tc atoms. On the other hand, the phonon vibration characteristic for the HfRh compound is somehow different from other two compounds. Owing to the fact that the Rh atom is lighter than Hf atom, it is expected that Rh atoms dominate at optical frequencies region. However, the contribution of Rh atoms is mostly stronger at acoustic region. The lowest frequencies of Rh vibration confirm rather weak bonding forces between Rh and Hf atoms. In the B2 phase, we compared HfC and HfN compounds with these calculated results for HfX (X = Rh, Ru and Tc) compounds. The phonon spectra of HfC and HfN have a large band gap. On the other hand, our results indicate that there are no band gaps because of severe overlapping of the acoustic and optical branches
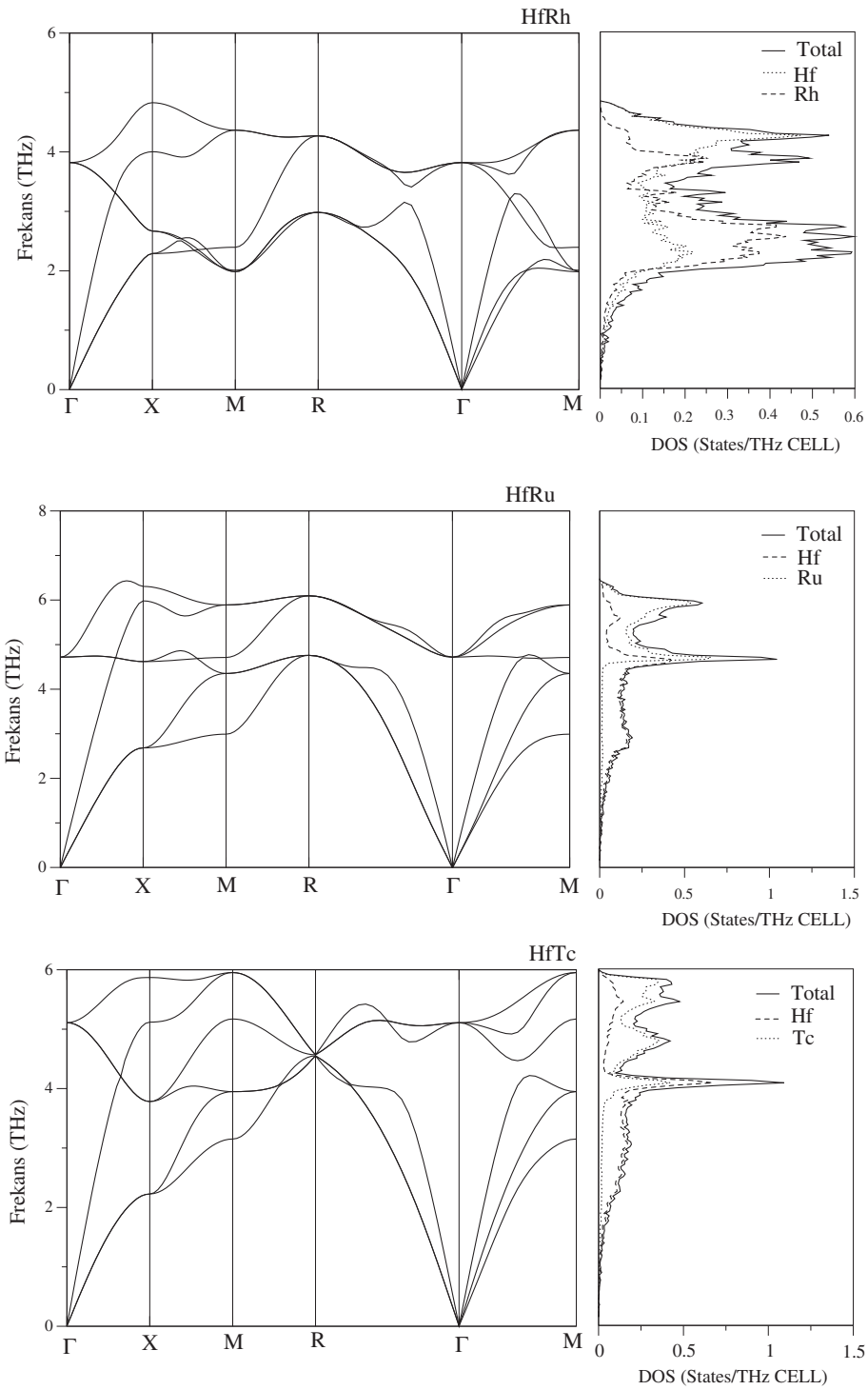
Figure 4. The phonon dispersion curves and partial density of states for HfRh, HfRu and HfTc compounds in the CsCl structure.

for the three compounds. These compounds in the B2 phase are dynamically stable because all phonon frequencies in the Brillouin-zone are not imaginary.

Conclusions

In this work, the structural, elastic, electronic and phonon properties of HfX (X = Rh, Ru and Tc) in the caesium-chloride phase have been investigated using the density functional theory (DFT) within the generalized gradient approximation (GGA). The structural parameters (the lattice constants, bulk modulus and its pressure derivative) and the elastic constants (C_{ij}) have been evaluated and compared with the available data. The calculation of elastic constants showed that these compounds are mechanically stable by Pugh criterion. The electronic band structure of HfX (X = Rh, Ru and Tc) compounds have been compared and analyzed in the B2 phase. All compounds exhibit metallic character. Full Phonon dispersion curves and density of states of HfX (X = Rh, Ru and Tc) compounds in the B2 phase have been calculated using the MedeA-Phonon in conjunction with MedeA-Vasp by the direct method. These compounds in the B2 phase are dynamically stable.

Disclosure statement

No potential conflict of interest was reported by the authors.

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