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Ab-initio studies of thermal and superconducting properties of HfX$_2$ alloys (X = Tc, Re, and Os)

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A systematic study of thermal properties such as the Debye temperature, specific heat coefficient, Grüneisen constant, electron-phonon coupling constant and transition temperature have been carried out using the results of electronic band structure and related characteristics, for hafnium superconducting alloys, namely, HfTc$_2$, HfRe$_2$ and HfOs$_2$. Computation of the electronic band structure and associated properties has been carried out using the tight-binding-linear-muffin-tin-orbital (TBLMTO) method within atomic sphere approximation (ASA). The calculated values have been compared with the available results of literature data.

Keywords: *Debye temperature; specific heat coefficient; Grüneisen constant; electron-phonon coupling constant; transition temperature*

1. Introduction

Hafnium forms a number of intermetallic binary alloys [1, 2] of the general formula HfX$_2$. Several are hexagonal C14 Laves structure alloys. Some intermetallic compounds of Hf and the transition metals Fe, Co, Pd and Pt have been investigated as hydrogen-storage materials because of their capability to form hydrides with high hydrogen to metal ratios at room temperature [3]. Hafnium is primarily used in the control and safety mechanisms of nuclear reactors because of its high cross-section for neutron absorption and its high corrosion resistance [4]. Hafnium cladding of nuclear fuel rods is expected to be an important element in the design of future advanced reactors [5]. Hafnium alloys are also used in medical implants and devices, due to their biocompatibility and corrosion resistance [6]. Hafnium is added to aluminum-magnesium-scandium alloys, widely used in aerospace applications, to increase their strength during high temperature thermo mechanical processing [7]. The hafnium dirhenide compound was first reported by Compton and Matthias [8]. Krikorin et al. [9] determined the lattice parameters for the analyzed composition HfRe$_{2.02}$. The phase diagram for the hafnium-rhenium was published by Taylor, Kagle and Doyle [10]. They found that the HfRe$_2$ phase occurs over a range of homogeneity with the lattice parameters varying. In a similar study Savitskii et al. [11] also reported a range of homogeneity but listed the variation of lattice parameters. The superconducting transition temperature for the HfRe$_2$ has been variously reported as 4.80 K by Compton and Matthias [8] and 5.61 K by Blaugher, Taylor and Hulm [12] suggesting Tc changes with composition. The lattices parameters of the HfTc$_2$ compound have been given by Darby et al. [13]. The richness of phenomena and the properties observed in these materials have motivated the study on the properties of their fundamental electronic structures. Hence, in order to have such a comprehensive understanding of the basic electronic properties of these materials, we have carried out the electronic band structure studies using the well-known and versatile TBLMTO method and the results of electronic, ground state, thermal and superconducting properties of HfTc$_2$, HfRe$_2$ and HfOs$_2$ are presented here. The results have been analyzed and compared with the literature data.

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2. Computational method

The hexagonal C14 Laves structure alloys HfTc$_2$, HfRe$_2$ and HfOs$_2$ are interesting due to their thermal and superconducting properties [14, 19]. Space groups of HfTc$_2$, HfRe$_2$ and HfOs$_2$ are the same as P6$_3$/mmc (no. 194). The atomic position in HfTc$_2$, HfRe$_2$ and HfOs$_2$ are: Hf1: 1/3, 2/3, 0.5629 and Tc$_1$ or Re$_1$ or Os$_1$: 0.1697, 0.3394, 1/4 and Tc$_2$ or Re$_2$ or Os$_2$: 0, 0, 0. The electronic configurations of elements in these materials are Hf: [Xe] $4f^{14}5d^26s^2$; Tc: [Kr] $4d^65s^1$ Re: [Xe] $4f^{14}5d^56s^2$ and Os: [Xe] $4f^{14}5d^66s^2$. The band structure calculations for these intermetallic compounds were carried out by using the TB-LMTO method within the ASA [15, 16]. The density of states (DOS) was calculated by the method of tetrahedron [17]. All the muffin-tin radii and number of k-points were varied to ensure total energy convergence. The ground-state properties were calculated for the lattice parameters that corresponded to the minimum of the total energy.

3. Results and discussion

All the electronic properties such as the DOS and energy bands were calculated for the equilibrium lattice parameters. For each case, equilibrium lattice parameters were obtained by minimizing the electronic total energy (E$_T$) with respect to the cell volume. The plots of total energy as a function of volume for HfTc$_2$, HfRe$_2$ and HfOs$_2$ are shown in Fig. 1 (a – c) respectively. The cell volumes have been varied by varying the a-parameter and maintaining c/a ratio constant. The curve was obtained by fitting the E$_T$-V data to Murnaghan's equation of state [18]:

$$E(V) = V \frac{B_0}{B'_0} \left[\frac{(V_0/V)^{B'_0}}{B'_0 - 1} + 1 \right] + \text{const.} \quad (1)$$

where B$_0$ is bulk modulus and B'_0 is the pressure derivative of B$_0$. The equilibrium lattice parameters were obtained by minimizing the total energy by varying the cell volumes of HfTc$_2$, HfRe$_2$ and HfOs$_2$ alloys. The minimum energy value corresponds to the volume of 1320.8 Å^3 for HfTc$_2$ and the corresponding lattice constant is 5.1475 Å. In
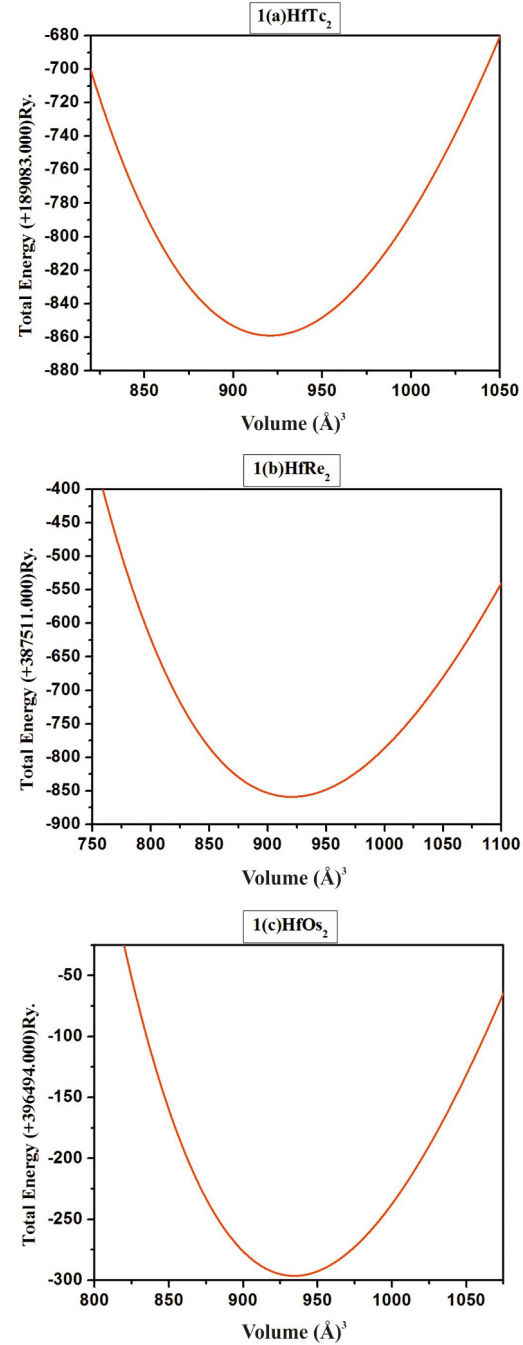

Fig. 1. Variation of total energy with cell volume for (a) HfTc$_2$, (b) HfRe$_2$ and (c) HfOs$_2$.

a similar manner to volume optimization, the lattice constants were calculated; they are: 5.2187 Å and 5.1652 Å for HfRe$_2$ and HfOs$_2$, respectively. The variations of lattice constants are in compliance with the variation of the size of atoms in their

alloys. A comparison with the experimental lattice parameters of $HfTc_2$, $HfRe_2$ and $HfOs_2$ [14, 19] is given in Table 1.

Table 1. Comparison of the calculated lattice parameters with the experimental results.

Alloys	Lattice parameter Å	
	Present	**Experimental**
$HfTc_2$	a = 5.1475	a = 5.2001 [14]
	c = 8.5305	c = 8.6175
$HfRe_2$	a = 5.2187	a = 5.2540 [14]
	c = 8.5423	c = 8.6000
$HfOs_2$	a = 5.1652	a = 5.2000 [19]
	c = 8.4350	c = 8.4920

Transition metals have large d-electron shells and are characterized by high binding energy [20]. The electronic band structures of $HfTc_2$, $HfRe_2$ and $HfOs_2$, along the high symmetry directions of the Brillouin zone are displayed in Fig. 2 (a – c). The Fermi level is set to 0 Ry. The bands are intense around the Fermi energy and are mainly derived from the d-states of Tc_1, Re_1, and Os_1 atoms of $HfTc_2$, $HfRe_2$ and $HfOs_2$, respectively. These are indicating the domination of d-bands. It is clearly evident in all the three materials that these states dominate the conduction in these materials. At higher energies there is a hybridization of the d-states of the hafnium. Just above the Fermi level the bands arise mostly from the p-states Tc_1, Re_1, and Os_1 atoms of $HfTc_2$, $HfRe_2$ and $HfOs_2$, respectively. They are also very strongly hybridized. The Fermi energies of $HfTc_2$, $HfRe_2$ and $HfOs_2$ are: 0.796676Ry, 0.83377Ry and 0.841479Ry, respectively. A relatively larger value of E_F for $HfOs_2$ is attributed to the more occupied p- and d-bands, relative to the other two compounds.

The DOS of all the three alloys, namely $HfTc_2$, $HfRe_2$ and $HfOs_2$, are presented in Fig. 3 (a – c). The DOS at E_F for $HfTc_2$, $HfRe_2$ and $HfOs_2$, are presented in Table 2. The high DOS around E_F is evidently due to the strong piling up of p- and d-bands in all the three alloys and accounts for the structural stability. It is clearly evident that d-bands of Tc_1, Re_1, and Os_1 atoms of $HfTc_2$, $HfRe_2$
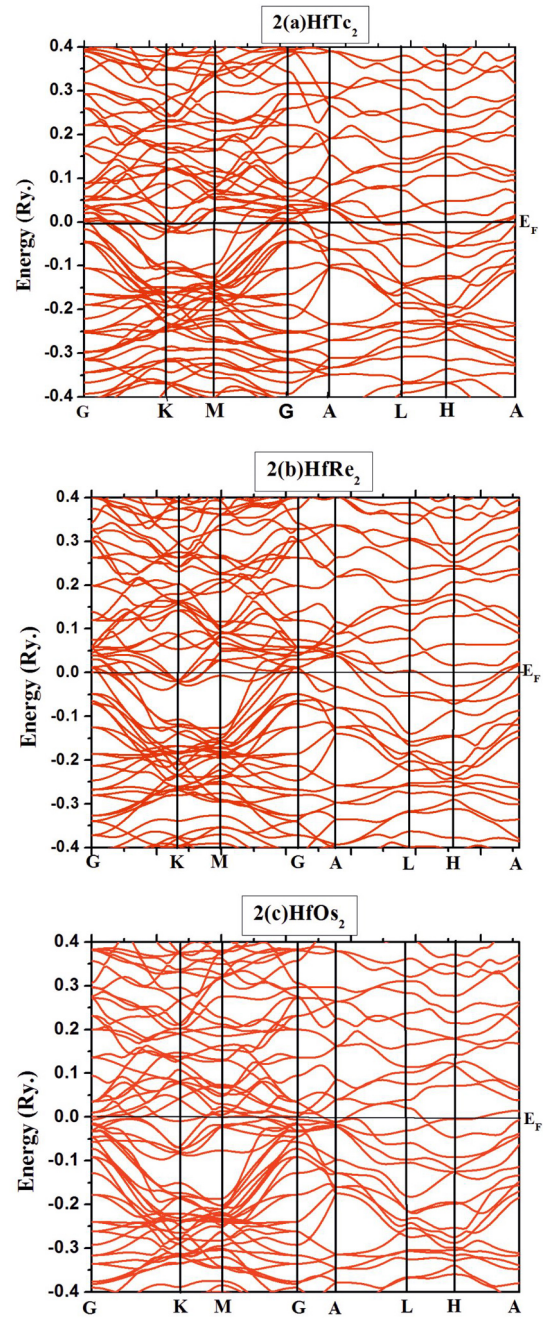

Fig. 2. Energy band structure for (a) $HfTc_2$, (b) $HfRe_2$ and (c) $HfOs_2$.

and $HfOs_2$, respectively contribute predominantly to the Fermi level for all the materials. The p-bands of Tc_1, Re_1, and Os_1 atoms of $HfTc_2$, $HfRe_2$ and $HfOs_2$, respectively also contribute a little to E_F but there is no contribution from p-bands of Tc_2,

Table 2. Electronic density of states at the Fermi energy for HfTc$_2$, HfRe$_2$ and HfOs$_2$ for s-, p-, d- and f-bands of various atomic elements.

| Bands | DOS at E$_F$ ((states/Ry)/atom) | | | | | | | | | | |
| | HfTc$_2$ | | | | HfRe$_2$ | | | | HfOs$_2$ | | | |
	Hf$_1$	Tc$_1$	Tc$_2$	Total	Hf$_1$	Re$_1$	Re$_2$	Total	Hf$_1$	Os$_1$	Os$_2$	Total
s	1.565	0.596	0.677	2.838	1.338	0.616	0.301	2.255	2.757	0.704	0.186	3.647
p	2.939	7.020	1.955	11.914	3.974	6.502	2.562	13.038	3.748	13.643	1.759	19.150
d	38.222	68.828	17.748	124.798	44.618	62.998	15.925	123.541	31.749	45.126	14.625	91.500
f	2.216	1.584	1.123	4.923	2.619	1.926	1.350	5.895	2.324	1.189	0.962	4.475

Re$_2$, and Os$_2$ atoms of HfTc$_2$, HfRe$_2$ and HfOs$_2$ to E$_F$. The DOS at the Fermi level is intense due to d-states. The DOS at E$_F$ is found to decrease drastically for HfOs$_2$ in comparison to HfTc$_2$ and HfRe$_2$. This is due to the increase in atomic number of X$_2$ elements. The Fermi energy moves towards the valley point next to the d-band peak in the DOS for HfOs$_2$. For HfTc$_2$ and HfRe$_2$, the valley point is near the Fermi level lying around the maximum region of the DOS plots and hence, the DOS at E$_F$ for these alloys are high.

The Debye temperature (Θ_D) and Grüneisen constant (γ_G) are important parameters, related to the thermal properties of materials. To calculate the thermal properties of a vibrating Debye lattice we have used the Debye-Grüneisen model [21]. In the present work, the Debye temperature is calculated using the equation 2:

$$\Theta_D = 67.48 \sqrt{\frac{r_0 B_0}{M}} \qquad (2)$$

where r is the Wigner-Seitz radius in a.u., $r = r_0$ (at equilibrium) B$_0$ is the bulk modulus in kbar and M is the average atomic weight. The Grüneisen constant (γ_G) is related to the Debye temperature (Θ_D) and the volume of the unit cell (V) by the relation [22]:

$$\gamma_G = \frac{\partial \ln \Theta_D}{\partial \ln V} \qquad (3)$$

The calculated values of Θ_D and γ_G are shown in Table 3. The Debye temperature is found to agree reasonably well with the existing experimental reports [19]. The electronic specific heat coefficient

Table 3. Equilibrium Wigner-Seitz radii (r$_0$), bulk modulii (B$_0$), Debye temperature (Θ_D) and Grüneisen constant (γ_G) for HfTc$_2$, HfRe$_2$ and HfOs$_2$.

| Alloys | r$_0$ (a.u.) | B$_0$ (GPa) | Θ_D (K) | | γ_G |
			Present	Exp.	Present
HfTc$_2$	2.97297	356.29	359	–	1.05
HfRe$_2$	3.00171	395.42	313	–	1.20
HfOs$_2$	2.96860	434.29	324	330 [19]	0.78

(γ) is related to the density of states N(E$_F$) and the electron phonon mass enhancement factor (λ) by the expression

$$\gamma = (1 + \lambda) \frac{1}{3} \pi^2 k_B^2 N(E_F) \qquad (4)$$

where k$_B$ is the Boltzmann constant. The electron-phonon coupling constant (λ) can be estimated using the electronic band structure results from the relation:

$$\lambda = \frac{N(E_F) \langle I^2 \rangle}{M \langle \omega^2 \rangle} \qquad (5)$$

where I^2 is the electron-phonon interaction matrix element averaged over the Fermi surface [23], M is the molecular mass, and $\langle \omega^2 \rangle$ is the average phonon frequency square given by [24]:

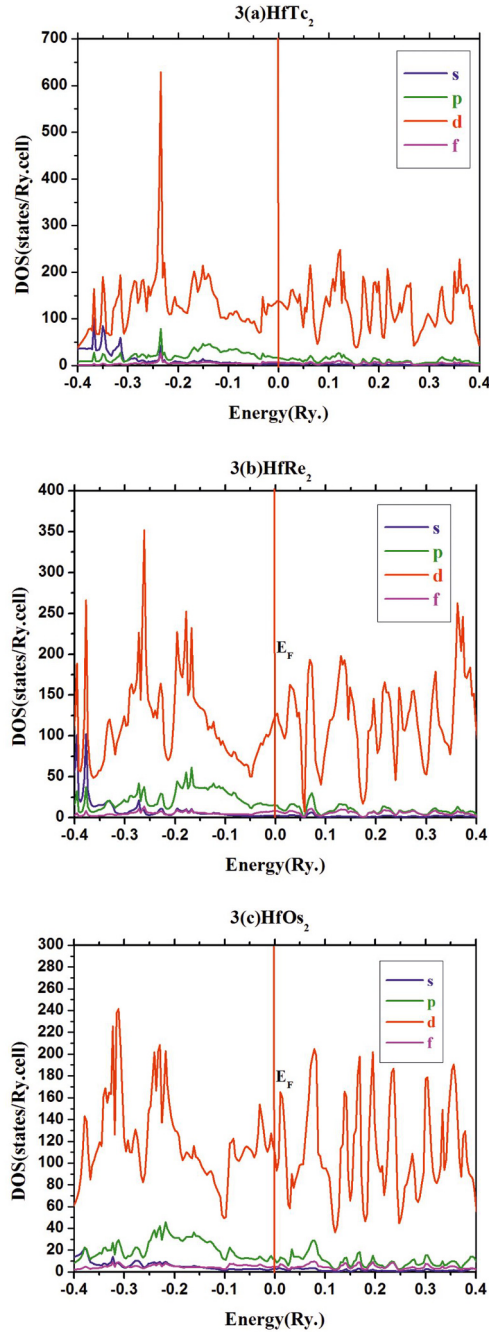$$\langle \omega^2 \rangle = \frac{1}{2} \Theta_D^2 \qquad (6)$$

Fig. 3. Density of states for (a) HfTc$_2$, (b) HfRe$_2$ and (c) HfOs$_2$.

with Θ_D in energy units. The quantity $\langle I^2 \rangle$ is determined by the relation:

$$\langle I^2 \rangle = 2 \sum_l \frac{(l+1)}{(2l+1)(2l+3)} M_{l,l+1}^2 \frac{N_l(E_F) N_{l+1}(E_F)}{N(E_F) N(E_F)} \quad (7)$$

where $M_{l,l+1}$ is the electron-phonon matrix element which can be expressed in terms of the logarithmic derivates (D_l):

$$M_{l,l+1} = -\varphi_l \varphi_{l+1} [(D_l(E_F) - l)(D_{l+1}(E_F) + l + 2) + (E_F - V(S)) S^2] \quad (8)$$

where $V(S)$ is the one electron potential and φ_l is the sphere boundary amplitude of the l partial wave function evaluated at E_F. N_l in equation 7 is the partial density of states function for the angular momentum quantum number l. The values of the electronic specific heat coefficient (γ) for HfTc$_2$, HfRe$_2$ and HfOs$_2$ are given in Table 4. For HfOs$_2$, $\gamma^{exp} = 2.84$ mJmol^{-1}K^{-2} [19]. No such data have been found in the literature for other two compounds for comparison. The superconducting transition temperature (T$_C$), which is obtained by using the procedure is detailed below. The superconducting transition temperature has been calculated using McMillan's formula [25], which is:

$$T_C = \frac{\langle \Theta_D \rangle}{1.45} \exp \left[\frac{-1.04(1+\lambda)}{\lambda - \mu^*(1+0.62\lambda)} \right] \quad (9)$$

where λ is the electron-phonon coupling constant which can be estimated as detailed above, and μ^* is the electron-electron interaction constant. The μ^* can be obtained from the empirical relation given by Bennemann and Garland [26]:

$$\mu^* = \frac{0.26 N(E_F)}{1 + N(E_F)} \quad (10)$$

It is evident from Table 4 that among the three compounds HfRe$_2$ has the highest T$_C$ value. The T$_C$ values estimated by the present work for HfTc$_2$, HfRe$_2$ and HfOs$_2$ agree well with the experimental values reported earlier [14, 19]. No such results have been available for λ, Θ_D and γ of HfTc$_2$ and HfRe$_2$ in the literature for comparison. As the atomic number of X in HfX$_2$ (X = Tc, Re, and Os) increases, the values of λ, γ and superconducting transition temperature Tc, are found to decrease.

4. Conclusions

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Table 4. Electron-phonon interaction constant (λ), electronic specific heat coefficient (γ), and superconducting transition temperature (T$_C$) for HfTc$_2$, HfRe$_\mathbf{2}$ and HfOs$_2$.

Alloys	λ		γ (mJmol^{-1}K^{-2})		Tc (K)	
	Present	**Exp.**	**Present**	**Exp.**	**Present**	**Exp.**
HfTc$_2$	0.6	–	2.26	–	4.50	5.60 [14]
HfRe$_2$	0.51	–	2.09	–	5.10	5.20 [14] 4.80 [27]
HfOs$_2$	0.43	0.49 [19]	1.75	2.84 [19]	1.86	1.85 [19] 2.69 [27]

of HfTc$_2$, HfRe$_2$ and HfOs$_2$ superconductors have been studied using the self-consistent tight binding linear muffin-tin orbital method. The ground state lattice parameters and primitive cell volume have been obtained by fitting the electronic total energy with the Murnaghan equation of state and are in good agreement with the experimental results. The electronic band structures show a strong hybridization between p- and d-bands and are also narrowly piled up around the Fermi energy for all the three materials and it is also evident in the density of states results. Furthermore, it has been found that the band structure and related properties at the Fermi energy are dominated by the d-bands in general. The density of states at Fermi energy is found to be strongly influenced by the d-bands due to X-atoms (X = Tc, Re, Os) in all the three compounds. The total d-band density of states at Fermi energy is found to decrease with the increasing atomic number of X-atoms in the compound, and therefore, the electron-phonon interaction parameter, electronic specific heat, and superconducting transition temperature have all been found to follow the same trend of variation. There are however, some discrepancies between the present theoretical estimates of Tc and the corresponding experimental values. The probable source of this difference is mainly attributed to the empirical estimation of the pseudo potential parameter (μ^*) for the electron-electron interactions using the Bennemann-Garland formula (the correct estimation of it requires more involved renormalization procedure by taking into account spin fluctuation as suggested earlier by Picket et al. [28]). Thus, within the approximations involved in the calculations, the present results are found to agree reasonably well with the available experimental results.

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