Electron-phonon interaction and superconducting behaviour of ZrB and HfB: A first principle study

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Abstract. The electronic, phonon and superconducting properties for ZrB and HfB in cubic NaCl phase have been studied by using a first principles scheme, based on the application of the plane-wave pseudopotential method, density functional theory, and a linear response technique. The electronic band structure and density of states show metallic behaviour of ZrB and HfB. Positive phonon frequencies confirm the stability of these compounds in cubic NaCl phase. The detailed discussion of superconductivity is given in terms of Eliashberg spectral function ($\alpha^2 F(\omega)$), electron-phonon coupling constants ($\lambda$) and superconducting transition temperature ($T_c$). The calculated superconducting transition temperatures are 3.42 K and 2.97 K for ZrB and HfB respectively which are in good agreement with their experimental values of 3.4 K and 3.1 K.

1. Introduction
The transition metal carbides show exclusive properties such as hardness, high melting points, inertia, metallic property, chemical stability, high ferromagnetism and superconductivity. Similarly the transition metal borides also show similar properties [1-7]. Among the various transition metal borides, Zr-B and Hf-B are the most attractive systems due to their extra ordinary chemical and physical properties [8,9]. A detailed review of Zr-B system was reported by Okamoto et al. [10]. Previous studies have found that the Zirconium monoboride (ZrB) phase can exist in the range from 1073 K to 1523 K [11]. Further the existence of ZrB with peritectoid reaction by XRD and TEM analysis confirmed by Champion et al [12] and even found that this phase can be easily stabilized to room temperature. On the other hand the Hafnium monoboride (HfB) play a vital role in various alloys, especially in Ti matrix alloys [13]. A large number of experimental and theoretical works have been done on the structural electronic and optical properties of ZrB and HfB compounds [13-15]. In the present paper we investigate the superconducting properties of ZrB and HfB. We also report the electronic, phonon properties and electron-phonon interaction of ZrB and HfB in NaCl phase using plane wave pseudopotential method with generalised gradient approximation. For electron-phonon interaction we have used linear response method and Migdal-Eliashberg approach from which the superconducting properties of ZrB and HfB can be calculated. The calculated superconducting parameters are favourably compared with their corresponding experimental values [16].

2. Computational method
The plane wave pseudopotential method of density functional theory DFT [17] as implemented within the QUANTUM ESPRESSO code [18] has been used for structural, volume optimization and
The electronic properties of ZrB and HfB compounds which crystallize in cubic (Fm3m no.225) NaCl-type structure. The phonon dispersion and electron-phonon interactions are calculated using density functional perturbation theory (DFPT) [19]. We have used the generalized gradient approximation (GGA) scheme of Perdew, Burke and Ernzerhof (PBE) [20] for exchange and correlation effects and the norm-conserving pseudopotential of Troullier and Martins type, generated with the FHI (Fritz-Haber-Institut) code for describing the interaction between the valence electron, nuclei and the core electrons. The smearing of Marzari-Vanderbilt is used to select the occupation distribution. The convergence is achieved with a kinetic energy cut-off 80 Ry. which is sufficient to fully converge all properties. For Brillouin zone integration, we take the zone-centered 14x14x14 Monkhorst-Pack [21] k-points mesh and the dynamical matrices are computed on a 4x4x4 q-mesh. The superconducting transition temperature has calculated by means of Mc-Millan’s equation modified by Allen and Dynes [22-25].

3. Results and discussion

3.1 Structural and electronic properties

The ground state properties of ZrB and HfB are obtained by a minimization of the total energy with respect to the unit cell volume and fitted to Birch-Murnaghan’s equation of state (EOS) [26]. The calculated all equilibrium structural properties such as lattice constants (a0), bulk modulus (B) and pressure derivative of bulk modulus (B’) of ZrB and HfB are listed in table 1, together with some available experimental and theoretical data [13-15, 27, 28]. It is seen from table 1 that the calculated values of lattice parameter and bulk modulus for both the compounds are in good agreement with available experimental and theoretical results. To elucidate the electronic properties of ZrB and HfB, we have calculated the electronic band structures (BS) and density of states (total and partial) for both the compound and presented in figure 1(a,b) and 2(a,b). From figure 1(a) and 2(a), it can be seen that there is no energy gap at the Fermi level EF which indicates the metallic behavior of ZrB and HfB compounds. The overall nature of BS and DOS for both the compounds is similar. The lowest lying band is due to the hybridization of Zr(Hf)-d and B-s states, which makes the peak at -5 eV (see figure 1(b) and 2(b)). The typical behavior of the total DOS in both the compounds is the presence of “pseudogap” (a sharp energy valley below the Fermi level) and this results is in good agreement with the Refs. [14,15]. The next group of the band between the energy range -2 eV to 8 eV appear due to the hybridization of Zr(Hf)-d and B-p states. Therefore these compounds show the covalent nature and the forces between them are central.

Table 1. Calculated lattice parameter (a0), bulk modulus (B), pressure derivative of bulk modulus (B’), density of states at Fermi level N(EF) and superconducting transition temperature (Tc) of ZrB and HfB compounds in NaCl phase.

| Compound | a0 (Å) | B (GPa) | B’ | N(EF) States/eV | Tc (K) |
|----------|--------|---------|----|-----------------|--------|
| ZrB (Pre.) | 4.914 | 156.0   | 4.68 | 1.21            | 3.42   |
| Exp. | 4.65<sup>a</sup> | - | - | - | 3.4<sup>d</sup> |
| Theo. | 4.90<sup>bc</sup> | 160.4<sup>b</sup>,163<sup>b</sup> | 160.6<sup>c</sup>,161<sup>c</sup> | 148.2<sup>c</sup> | 4.827<sup>bc</sup> |
| HfB (Pre.) | 4.860 | 164.1   | 6.48 | 1.14            | 2.97   |
| Exp. | 4.62<sup>d</sup> | - | - | - | 3.1<sup>f</sup> |
| Theo. | 4.855<sup>bc</sup> | 179.7<sup>b</sup>, 269.30<sup>b</sup> | 179.7<sup>b</sup>, 269.30<sup>b</sup> | 179.7<sup>b</sup>, 269.30<sup>b</sup> | 4.850<sup>c</sup> |

<sup>a</sup>Ref. [13], <sup>b</sup>Ref. [27], <sup>c</sup>Ref. [15], <sup>d</sup>Ref. [28], <sup>e</sup>Ref. [14], <sup>f</sup>Ref. [16]
3.2 Phonon dispersion curves and superconductivity

The lattice dynamical study is used to determine the structural stability and to explain superconductivity. The calculated phonon dispersion curves and phonon density of states of ZrB and HfB along the principles symmetry directions of the Brillouin zone are shown in figure 3 and 4. As is seen in figure 3(a) and 3(b), all the phonon modes are positive throughout the Brillouin zone which indicates that the ZrB and HfB are dynamically stable in cubic NaCl phase. In the PDC, the transverse optical (TO) and longitudinal optical (LO) branches are degenerate (around 450 cm\(^{-1}\)) at the zone centre, which shows the metallic nature of ZrB and HfB compounds. From figure 3 and 4, it is noticed that, there is large gap between acoustic and optical branches. This is due to large mass difference between Zr(Hf) and B atoms. Our calculated PDC for ZrB agree well with Ref. [15]. However there has been no experimental or theoretical work on phonon properties of HfB reported in the literature so far. From figure 4(a) and 4(b) it can be noted that, the phonon state in the acoustic region is mainly
contributed by the vibration of Zr and Hf atoms due to their heavier mass with considerable contribution of B atom. B atom shows the most contribution in the optical phonon branches. The highest peaks in the phonon DOS are observed at 195 cm$^{-1}$ and 150 cm$^{-1}$ for ZrB and HfB respectively.

In the present work, our main aim is to explore the strength of electron-phonon interaction in ZrB and HfB to clearly understand the origin of superconductivity in these compounds. The electron-phonon interaction is studied by employing the linear response method and Migdal-Elishberg theory [22, 23]. Figure 5(a) and 5(b) shows the behaviour of Eliashberg spectral function $\alpha^2 F(\omega)$ (which actually governs the strength and spectrum of electron-phonon coupling as a function of phonon frequency) with frequency for ZrB and HfB compounds. The features of this function are very similar to that of phonon density of states. With the help of Eliashberg spectral function, we can express the electron-phonon coupling parameter ($\lambda$) as

$$\lambda = 2 \int \frac{d\omega}{\omega} \alpha^2 F(\omega)$$

(1)

Further, the similarity of spectral function with phonon density of states confirms that, the acoustic as well as optical phonon branches make considerable contribution to $\lambda$. The calculated values of $\lambda$ for ZrB and HfB are 0.54 and 0.44 respectively. We have also calculated the superconducting transition temperature $T_c$ using Allen-Dynes formula [24,25]

$$T_c = \frac{\omega_{\text{trap}}}{1.2} \exp \left( \frac{1.04(1 + \lambda)}{\lambda - \mu^*(1 + 0.62\lambda)} \right)$$

(2)
where $\omega_L$ is the logarithmic averaged frequency and $\mu^*$ is the screen coulomb repulsion constant, whose value lies between 0.10 and 0.16 [29,30]. For $T_C$ we have taken $\mu^*$ is 0.11 (ZrB) and 0.08 (HfB) in the present calculations and found $T_C = 3.42$ K and 2.97 K for ZrB and HfB respectively, which agree well with experimental value of $T_C = 3.4$ K (ZrB) and 3.1 K (HfB) [16]. The calculated value of Debye temperature in the quasi harmonic approximation was found to be 509 K and 362 K for ZrB and HfB respectively.

4. Conclusion
In conclusion, our systematic theoretical work demonstrate that the ZrB and HfB compounds have been optimized to calculate the structural and electronic properties in cubic NaCl phase by performing the generalized gradient approximation (GGA) scheme with in the framework of density functional theory. The calculated lattice constants are in good agreement with the experimental and theoretical data. The electronic band structures and DOS suggest metallic behaviour of ZrB and HfB compounds. Moreover, we have presented the phonon properties and electron-phonon interaction for ZrB and HfB by employing the plane wave pseudopotential method. The calculated phonon dispersion curve confirms the dynamical stability of ZrB and HfB in cubic NaCl phase. The obtained values of electron-phonon coupling parameters are 0.54 and 0.44 for ZrB and HfB respectively. Further ZrB and HfB in cubic NaCl phase are found to be superconducting with transition temperature $T_C = 3.42$ K and 2.97 K, in good agreement of experimental values. The calculated Debye temperatures are 509 K and 362 K for ZrB and HfB respectively.

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