Structural and Electronic Properties of HfN: *ab initio* calculation

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Abstract: The structural and electronic properties of HfN from an electronic structure calculation have been presented. The calculation is performed using self-consistent tight binding linear muffin tin orbital (TB-LMTO) method within the local density approximation (LDA). The calculated equilibrium structural parameters are in good agreement with the available experimental results. It is found that this compound shows metallic behavior under ambient condition. The electronic structures of HfN in B_1 phase are investigated. It is found that HfN have strong metallization and the hybridizations of atoms in B_1 phase.

Keywords: Bulk modulus, band structure, density of states.

1. Introduction

The development of the technique for electronic structure calculation and hardware is remarkable in decades. In past it is difficult to calculate the total energy pseudo potential calculation of Transition metal compounds. Now this difficulty has been solved with the advance computing techniques. Transition metal carbides (TMC) and Transition metal nitrides (TMN) are known to be extremely hard and high melting points materials [1]. Technically, it is very important as high stable field electron emitters [2-4] and catalyst for various chemical reactions on the surface [5-7]. Theoretically, the cohesive properties of NaCl-type structure nitrides of the 4*d*-transition metals have been performed by Gelatt *et* al. [8] with use of the augmented-spherical-wave method. Their emphasis is on the contribution of the various electron states to the bonding properties. Papaconstantopoulos *et* al. [9] studied the electronic properties of VN, NbB, TaN, CrN, MoN and WN. Guillermet *et* al. [10] have investigated the electronic, cohesive and thermodynamics properties of 3*d*- and 4*d*-transition-metal monocarbides and mononitrides in the NaCl structure. Recently Stampft *et* al. [11] investigated the bulk electronic and physical properties of the early 4*d*-transtion-metal monotrides (YN, ZrN, NbN) also in the NaCl structure. The equation of states, elastic properties and hardness of TMN (TM = Zr, Nb and Hf) [12] are investigated by angle-dispersive synchrotron powder X-ray diffractometry with a diamond anvil cell. Isaev *et* al. [13] have investigated the anomalously enhanced superconductivity and lattice dynamics in transition metal carbides and nitrides.

In this paper, we emphasize the ground state electronic and structural properties for B_1-type HfN compound is studied by the first principles tight binding linear muffin tin orbital (TB-LMTO) method. We show that these solids crystallize in NaCl-type structure. We further report the electronic band structure (BS) and density of states (DOS). The outline of this paper is as follows: The method of calculation is described in section 2. The results and discussion are presented in section 3, and concluding remarks is given in section 4.

2. Method of Calculation

The total energy, BS and DOS for HfN are calculated using a similar procedure as reported in our pervious work [14-16] using the TB-LMTO method [17, 18] within the local density approximation (LDA) [19]. Van Barth and Hedin [20] parameterization scheme has been used for exchange correlation potential. The HfN compound crystallize in the NaCl-type structure (*fcc* lattice with space group, *Fm3m*, No. 225). In the NaCl structure, the Hf and N atoms are located at the position: Hf: (0, 0. 0) and N: (0.5, 0.5, 0.5). As mention earlier work [14, 16, 21], the TB-LMTO method works well for the close-packed structure and since the HfN compounds belongs to NaCl-type (B_1-phase) structure at ambient conditions, which is not a close-packed one. We have therefore introduced two equivalent empty spheres at position (0.25, 0.25, 0.25) and (0.75, 0.75, 0.75) in such a way that they do not break the crystal symmetry [22]. The Wigner-Seitz sphere was chosen in such a way that the sphere boundary potential is minimum and the charge flow between the atoms is in accordance with the electro negativity criteria [16, 21]. The E and **k** convergences are checked subsequently to achieve better accuracy. The calculations were performed for 512 **k** points (grid of 8×8×8) in the Brillouin zone for the B_1 phases. The tetrahedron method [23] of Brillouin zone integration has been used to calculate the DOS. The total energy was computed by reducing the volume from 1.05 V_0 to 0.60 V_0, where V_0 is the equilibrium cell volume.

3. Results and discussion

3.1. Structural properties

The electronic BS calculations are performed to estimate the total energy of HfN compound by using the first principle TB-LMTO method. The total energies for HfN compound are plotted against different compressions

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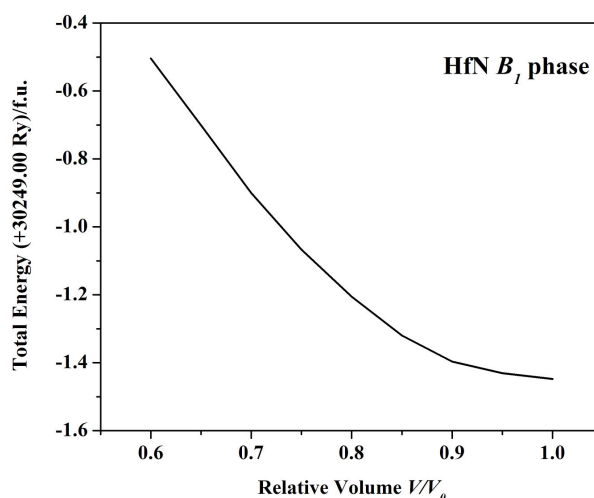
and are shown in Figure 1.

Figure 1.Variation of total energy with relative volume for the B_1 phase for HfN.

The minimum of all the curves define the equilibrium volume V_0 (or equilibrium separation a_0), which is found to be 62.5 Å^3 and the corresponding lattice parameter is 4.48 Å.

Table 1. Calculated equilibrium lattice parameter a_0 (Å), bulk modulus B_T (GPa), number of f-states at the Fermi level N(E_f) (states/Ry cell), of HfN in the B_1 phase.

Solids		a_0 = 2r (Å)	B_T (GPa)	N(E_f) (states/Ry cell)
HfN	Pres.	4.48	271	9.05
	Other	4.52[a], 4.54[b,c], 4.47[d]	278[b], 269[c], 303[d], 306[e,f]	--

[a]Ref [24].

[b]Ref [11], FLAPW+GGA.

[c]Ref [13], FP DFT perturbation

[d]Ref [25], pseudopotentials+LDA.

[e]Ref [12], neutron scattering experiment.

[f]Ref [26], LDA+DFPT

The present values of lattice parameters are in good agreement with the theoretical values [13, 24, 25, 26]. However, these reported values of the lattice parameter for HfN is little larger than our results. This is primarily due to usage of LDA [19] in the present calculation. Regarding the LDA contraction, it is often found that the LDA leads to some over binding which yields lattice parameters that are somewhat smaller when compared with the experimental.   The bulk modulus is in good agreement with available theoretical [13, 25, 28] and experimental results [27] which is listed in Table 1.

3.2. Electronic properties

The electronic BS and the DOS for the HfN in their B_1-phase under ambient conditions are shown in Figure 2. From these figures, it can be noticed that these compounds show metallic property which is manifested by the presence of large number of d-states at the Fermi level for HfN, as mentioned in Table 1.
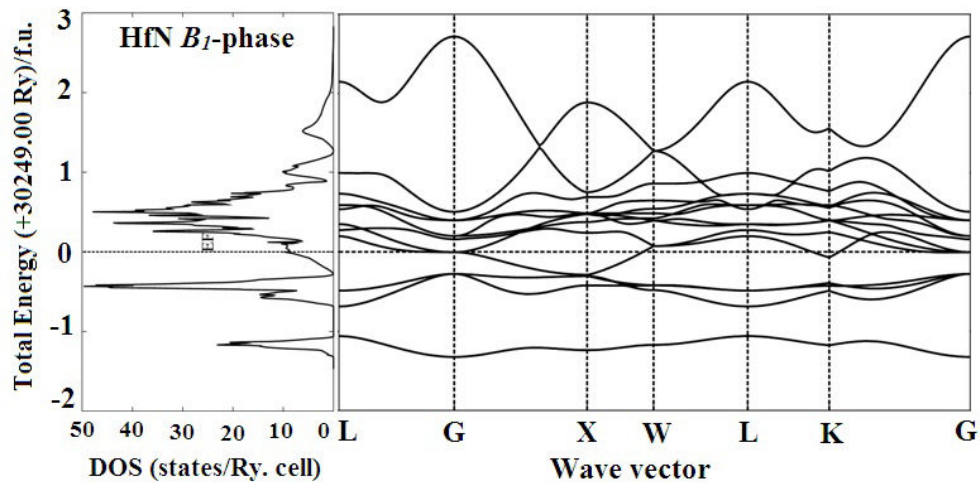
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Figure 2 BS and DOS in the B_1 phase for HfN.

To understand the elementary contribution of all atoms, we have studied the partial density of states (PDOS) which are shown in Figure 3. From the PDOS analysis, it has been found that the lower valence band lying around -1.25 Ry is due to the N-p states for HfN.
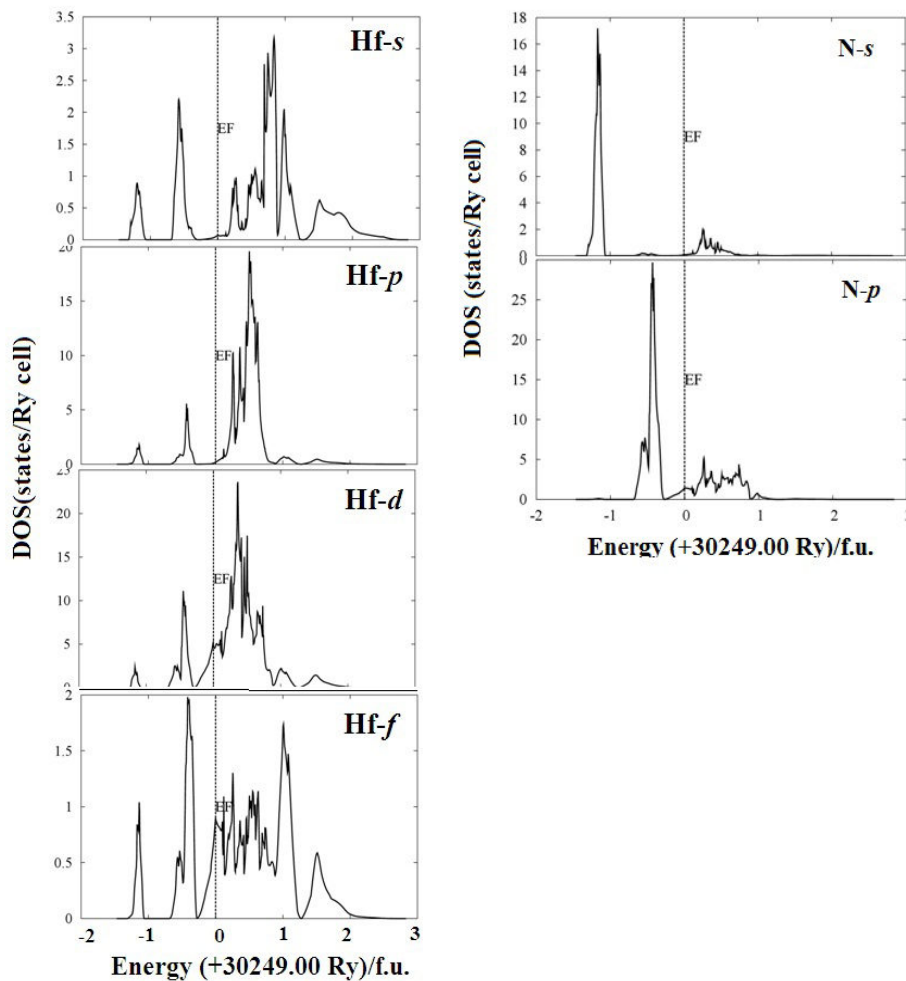

Figure 3. PDOS in the B_1 phase for HfN.

The upper valence band lying between 1.0 and 0.0 Ry are due to hybridization of Hf-s, p-, d- and N-p states for HfN. The Hf-d and N-p states are highly localized at the Fermi level. The conduction bands are due to the hybridization of the Hf-d and N-p states at the Fermi level for HfN.

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4. Conclusions

In summary, we have investigated structural and electronic properties for HfN using the TB-LMTO method within the LDA. At ambient conditions, this compound is stable in the NaCl-type structure. The lattice parameters and bulk modulus are obtained which are in good agreement with the experimental data. The electronic properties of HfN under pressure are also calculated, and it is found that HfN exhibit a metallic behavior.

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