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Pressure induced phase transition of ZrN and HfN: a first principles study

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Abstract. The structural, elastic, and electronic properties of zirconium nitride (ZrN) and hafnium nitride (HfN) are investigated by first principles calculation with density functional theory. The obtained cubic NaCl structure is energetically the most stable structure at ambient pressure. A pressure induced structural phase transition from B1 to B2 phase is predicted. The estimated superconducting transition temperature (T_c) of ZrN and HfN are 9.17 K and 8.66 K respectively. As pressure increases the superconducting transition temperature also increases.

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Key words: electronic structure, elastic properties, structural phase transitions, superconducting transition temperature

1 Introduction

The physical properties of materials undergo a variety of changes when subjected to high pressure [1]. The increase of pressure means the significant decrease in volume, which results in the change of electronic states and crystal structure. The recent developments in diamond anvil cell [2] enable the experimentalist to perform the investigation at high pressure. With the development of high pressure experimental techniques, investigations on pressure induced structural phase transition and superconductivity are getting the attention of all.

Transition metal nitrides ZrN and HfN are of great technological and fundamental importance because of their strength and durability as well as their useful optical, electronic, magnetic and superconducting properties. The technological application of all

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the above compounds requires significant progress in the fundamental understanding of their behavior at normal and high pressures. At ambient pressure both ZrN and HfN crystallize in the NaCl structure .Recently Chen *et al*.[3] ,using zone annealing technique grown hafnium nitride(HfN) and zirconium nitride(ZrN) crystals in the rock salt structure and they were identified as superconductors at ambient pressure. The measured bulk modulus was 215 GPa (ZrN) and 306 GPa (HfN) by neutron scattering experiments. There are many theoretical as well as experimental investigations on the structural stability ZrN and HfN [4-11]. But there are many disagreements between the theory and experiments in the prediction of stable structure, equilibrium lattice constant and bulk modulus of these transition metal nitrides TMNs (TM-Zr, Hf). This necessitated further theoretical studies in these systems. Moreover, the pressure dependence of elastic moduli and superconductivity have not been reported yet.

In the present investigation, the electronic structure, structural phase transition and mechanical stability of ZrN and HfN have been investigated using Vienna ab-initio simulation package (VASP) for all possible cubic and hexagonal structures. The superconducting transition temperature is also estimated using tight binding linear muffin tin orbital (TB-LMTO) method.

2 Computational details

The total energy calculations are performed in the frame work of density functional theory using the generalized gradient approximation (GGA) [12-14] as implemented in the VASP code [15-17]. Ground-state geometries are determined by minimizing stresses and Hellman-Feynman forces using the conjugate-gradient algorithm with force convergence less than 10^{-3} eV $Å^{-1}$. Birllouin zone integration is performed with Gaussian broadening of 0.1eV during all relaxations. The wave function of the valence electron is expanded by a plane wave basis with an energy cutoff of 600eV, which is tested to be fully converged with respect to the total energy for many different volumes. Birllouin-zone integrations are performed using the Monkhorst-Pack scheme [18] with a grid size of $12\times12\times12$ for structural optimization. A similar density of k-points and energy cut-off are used to estimate total energy as a function of volume for all the structures considered for the present study. Scalar-relativistic corrections are also included in all the calculations. Iterative relaxation of atomic positions is stopped when the change in total energy between successive steps is less than 1 meV/cell. With this criterion, the force on the atoms is generally less than 0.1 eV/Å.

To search for the most stable structure of the transition metal nitrides TMNs (TM= Zr, Hf), 5 types of the potential structures have been considered. They include NaCl (B1), Zinc blende (ZB)(B3), CsCl (B2), WC(Bh) and NiAs(B8). The space group and atomic position of atoms in the five different phases of TMNs are tabulated in Table 1. The electronic configurations of Zr, Hf and N atoms are [Kr] $4d^2 5s^2$ (Z=40), [Xe] $4f^{14} 5d^2 6s^2$ (Z=72), and [He] $2s^2 2p^3$ (Z=7) respectively. The valence electronic configurations chosen