Electronic and structural properties of transition metal mono nitrides

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The electronic and elastic properties of rock-salt structured nitrides, namely TiN and VN have been studied using ab-initio pseudopotential scheme and local density approximation. Both the compounds show metallic behaviour, with a large gap between occupied and unoccupied states. The mechanical and the elastic properties show excellent agreement with experimental results and well compared with other theoretical results because of the inclusion of partial core correction in the present calculation.

Keywords: ab-initio calculations, Atoms electronic structural calculation, Electronic properties, Structural properties

1 Introduction

During the past decade, interest in transition metal nitrides has grown considerably. Nitrides of various elements play an important role in industry, science and technology for their interesting and useful resilient properties, e.g. titanium nitride, which is a metallic compound characterized by high melting point, ultra hardness and high resistance to corrosion is used as electrically conducting barrier. Their technological importance has made them attractive for theoretical and experimental investigations. Vanadium nitrides are found in many technologically important materials, e.g. as precipitates in steels and in hard metals or in hard coatings on cutting and shaping tools. From theoretical point of view, the local density approximation (LDA) with in the density functional theory (DFT) has been used for calculating electronic and ground state properties of solids, molecules and atoms. This approach works for most systems like for 3d transition metals, where it underestimates the bulk modulus¹². But to remove their drawbacks they proposed approximations. Perdew and Wang (PW)³ have proposed the generalized gradient approximation (GGA) which hereafter is referred to as PW91⁴. This gives considerable improvement of the ground state properties of many atomic, molecular and solid-states systems. Ozolins and Körling had calculated GGA based on full potential linear muffin-tin orbital (FPLMTO) method using PW91 for structural and cohesive properties of transition metals.

In the present paper, the equilibrium lattice constants, the bulk modulus, the electronic band structures and density of states (DOS) for the compounds TiN and VN have been examined. The local density approximation (LDA) type exchange potential for defined studies is used. The comparison of the present calculated results with other ab-initio methods has been done.

2 Theory

The first-principles total energy calculations are performed with in the local density approximations (LDA) to the density functional theory (DFT) using the suit of code SIESTA⁵-⁷. This ab-initio method is based on density functional theory adopting a localized linear combination of numerical atomic orbital basis sets for the description of valence electron and norm conserving non-local pseudopotential for atomic core. The pseudopotentials were constructed using the Troullie-Martins scheme⁸ to describe the valence electron interaction with the atomic core; the non-local components of the pseudopotential were expressed in the fully separable form of Kleinman and Bylander⁹,¹⁰. Ceperley-Alder (CA)¹¹ form local density approximations (LDA) with relativistic calculations were used for the exchange correlation potential. The cutoff radius used for pseudopotential for Ti is 2.42 and 3.25 Bohr, for 4s and 3d orbitals respectively, while for V it is 2.50 Bohr for 4s and 2.00 Bohr for 3d state. In case of N cutoff radius used for pseudopotential is 1.00 Bohr for
2s, 2p and 3d orbitals. For Ti and V the atomic orbital basis set employed is double-$\zeta$ with polarization for 4s state and only double-$\zeta$ for 3d state. For nitrogen, basis set with soft confinement is used for the calculation. The total energy and band structures, were calculated according to the Monkhorst-Pack approximation\(^{12}\). The whole Brillouin-zone is sampled with 320 $k$-points for TiN and VN. Atoms are allowed to relax until a force tolerance of 0.01eV/Å and stress tolerance of 0.1 GPa is reached for each atom, while retaining the structure to be cubic. The elastic constant is calculated by applying tetragonal strains\(^{14}\).

### 3 Results and Discussion

The electronic properties of two transition metal nitrides viz. TiN and VN in rocksalt structure (space group Fm $\bar{3}$ m) are investigated by using efficient $ab$-initio code, known as SIESTA. The mechanical properties of TiN and VN are given in Table 1. The calculated equilibrium lattice parameters of TiN and VN with LDA are 4.16 Å and 4.03 Å, respectively. The values of calculated lattice parameters differ from the experimental values\(^{13}\) (4.24 and 4.14) by 2%. The bulk modulus obtained for TiN and VN are 278 and 282 GPa, respectively. So the calculated results for TiN and VN deviate from experimental values with 3% and 21% respectively. If the present study results are compared with the other first principle methods, it has been found that FLAPW reported higher bulk modulus from experimental results with 12% and 61% error for TiN and VN respectively, while LMTO-ASA method reported 35% and 21% error from experimental values. Table 1 also gives the comparison of calculated values of elastic constants of TiN and VN with available experimental values. The

<table>
<thead>
<tr>
<th>Methods</th>
<th>Lattice parameter a (Å)</th>
<th>Elastic Constants (Mbar)</th>
<th>Bulk Modulus $B_T$(GPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>TiN VN</td>
<td>$C_{11}$, $C_{12}$, $C_{44}$</td>
<td>TiN VN</td>
</tr>
<tr>
<td>FLAPW</td>
<td>4.18(^{a}), 4.06(^{a})</td>
<td>-</td>
<td>322(^{a}), 376(^{a})</td>
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<tr>
<td>LMTO-ASA</td>
<td>4.32(^{a}), 4.23(^{a})</td>
<td>-</td>
<td>389(^{a}), 282(^{a})</td>
</tr>
<tr>
<td>LDA (Present)</td>
<td>4.16, 4.03</td>
<td>6.74, 6.45</td>
<td>278, 282</td>
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<td></td>
<td>1.30, 3.49</td>
<td>1.62, 1.24</td>
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<tr>
<td>Expt.</td>
<td>4.24(^{a}), 4.14(^{a})</td>
<td>6.25, 1.65</td>
<td>288(^{a}), 233(^{a})</td>
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<td></td>
<td>1.63</td>
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\(^{a}\)Ref. 13

Fig. 1—Electronic (a) band structure of TiN; (b) density of state of TiN, Fermi level $E_f$ is set to zero

band structure and electronic density of states of TiN and VN with rock-salt phase along high symmetry direction is shown in Figs 1 and 2, respectively. The overlapping of bands in Fermi level shows the metallic nature of these compounds. There is a large gap between unoccupied and occupied states, as can
be seen in the band structure plots of Figs 1(a) and 2(a). In Figs 1(b) and 2(b), the DOS near the fermi level is mainly contributed by 3d orbital of the transition metals and less contributed by 2p orbital of nitrogen. The peak at DOS plot from −5 to −10 eV is due to the hybridization of 3d orbital of the transition metals and 2p orbital of nitrogen. Another peak near −18 eV is contributed by nitrogen 2s orbital only.

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**References**


Fig. 2—Electronic (a) band structure of VN; (b) density of state of VN, Fermi level $E_f$ is set to zero.