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Structural and electronic properties of isostructural transition metal nitrides

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ABSTRACT

The structural and electronic properties of three isostructural transition metal nitrides VN, NbN and TaN have been calculated using the full-potential linearized augmented plane-wave method within a generalized gradient approximation scheme for the exchange-correlation potential. Perfect NaCl structures as well as lattices containing nitrogen vacancies (M_4N_3), and an hexagonal ε-M_2N structure are considered. The trends are discussed and compared with available experimental and other theoretical results.

1. Introduction

Transition metal nitrides (TMNs) are hard refractory materials that are used in multiple types of applications [1–7] because of their renowned hardness [4,5], excellent thermal stability [1,2,8,9], defect impermeability [6] and resistance to wear, oxidation and corrosion. These compounds normally exist in substoichiometric phases with a substantial amount of vacancies [10–12]. Non-metal deficiency is known to be a major source of the non-stoichiometry, and the control of the stoichiometry and the understanding of its effect on mechanical properties are crucial to the design of hard materials based on these compounds. Moreover, the electronic structures should be sensitive to the presence of vacancies and differ significantly from those for the stoichiometric phase. The vacancy concentration as well as the alloy composition is shown crucial to the electronic and mechanical properties in these materials [13,14]. However, there are still some unresolved questions to be discussed. In our opinion, the vacancy effects in these compounds need more profound investigations; detailed calculations are required to understand the mechanical and electronic properties of the substoichiometric transition metal compounds. Among these compounds, there is increasing interest on vanadium nitride as an important industrial catalyst known for its selectivity and stability [15,16]. Also VN is a superconductor with transition temperature ranging from 2 to 9 K [17]. In the phase diagram of V–N, several binary phases have been reported: vanadium mononitride VN, which exhibits the rock salt structure and exists over the compositions from $VN_{0.7}$ to $VN_{1.0}$ [18]. In a previous paper [19], X-ray diffraction (XRD) measurements of VN samples showed that films deposited at 150 °C and at low nitrogen gas flows exhibit a hexagonal sub-nitride phase ε-V_2N. Hofer et al. [20] have also reported a rapid thermal processing of vanadium layers in pure nitrogen at high temperature, and their electron diffraction patterns revealed different phases: a rock salt structure was identified at 1100 °C and vanadium sub-nitride with the hexagonal structure (ε-V_2N) was found at 900 °C. This latter phase was firstly identified by Christensen and Lebech [21]. Similarly, the phase diagram for niobium–nitrogen system is also complex and only partly investigated, in which three phases are stable up to 2100 °C: a trigonal β-Nb_2N, a tetragonal γ-NbN, and the cubic rock salt δ-TaN. All three compounds are non-stoichiometric [22,23]. δ-NbN is metallic and becomes superconductive at $T_c = 17.3$ K [24]. Moreover, the Ta–N equilibrium phase diagram is extremely rich [25–28] and relatively unexplored, in which four phases are stable up to 1860 °C: ε-TaN, δ-TaN_{1-x}, β-Ta_2N_{1-x} and α-Ta(N) [29]. The cubic rock salt structure (δ-TaN_{1-x}) is obtained over a wide range of compositions from $TaN_{0.69}$ to $TaN_{1.04}$. Theoretically, Papaconstantopoulos et al. [30] also predicted that cubic TaN has high superconducting critical temperature.

These materials exist over a wide range of compositions outside stoichiometry and their physical properties vary as a consequence. Despite many physical properties, previously determined for cubic MN (M = V, Nb and Ta) and summarized in

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Ref. [31], no studies have been yet determined for the stable phase β-M_2N (M=V, Nb and Ta). These substoichiometric compounds exhibit a hexagonal ε-Fe_2N-type structure with a space group P-31m [32]. The aim of this paper is to present the results of a theoretical investigation of the structural and electronic characteristics of a bulk of three isostructural compounds VN, NbN and TaN, which crystallize in a cubic NaCl-type and in a hexagonal ε-Fe_2N-type lattices. The ε-Fe_2N structure is hexagonal; the space group is P-31m (no. 162) with three formula units per unit cell. The metal atoms can be placed in the 6k site with (0.323, 0.0, 0.272) coordinates, and the nitrogen atoms can be placed in the 2d and in the 1a sites with (1/3, 2/3, 1/2) and (0.0, 0.0, 0.0) coordinates, respectively. In addition to these two phases (δ-MN and β-M_2N), which have been observed in nature, we performed calculations for another substoichiometric rock salt structure (M_4N_3) for comparison purpose.

The paper is organized as follows: we explain the computational method in Section 2. The results are presented and discussed in Section 3 for the electronic structure properties. A brief conclusion is drawn in Section 4.

2. Computational method

The electronic structure calculations were performed using the full linearized augmented plane-wave method using the package *Wien2k* [33]. The unit cell is separated into non-overlapping atomic spheres and an interstitial region. The wave functions are described using radial solutions of Schrödinger's equation inside the spheres and plane waves in the interstitial regions. Exchange and correlation effects were treated using the generalized gradient approximation (GGA) [34]. For each calculation, typically, more than 100k-points were used in the irreducible Brillouin zone, a maximum angular momentum for the radial wave functions (l_{max}) of 12 and a plane-wave cutoff ($R_{MT}K_{max}$) of 8. Local orbitals were added to the basis set. This allows a better treatment of the problem of semicore states present in transition metal compounds; semicore states are high lying, relatively extended core states (e.g., the M p states) [35]. Also, addition of extra local orbitals, e.g., non-metal s and p and metal d orbitals, at energies high above the Fermi energy, enables a better and more reliable description of the unoccupied states. We have chosen the muffin-tin radii (R_{MT}) for V, Nb and Ta to be 2.09 (1.93), 2.05 (1.93) and 2.01 (1.91) a.u., respectively, in the cubic (hexagonal) structures of VN (V_2N), NbN (Nb_2N) and TaN (Ta_2N), and finally 1.85 (1.85) a.u. for the nitrogen atom. We compute lattice constants and bulk moduli by fitting the total energy versus volume according to the Murnaghan's equation of state [36]. The total density of states (DOS) was obtained using a modified tetrahedron method of Blöchl et al. [37]. A non-stoichiometric $MN_{0.75}$ was also simulated by substituting a vacancy on one non-metal N atom in unit cell of 8 atoms in a NaCl structure.

3. Results and discussions

We have calculated the ground state properties for transition metal (TM) nitrides. Results are summarized in Table 1 and compared with available experiments and results of other calculations. We have found excellent agreement between our calculated and available experiment and theoretical lattice parameters for all the compounds. Our calculated bulk moduli are in very good agreement with most of the available data. From Table 1 the agreement between our results and the pseudopotential calculations of Isaev et al. [31] appears to be excellent for both lattice parameter and bulk moduli.

Table 1
Ground state parameters for transition metal nitrides within cubic and hexagonal structures. Results of other calculations and experimental data are shown on the next line after results of our calculations.

Compounds	**a (Å)**	**c (Å)**	**V ($Å^3$)**	**B (GPa)**
δ-VN	4.12		69.934	305
	4.11[a], 4.136[b], 4.12[c], 4.14[d,e], 4.132[f], 4.19[g], 4.092[h]			313[a], 333[c], 316[f], 282[e], 338[g], 370[h], 268[i]
V_4N_3	4.07		67.419	285
β-V_2N	4.98	4.53	97.294	258
	4.917[j]	4.568[j]		
δ-NbN	4.43		87.275	314
	4.41[a], 4.394[b], 4.42[c], 4.378[g], 4.392[k], 4.379[l]			309[a], 317[c], 350[m], 292[n], 287[i], 354[n,o]
Nb_4N_3	4.39		84.604	282
β-Nb_2N	5.39	4.99	125.547	263
	5.267[p]	4.988[p]		
δ-TaN	4.43		87.275	332
	4.408[a], 4.33[b], 4.42[c], 4.397[l], 4.385[c], 4.336[q]			329[a], 338[c], 372[o]
Ta_4N_3	4.38		84.027	304
β-Ta_2N	5.38	4.98	124.831	265

[a] Ref. [31] (Calc.)
[b] Ref. [38] (Exp.)
[c] Ref. [39] (Calc.)
[d] Ref. [40] (Exp.)
[e] Ref. [41] (Calc.)
[f] Ref. [42] (Calc.)
[g] Ref. [43] (Calc.)
[h] Ref. [44] (Calc.)
[i] Ref. [45] (Exp.)
[j] Ref. [21] (Calc.)
[k] Ref. [46] (Calc.)
[l] Ref. [20] (Exp.)
[m] Ref. [47] (Exp.)
[n] Ref. [48] (Calc.)
[o] Ref. [49] (Calc.)
[p] Ref. [22] (Calc.)
[q] Ref. [50] (Exp.)