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First-principles studies of the superconductivity and vibrational properties of transition-metal nitrides TMN (TM = Ti, V, and Cr)

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HIGHLIGHTS

- The electronic band structure and density of states-calculations show metallic nature.
- Rocksalt structure of TMN indicating dynamical stability.
- The calculated superconducting transition temperature agrees well with the experimental data.
- These compounds behave as a conventional phonon-mediated superconductor.
- Using quasi-harmonic approximation, thermodynamical properties are investigated.

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ABSTRACT

The present paper reports the structural, electronic, phonon and thermodynamical properties of some transition-metal nitrides (TMN: TiN, VN and CrN) by means of first-principles calculations. The computed equilibrium lattice constant and bulk modulus agree well with the available experimental and theoretical data. The electronic band structure and density of states calculations show metallic nature. The phonon frequencies are positive throughout the Brillouin zone for these compounds in rocksalt structure indicating dynamical stability. The calculated electron–phonon coupling constant λ and superconducting transition temperature agree reasonably well with the available experimental data. These compounds behave as a conventional phonon-mediated superconductor. Within the GGA and quasi-harmonic approximation, thermodynamical properties are also investigated.

1. Introduction

Nowadays, the advancement in the *ab-initio* quantum-mechanical calculations of the atomic and electronic structures allows the theoretical modeling of new materials which permits the prediction of their properties and suggestions to new synthesis. In last years, transition metal nitrides (IV to VI *i.e.* 3*d* compounds) have received great experimental and theoretical attention in connection with their potential technological applications in optoelectronics, information storage technology (for coating of magnetic sheets), high power energy industry and spintronics [1–29]. They are characterized by hardness, high melting point, which class them among the refractory compound, excellent electrical and thermal conductivity, high chemical and thermal stability and good wear and high corrosion resistance.

It is however important to note that the transition or noble metal nitrides continues to attract enormous interest in recent times not only due to their unique and unusual properties but also due to a resulting spectacular high pressure synthesis of platinum nitride (PtN) [30]. PtN was prepared by compressing Pt metal and N_2 at pressure of 45–50 GPa and temperature above 2000 K. This was further followed by the synthesis of IrN_2 and OsN_2, with a high bulk modulus of 428 and 358 GPa respectively [30–32] similar to the PtN, having bulk-modulus of 372 GPa [22]. These works therefore have important implication for high pressure research and superconductivity, particularly the possibility to synthesize other nitrides with noble and transition metals.

Akhiyama et al. [33] reported a phase transition in the thin film of scandium aluminum nitride ($Sc_xAl_{1-x}N$) alloy and demonstrated the new route to design of a ScN based high-temperature piezoelectric material. The crystal structure of scandium nitride (ScN) is

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rocksalt. Thermoelectric properties of ScN thin films grown by reactive magnetron sputtering on Al_2O_3 (0001) wafers are reported by Kerdsongpanya and co-workers [34]. They observed a low electrical resistivity. The effect of the stoichiometry on the lattice parameter and other properties of scandium nitride is studied by Moreno-Armenta and Soto and found that the ScN behaves as a heavily doped p-type semiconductor [35].

Early members of first few transition metal nitrides are known to have rocksalt (RS) structure with metal atom retaining a *fcc* lattice, while nitrogen atom occupy the octahedral interstitial site. The theoretical studies done to date diverge in their dynamical stability as well as superconducting behavior for the rocksalt noble metal nitride compounds.

The electronic structure and physical properties of early transition metal carbides and nitrides in the rocksalt (B1) structure have been studied by means of the LMTO [9] and FP-LAPW [15] and *ab-initio* pseudopotential [22–24,36] techniques. Besides, band structure calculations performed by means of the screened-exchanged LDA method have shown that the semiconducting nature with indirect band gap for some of the nitrides (ScN, YN and LaN). Recently, Kerdsongpanya el al [37] investigated the effect of defects and impurities of the electronic density of ScN using first principles calculation and results envisage ways for improving the thermoelectric figure of merit of ScN. Xu et al. [38] investigated the lowest energy structure, binding energies, HOMO–LUMO gaps and ionization potential with size of ScN nanocrystals and observed that Sc_4N_4 units is energetically favorable with cage like structure.

The study on phonons and disorder-induced first order Raman spectra in rocksalt ScN using density functional perturbation theory (DFPT) approach has been reported in Refs. [39,40]. Kress et al. [41] using double shell model found anomalies in the phonon spectrum of TiN showing a dip of the longitudinal acoustic (LA) mode at $q \sim 2\pi/a(0.7, 0, 0)$ point and softening near L-point of Brillouin zone (BZ). Spengler et al. [42] argued that the nitrogen vacancies have strong influence on the Raman spectrum, phonon density of states and, consequently on the superconductivity of TiN_{1-x} compounds. Inelastic-neutron-scattering measurements [43] reveled that the acoustic branches of the phonon spectrum of VN are completely different from TiN, and the anomalies in the phonon spectra are shifted to the X-point of the Brillouin zone (BZ). In the case of other metal nitrides having rocksalt structure the special features (anomalies) of the phonon spectra are located near the point $2\pi/a(q, 0, 0)$ along the high symmetry Δ direction where $q \sim 0.65–0.70$. Tunneling measurements [44] for VN shows that Eliashberg spectral function $\alpha^2F(\omega)$ is similar to that of NbN for which optical phonons are believed to play an important role in superconductivity. Recently, Ivashchenko et al. [45] have proposed a possible mechanism of phase transformation in VN_x that accounts spontaneous volume and shear strains induced indirectly by the collapse of the X_3' mode, indicating that the tetragonal phase exhibits improper ferroelasticity. Nevertheless, the approach that is based on an analysis of the total energies of various structures as a function of Gaussians width 'σ' enabled one to correctly describe the main features of the complex phase transition in VN.

Recently, the chromium carbide (CrC) in the rocksalt phase has been synthesized [8] and paved the possibility of synthesizing CrN [46]. CrN, in recent time has received attention due to easy deposition of films, high thermal stability, good corrosion resistance, high bulk modulus and potential electronic and spintronic material [47–49]. However, there exists controversial informations concerning the fundamental properties such as lattice structure and bulk modulus [8,14]. Moreover, an antiferromagnetic phase was found for almost stoichiometric CrN [3,14]. Not surprisingly, the theoretical results are scarce and unprevailing for rocksalt CrN that undergoes reconstructions accompanied by, and perhaps driven by, magnetic ordering [50]. In addition, some reported $\rho(T)$ curves are monotonous [51] while others show a discontinuity at 260–280 K, which is associated with a magnetic and structural phase transition with a Neel temperature $T_N = 273–286$ K [52], from a paramagnetic RS structure above room temperature to a low-temperature antiferromagnetic (AFM) orthorhombic *Pnma* phase [53,54], with a 0.56–0.59% increase in atomic density [54] and a 25% lower bulk modulus [55]. Recent works of Alling et al. [56], and Wang et al. [57] confirmed experimentally as well as theoretically respectively that the bulk modulus to be 257 GPa (rocksalt) and 262 GPa (orthorhombic) while in a calculation the correct paramagnetic configuration gave the value 252 GPa, very close to the value for the orthorhombic phase (255 GPa) which discarded or justify the work with of Rivadulla et al. [55]. Electronic structure calculations indicate that a distorted antiferromagnetic phase is energetically more stable than paramagnetic and magnetic stress relief couples magnetic ordering with the structural change during the phase transition [14], which may also be induced by increasing the pressure above ~1 GPa [55]. Herwadkar et al. [58] reported a depletion of electron states near the Fermi level and the opening of a band gap when using a Hubbard coulomb interaction term $U = 3–5$ eV, and concluded that CrN is close to a "charge-transfer insulator". Recently, Zhang et al. [59] reported the optical properties of paramagnetic CrN. They showed that the imaginary part of the dielectric function exhibits a steep onset due to direct inter-band transitions and indicates depletion in the density of states at the Fermi level. In summary, both experimental and theoretical approaches have not been yet able to resolve the question whether CrN is a metal or a semiconductor, and to what extend the electronic and vibrational properties affects the possible band gap.

The present work pursues two main goals; first to carry out *ab-initio* calculation of the phonon spectra of some transition metal nitrides TMN (TM = Ti, V and Cr) in rocksalt and orthorhombic phases of CrN, and secondly, understanding the superconducting mechanism which is always full of interest. Theoretical calculations of electronic structure, phonon structure and electron–phonon interaction can serve as an useful tool to gain a preliminary insight into the superconductivity. Therefore, in this work we start from first-principles calculation to get the superconducting mechanism of TMN (TM = Ti, V and Cr) rocksalt phase compound and orthorhombic phase of CrN compounds via a complete knowledge of the electron–phonon-related properties in their normal state. This paper is organized as follows: the detailed computational method is described in Section 2, the results and discussion of electronic structure, phonon spectra as well as electron–phonon interaction and thermodynamical properties are given in Section 3 followed by conclusion in Section 4.

2. Computational details

We have performed first-principles total energy calculations within the density functional theory (DFT) using the plane-wave self-consistent field (PWSCF) implementation, with a generalized gradient approximation (GGA) [60] to exchange correlation energy and ultra soft pseudopotential [61] to represent the interaction between ionic cores and valence electrons. Plane waves (PWs) with a cutoff energy for plane wave expansion were 40 Ry (for TiN-RS), 100 Ry (for VN-RS), 60 Ry (for CrN-RS) and 40 Ry (orthorhombic structure of antiferromagnetic CrN) and Brillouin zone sampling was performed on a $8 \times 8 \times 8$ (for rocksalt structure) and $8 \times 4 \times 6$ (for orthorhombic structure) k-point Monkhorst-Pack grid respectively. We have used smearing of Methfessel–Paxton scheme [62] and Gaussian [60] scheme with a broadening of 0.05 Ha for TiN and CrN respectively, while 0.1 Ha with Fermi–Dirac [61] scheme is used for VN. The Fermi–Dirac smearing alone gives only a modest