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First principles study of pressure-induced magnetic transition in CrN

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ABSTRACT

First principles calculation was performed using tight-binding LMTO method with local density approximation (LDA) and atomic sphere approximation (ASA) to understand the electronic properties of chromium nitride. The equilibrium geometries, the magnetic moment, the electronic band structure, the total and partial DOS are obtained under various pressures and are analyzed in comparison with the available experimental data. The most stable structure of CrN is NaCl structure in the FM state. A pressure-induced second order magnetic phase transition from ferromagnetic (FM) to non-magnetic (NM) at very high pressure of 0.5549 Mbar is predicted. Our results indicate that CrN can be used as a hydrogen storage material.

1. Introduction

Transition metal nitrides are of intense interest for researchers because they have important technical applications [1]. They are known as refractory, hard, metallic compounds, characterized by hardness, excellent electrical and thermal conductivity and good corrosion resistance [2]. They are extremely good for high temperature oxidation protection coatings. Most of their technological applications in thin film or bulk form are based on this favorable combination of properties, which are attributed to their unusual electronic bonding (a mixture of covalent and ionic bonding) and strong electron phonon interaction. Recently, their electronic and magnetic properties have received renewed attention [3] and some have been found to be superconducting [4]. Among the transition metal nitrides, CrN has unique ferromagnetic configuration. A higher Valence Electron Density (VED) and a stronger hybridization between transition metal d electrons and non-metal p electrons make some of them to exhibit large incompressibility and high hardness [5]. Eck et al. [6] estimated theoretically, the magnetic moment of NaCl-CrN to be 1.4 and 1.0 for ZB-CrN. Herle et al. [7] did measurements on chemically synthesized CrN powder and their resistivity measurements indicate semiconductor behavior with a band gap of 0.09 eV as measured from resistivity. Constantin et al. [8] measured resistivity of single-phase CrN_{1-x} with $x \leq 0.05$ thin films, which shows semiconductor behavior for temperature above 285 K with a band gap of 0.07 eV. On the other hand, Gall et al. [9], using magnetron sputter deposition technique, grew crystalline thin films of CrN_{1-x} with $x \leq 0.03$. He also oriented along (0 0 1) and on MgO (0 0 1) substrates and reported distinct semiconductor characteristics for a large range in temperature without any discontinuities. In fact, no structural phase transformation is observed in their data, which pertains to the rock salt structure. One of the afore mentioned scientists has investigated the effect of pressure on the band structure, density of states and magnetic moment. Moreover, to the best of our knowledge, the mechanical properties and charge density distribution of CrN have not been reported yet.

In the present study, both spin- and non-spin polarized electronic band structure calculations at ambient and high pressure are performed to check the stability in magnetic and non-magnetic phases. CrN crystallizes in rock salt and Zinc blende structure and are stable in NaCl-ferromagnetic phase. Under pressure, NaCl-CrN shows magnetic phase transition from ferromagnetic to non-magnetic transition at 0.5539 Mbar whereas ZB-CrN shows magnetic phase transition from ferromagnetic to non-magnetic transition at 2.615 Mbar. The density of states (DOS), elastic constants, charge density distribution and magnetic moment per CrN at different pressures are reported for both the structures.

2. Method

The total energy, band structure and density of states for rock salt and zinc blende structures of CrN are calculated in non-magnetic (NM) and ferromagnetic (FM) states using tight-binding linear muffin tin orbital method with local density approximation

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(LDA) [10–14]. Von-Barth and Hedin parameterization scheme is used for exchange correlation potential. CrN crystallizes in the B1 (space group, Fm3m) and B2 (space group, Fm3m) type structure. It is magnetically stable in FM state. The Wigner–Seitz sphere was chosen in such a way that the boundary potential was minimum and charge flow between the atoms was in accordance with the electro-negativity criteria. The E and K convergence are also checked. The tetrahedron method [15] of Birllouin zone integration is used to calculate the total density of states. The total energy was computed by changing the volume from 1.05 to 0.65*Vo*, where *Vo* is the equilibrium cell volume relation. Pressure calculations are done with second order Birch Murnaghan equation of states [16,17].The bulk modulus $B=-V\mathrm{o}dP/dV$ is calculated from *P*–*V* relation. Young's modulus and Poisson's ratio are calculated by the formula $E=9BG/(3B+G)$, $v=3B-2G/2(3B+G)$.

3. Result and discussions

3.1. Mechanical property

Equilibrium volume Vo(Å^3), lattice parameters *a*(Å^3), magnetic moment $\mu(\mu_{B/CrN})$, Valence electron density ρ (electrons/Å^3), total energy (Ry), Density of states (DOS) at the Fermi level N(E_f)(DOS(States/Ry.Cell)), Radius of the Wigner–Seitz cell (Rwz), electron–electron interaction parameter(μ^*) obtained from TB-LMTO method are given in Table 1. The equilibrium volume per f.u is 19.8400 Å^3 for ZB-CrN and 16.24101 Å^3 for NaCl-CrN, which is higher than that of Cr metal (14.6743 Å^3) due to the addition of N atoms. Valence Electron Density (VED) is the total number of valence electrons divided by volume per unit cell, which is an important factor for analyzing the super hard materials. The calculated VEDs are 0.5544 electrons/Å^3 for ZB-CrN and 0.6772 electrons/Å^3 for NaCl-CrN. It is worth noting that all VEDs for these structures are higher than that of Cr metal (0.4261 electrons/Å$^{3)}$ and are comparable to 0.70 electrons/Å^3 for diamond [18]. The elastic constants, Bulk modulus B_0 (Mbar) and its derivative B_0', Youngs modulus *E*(Mbar), Shear modulus *G*(Mbar) and Poisson's ratio obtained using TB-LMTO method are compared and given in Table 2. The three independent elastic constants C_{ij} (C_{11}, C_{12}, C_{44}) should satisfy the well known Born–Huang criteria for the stability of cubic crystals [19]

$$C_{44}>0 \quad C_{11}>|C_{12}|, \quad C_{11}+2C_{12}>0 \tag{1}$$

Clearly, the obtained elastic constants of cubic NaCl- and ZB-CrN satisfy the Born–Huang criteria, suggesting that it is mechanically stable in both the phases. Young's modulus *E* and Poisson's ratio are the two important factors for technological and engineering application. The stiffness of the solid can be analyzed using Young's modulus (*E*) value. From Table 2 it is clear that the bulk modulus of CrN is larger than (2.84 Mbar) Cr metal. Thus, we conclude that CrN is less compressible than pure Cr and Poisson's ratio, reflects the stability of the crystal against shear. The ratio can formally take values between −1 and 0.5, which correspond to the lower limit where the material does not change its shape, in other words the upper limit when the volume remains unchanged. The obtained Poisson ratio of NaCl-CrN is 0.18, which indicates that CrN has central interatomic forces and is relatively

Table 1
Equilibrium volume *Vo*(Å^3), lattice parameters *a* (Å^3), magnetic moment $\mu(\mu_{B/CrN})$, Valence electron density ρ (electrons/Å^3), total energy (Ry), Density of states (DOS) at the Fermi level N(E_f)(Dos(States/Ry.Cell)), Radius of the Wigner–Seitz cell (Rwz), electron–electron interaction parameter(μ^*).

	FM ZB-CrN	FM NaCl-CrN
Vo	19.8400	16.2410
a	4.5468	4.2743
$\mu(\mu_{B/CrN})$	1.0152	1.3945
ρ	0.5544	0.6772
μ^*	0.2146	0.2182
$N_l(E_f)$	71.1918	64.2897
Rwz	1.9999	1.8709
E(total)	−2207.6025	−2207.6444

Table 2
Elastic constants C_{11}, C_{12} and C_{44} (Mbar), Bulk modulus B_0 (Mbar) and its derivative B_0', Youngs modulus *E* (Mbar), Shear modulus *G* (Mbar) and Poisson's ratio *v*.

	FM ZB-CrN	FM NaCl-CrN
B_0	2.81	2.84
B_0'	3.954	3.652
v	–	0.18
E	4.23	5.32
G	1.43	2.23
C_{11}	4.72	5.83
C_{12}	1.85	1.34
C_{44}	1.43	2.23

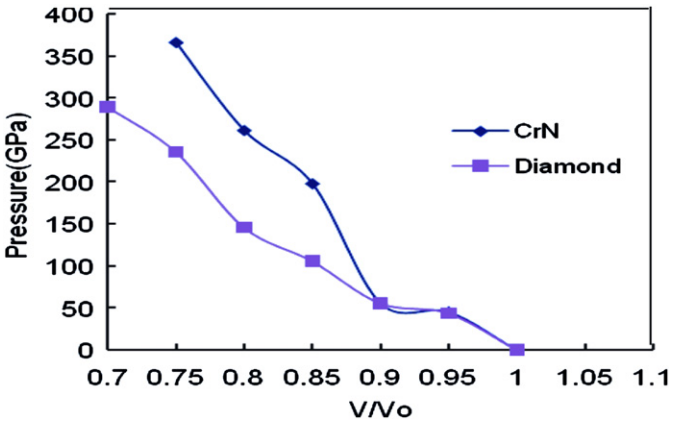

Fig. 1. Volume as a function of pressure with respect to the equilibrium volume, *Vo*.

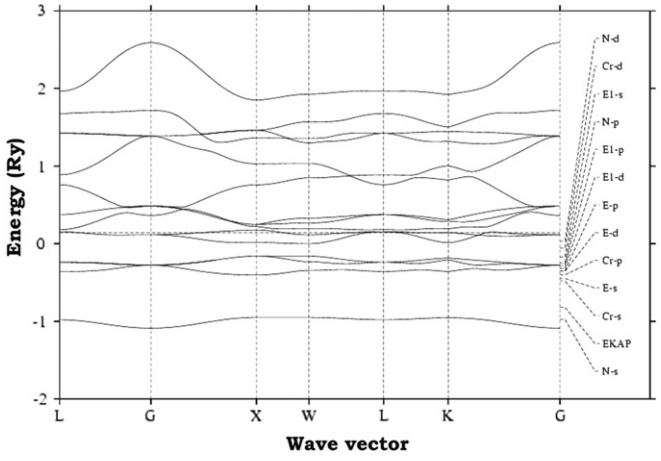

Fig. 2. Band structure of NaCl-CrN at normal pressure.