Structural, electronic, and magnetic properties of CrN under high pressure*

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The structural, electronic and magnetic properties of CrN under high pressure are investigated by first-principles calculations. The antiferromagnetic orthorhombic structure is identified to be the preferred ground state structure. It possesses a bulk modulus of 252.8 GPa and the nonzero magnetic moment of 2.33 μ_B per Cr ion, which agree well with the experimental results. CrN undergoes structural and magnetic transitions from an antiferromagnetic rocksalt structure to a non-magnetic *Pnma* phase at 132 GPa. Under compression, the magnetic moment of the Cr ion reduces rapidly near the equilibrium and phase transition point, and the distribution of the density of states is broadened, but the form of overlap between the orbitals of Cr d and N p remains unchanged. The broadening of the band induces spin flipping, which consequently results in the smaller magnetic moment of the Cr ion.

Keywords: CrN, pressure, electronic property, magnetic property

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1. Introduction

Transition-metal (TM) nitrides have attracted a great deal of attention due to their rich variety of properties, i.e., high hardness, high-temperature resistance, good electrical conductivities and corrosion resistance.[1−4] Their high melting points and chemical hardness values reflect unusual electronic bonding.[5] Recently, their electronic and magnetic properties have received renewed attention.[6−10] VN has been found to be a superconductor,[11] and some of these compounds also have interesting magnetic properties, e.g., [001] antiferromagnetic (AFM) order in MnN[12] and AFM-[110] in CrN.[13]

The competition between magnetic and structural transitions can be tuned or manipulated with external stimuli, such as temperature, pressure, electric or magnetic fields. Among these, the effect of pressure remains unclear. Although MnN and CrN are known to be antiferromagnetic, it is not clear whether the magnetic ordering of the phases could be changed under pressure, resulting in a different crystal structure. In addition, the 3d TM nitride is an interesting system composed of localized 3d electrons, and the band splitting due to the polarization arises mainly from 3d states. However, the behaviour of 3d electrons under high pressure has received less attention. Moreover, there is a strong interaction between 3d electrons and N 2p electrons in the TM nitride, and the interaction under high pressure is not yet clear. Clearly a better understanding of the structural preference and magnetic properties of the TM nitride as a function of pressure is desirable.

Among TM nitrides, CrN has raised many expectations over recent years as it possesses some advantages, such as easy deposition of film, high thermal stability and good corrosion resistance with the prediction of a large bulk modulus. In contrast to previous studies that mainly concentrated on the bulk properties,[13−16] recent research of TM nitrides has focused on films and nanosized particles.[6] The CrN film is grown on semiconductor substrates, and the compound volume can be very different from its bulk equilibrium value. This is the result of the large strain imposed by the substrate or the host. Therefore, studies of the volume dependence of the structural, electronic, and magnetic properties of CrN are important for understanding the properties of CrN in film form.

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However, investigations on CrN under pressure are lacking, and this lack of study is most probably due to the difficulty in preparing stoichiometric samples, which has resulted in different and even contradictory results about its electrical properties.[17−19]

While most TM nitrides have a rocksalt (RS) or closely relevant structure, CrN seems to be very peculiar in that it is the only one of the series that does not have a ground state of cubic symmetry. At room temperature, it is paramagnetic and has the RS structure like most of the TM nitrides, but at Neel temperature $T_{\rm N}$ from 273 K to 286 K, a phase transition in both structure and magnetism to the AFM orthorhombic *Pnma* phase was observed.[13] In the present paper we focus on CrN and investigate the relative phase stability of the RS and orthorhombic structures, the possibility of a high-pressure phase transition and their electronic and magnetic properties under pressure. We show that CrN undergoes structural and magnetic transitions from an antiferromagnetic RS structure to a non-magnetic *Pnma* phase at 132 GPa.

2. Computational details

Our calculation is carried out using the density functional method in the local density approximation (LDA) and generalized gradient approximations (GGA), as implemented in the VASP code.[20] The projector augmented wave (PAW) method[21] is adopted with the PAW potentials taken from the VASP library[22] where $2s^2\ 2p^3$ and $3d^5\ 4s^1$ are treated as valence electrons for N and Cr atoms, respectively. A plane-wave basis set with an energy cutoff of 520 eV is used and gives a well-converged total energy within 1×10^{-6} eV.

Our approach is to relax structure to minimum energy at fixed volume and plot the energy–volume (E–V) curves. The equilibrium volume (V_0), bulk modulus (B_0) and its pressure derivative (B_0') at ambient pressure are estimated by a least-square fitting of the obtained E–V curves to the third-order Birch–Murnaghan equation of state (B–M EOS)[23]

$$E = -\frac{9}{16}B_0\left[(4-B_0')\frac{V_0^3}{V^2} - (14-3B_0')\frac{V_0^{1/3}}{V^{4/3}} + (16-3B_0')\frac{V_0^{5/3}}{V^{2/3}}\right] + \text{const.}, \quad (1)$$

where E is the energy. Using the obtained B_0, B_0' and V_0, the hydrostatic pressure P is determined by the P–V form of the B–M EOS, which is the volume derivative of Eq. (1) as

$$P = \frac{3}{2}B_0\left[\left(\frac{V_0}{V}\right)^{7/3} - \left(\frac{V_0}{V}\right)^{5/3}\right] \times\left\{1+\frac{3}{4}(B_0'-4)\left[\left(\frac{V_0}{V}\right)^{2/3}-1\right]\right\}. \quad (2)$$

To estimate the transition pressure between the RS structure and the orthorhombic crystal structure we plot the enthalpy $H(P) = E[V(P)] + PV(P)$, where $V(P)$ is the volume corresponding to a given external pressure P obtained from Eq. (2), as a function of pressure for both structures, and the intersection point thus represents the occurrance of the transition.

We also perform calculations for the ferromagnetic (FM) and AFM alignments of the magnetic moments, where the AFM corresponds to [100] layers of parallel spin within the layer, but alternating spin direction between adjacent layers.

3. Results and discussion

3.1. Structural and magnetic properties

Table 1 shows a comparison between the equilibrium properties obtained with the different methods. As expected, the lattice constants calculated by GGA are closer to the experimental values than those by the LDA, and the bulk modulus obtained in GGA ($B_{0,Pnma} = 252.8$ GPa) is well comparable to the experimental result ($B_0 = 255(5)$ GPa) listed in Table 1.

Therefore, we only discuss the results from GGA in what follows. The phase transition can occur at the pressure where the enthalpies of the two phases are the same. As explained in Section 2, we determine this transition pressure very accurately by an intersection in the enthalpy plotting, as shown in Fig. 1. The data show that at zero pressure the enthalpy of AFM RS is −74.606 eV per unit cell, and the enthalpy of AFM *Pnma* phase is −74.623 eV per unit cell, indicating that the AFM *Pnma* phase has a preferred ground state structure, which is in accordance with the experimental result.[13] Nevertheless, as pressure increases up to 132 GPa, the AFM RS structure is favored overall. At 132 GPa we have a pressure-induced transition to a non-magnetic *Pnma* phase (see Fig. 1).

Table 1. Equilibrium properties of CrN: lattice constants, bulk modulus B_0 and its pressure derivative B_0'.

	Lattice constant/Å	B_0/GPa	B_0'
	RS structure, non-spin-polarized		
LDA	$a = 3.9823$	396.1	4.5
GGA	$a = 4.0534$	336.2	4.5
	RS structure, spin-polarized		
LDA	$a = 4.0648$	318.9	4.7
GGA	$a = 4.1382$	251.2	4.3
Expt.	$a = 4.13$[a)]		
	Pnma phase, non-spin-polarized		
LDA	$a = 5.6793$, $b = 2.7885$, $c = 3.9750$	391.4	4.4
GGA	$a = 5.7546$, $b = 2.8571$, $c = 4.0539$	334.7	4.3
	Pnma phase, spin-polarized		
LDA	$a = 5.7577$, $b = 2.8749$, $c = 4.0743$	312.6	4.3
GGA	$a = 5.8393$, $b = 2.9232$, $c = 4.1362$	252.8	4.2
Expt.	$a = 5.757$[a)], $b = 2.964$[a)], $c = 4.134$[a)]	255(5)[b)]	

[a)]Reference [13], [b)]Reference [4]

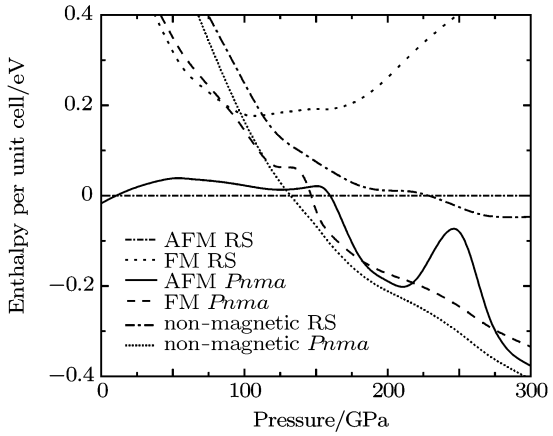


Fig. 1. Enthalpies per unit cell of various structures, each as a function of pressure, referenced to AFM RS structure.

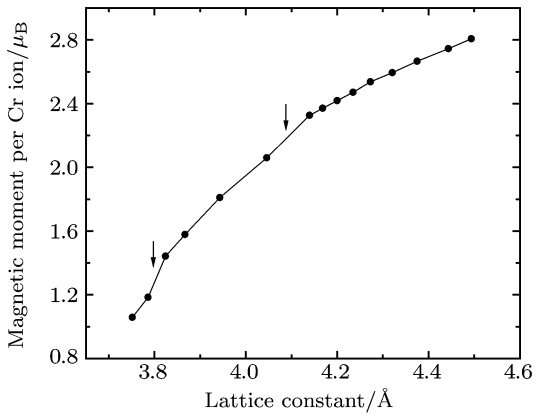


Fig. 2. Magnetic moment versus lattice constant in AFM RS structure.

The magnetic moment for the AFM *Pnma* phase is 2.33 μ_B per Cr ion, which is in fair agreement with the experimental result, 2.36 μ_B.[13] Figure 2 shows the magnetic moment per Cr ion in AFM RS structure as a function of lattice constant. It shows that with the increase of the pressure, the magnetic moment decreases rapidly near 3.803 Å (see the left arrow), which corresponds to the phase transition pressure of 132 GPa. The lower magnetic moments at a smaller lattice constant indicate a tendency to the non-magnetic state. Another rapid decrease of moment occurs near 4.086 Å (see the right arrow) slightly under the minimum-energy lattice constant. The bigger magnetic moments at expanded lattice constants indicate more atomic-like behaviour.

3.2. Electronic properties

Within 10–132 GPa, the AFM RS structure has the lowest enthalpy and the structure experiences the weakening process of magnetism. To clarify the physical mechanism of weakening magnetism, we present the total and partial densities of states (DOSs) of the AFM RS structure at the equilibrium lattice constant in Fig. 3. The DOS shows that the Cr d states form strong σ bonds with the N p states that lie in a range of from -8 to -2.6 eV, while around the Fermi level (E_F) at least 90% of DOS comes from Cr d states, and the remaining contribution is due to the N p states. The polarization on N is negligible, only holding about 0.01 μ_B. The DOS of Cr around E_F clearly resembles the total one, hence the exchange splitting due to the

polarization arises almost entirely from Cr d states.

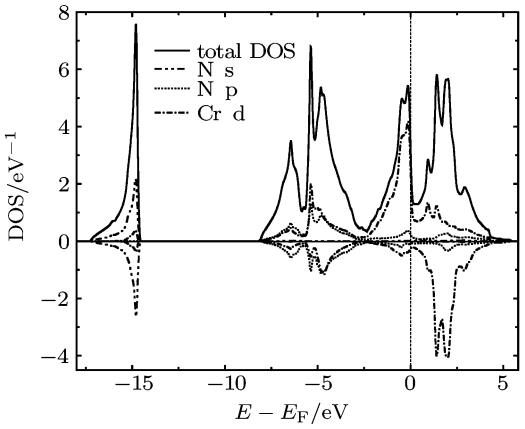


Fig. 3. DOS of the RS AFM structure at equilibrium lattice constant.

Figure 4 shows the partial DOSs (PDOSs) of Cr d and N p for the AFM RS structure at several pressures. The effect of pressure is to increase the volume of Brillouin zone and extend the motion range of electrons. It can be seen that the distribution of DOS is broadened as pressure increases: at equilibrium (0 GPa), the DOS lies in an energy range of from −8.2 to 5.0 eV, while at 120 GPa it is distributed in a range of from −11.0 to 6.0 eV. Furthermore, as the band is broadened, the energy of the valence band (E_1) of spin-up electrons is higher than that (E_2) of spin-down electrons due to electron number conservation (see Fig. 5), which induces spin flipping, which consequently results in a lower magnetic moment of the Cr ion. The resulting magnetic moments for the Cr ion at 0, 50, 80 and 120 GPa are 2.32, 1.81, 1.57, and 1.18 μ_B, respectively. In contrast, the magnetic moment of Cr increases under volume expansion, for example, it is 2.81 μ_B at −38 GPa.

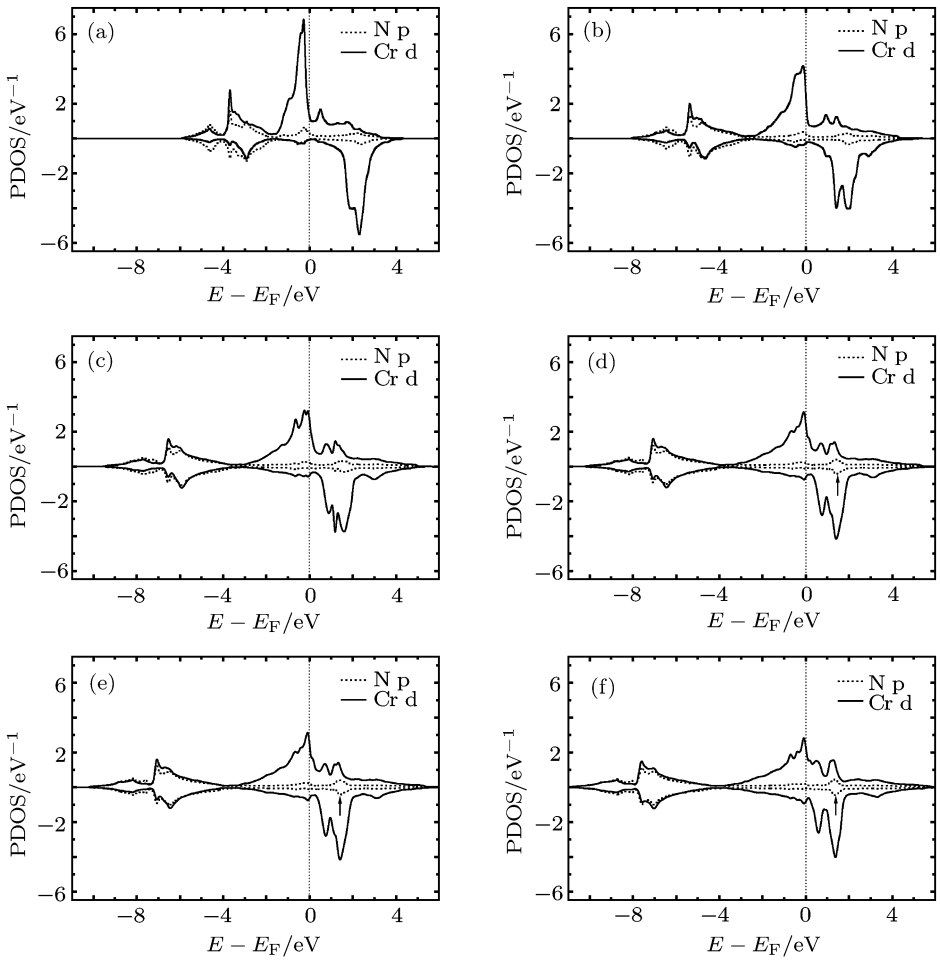


Fig. 4. PDOSs of the RS AFM structure at different pressures. (a) $P = -38$ GPa, (b) $P = 0$ GPa, (c) $P = 50$ GPa, (d) $P = 80$ GPa, (e) $P = 100$ GPa, (f) $P = 120$ GPa.

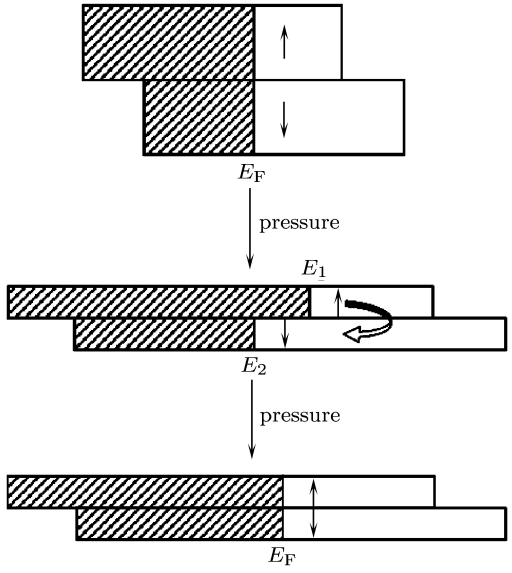


Fig. 5. Schematic DOS showing the process of spin flipping.

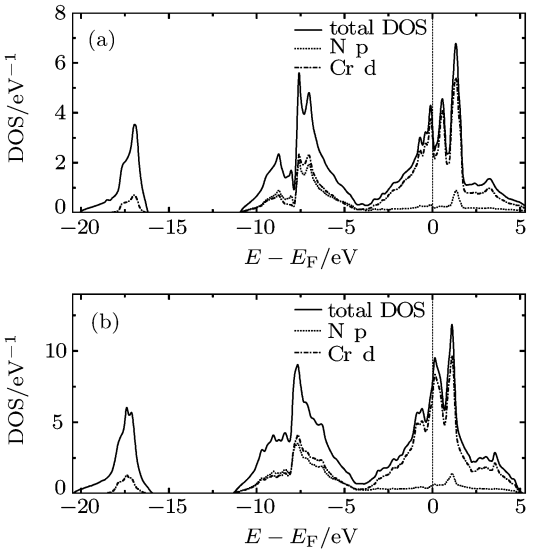


Fig. 6. Comparison of the DOS between (a) RS structure at 120 GPa and (b) *Pnma* phase at 140 GPa.

As shown in Fig. 4, under pressure the distribution of N p states is also widened: at zero pressure the Cr d orbital overlaps the N p orbital in the range of from −8 to −2.6 eV. While at 120 GPa they overlap in the energy region between −11 and −3.7 eV. Although the distribution of DOS is broadened, the form of overlap between the orbitals of Cr d and N p remains unchanged. With pressure increasing, the N p states near E_F are gradually reduced, while an apparent peak of N p appears above E_F (see the arrows), which means that more obvious antibonding states are formed by N p and Cr d states.

At 132 GPa, the AFM RS structure transforms into a non-magnetic *Pnma* phase. Figure 6 shows a comparison of DOS between an AFM RS structure at 120 GPa and a non-magnetic *Pnma* phase at 140 GPa. After the occurrence of phase transition, the distribution of DOS does not change much and the form of the overlap between the orbitals of Cr d and N p is unchanged. For *Pnma* phase, however, the DOS peak near E_F shifts above E_F compared with that of RS structure.

4. Conclusion

In conclusion, we use first-principles methods to investigate the structural, electronic and magnetic properties of CrN under high pressure. The orthorhombic structure is found to be the preferred ground state structure, being consistent with the experimental result. The transition pressure from AFM RS to a non-magnetic *Pnma* phase is determined to be 132 GPa. As pressure increases, the magnetic moment of Cr decreases, indicating a tendency to a non-magnetic state. Under pressure, the distribution of the DOS is broadened, but the form of overlap between the orbitals of Cr d and N p is invariable. It is also worth noting that the broadening of band induces spin flipping, which results in the lower magnetic moment of the Cr ion.

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