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ab initio Study on Electronic and Magnetic Structural Properties of $TiCr_3$ and $TiCr_3N$ Compounds

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Tight binding linear muffin tin orbital method has been used to investigate the electronic and magnetic structural properties of titanium chromium ($TiCr_3$) and titanium chromium nitride ($TiCr_3N$) under pressure. In the present study, the total energy of $TiCr_3$ and $TiCr_3N$ varied with relative volumes has been calculated and fitted into Birch Murnaghan equation of state. Under the pressure of about -19 Giga Pascal, a magnetic phase transition occurs from ferromagnetic to nonmagnetic phase for $TiCr_3$. The magnetic phase of $TiCr_3$ is nonmagnetic in lower volumes *i.e.* at high pressures, while it shows the ferromagnetic order in higher volume (at low pressures). Concerning with structural stability of $TiCr_3$, it shows stable phase as ferromagnetic phase than a nonmagnetic phase. Further the calculations are performed by including N in $TiCr_3$ compound shows nonmagnetic behaviour, which is evident from the density of state.

Keywords: Magnetic transition, Electronic structure, Density of states, Magnetic property.

INTRODUCTION

In recent years, transition metal-based nitride compounds have attracted much attention for its technological applications. These compounds are of prime importance for wear-resistant, protective and decorative coatings because of their broad range of functional properties in the field of machining and decoration in microelectronics [1-3]. The transition metal nitrides are of scientific interest and has a variety of properties. The titanium chromium nitride coating provides a complete solution for damage mechanism [4,5]. The titanium nitride increases the hardness of coating for drilling tools [6]. Though high-temperature applications are restricted beyond 500 °C, it can be used for high-speed dry machining process [7,8]. Titanium chromium nitride compound has improved oxidation resistance and better mechanical properties and it is used for multilayer coating on cutting tools, press molds and dies. Present study on spin polarized and non-spin-polarized electronic band structure calculations were carried out under various pressure for finding the stable magnetic phase of compounds under investigation.

EXPERIMENTAL

The basis set used for calculations are as: Ti: [Ar] $4s^2 3d^2$; Cr: [Ar] $4s^1 3d^5$; N: [He] $2s^2 2p^3$. $TiCr_3N$ and $TiCr_3$ compounds assumed to be in the cubic perovskite structure with space group Pm-3m (no: 221). The structural and magnetic properties of these compounds have been calculated using TB-LMTO method within atomic sphere approximation. The total energy calculations were performed for $TiCr_3$ in the cubic structure with face centered cubic (FCC) positions, where Ti atom situated in a corner position and Cr atom at face centered cubic position for the $TiCr_3$ compound. The $TiCr_3N$ compound crystallizes in cubic perovskite structure, having Ti at corner site, Cr at face centered cubic site and N at body centered cubic (BCC) site [9]. The exchange-correlation scheme of Von Barth and Hedin [10] has been employed in the present calculation. Hence, the most important relativistic corrections namely the Darwin's correction, mass velocity terms and spin-order coupling has been included. The total energy of this compound has been calculated as a function of reduced volume and fitted into Birch Murnaghan equation of state [11,12]. The calculation have been performed by 216 k-points in the entire Brillouin zone.

RESULTS AND DISCUSSION

The total energy of $TiCr_3$ and $TiCr_3N$ compounds with different volumes are calculated to determine the equilibrium structural parameter. The calculated equilibrium lattice parameter and bulk modulus are given in Table-1.

Fig. 1 shows the variation of total energies with cell volume in ferromagnetic and nonmagnetic phases at ambient condi-

TABLE-1
LATTICE PARAMETER AND BULK MODULUS OF $TiCr_3N$, $TiCr_3$-NM AND $TiCr_3$-FM COMPOUNDS

Compounds	Lattice constant 'a' (a.u)	B (Mbar)
$TiCr_3N$	7.275	2.645
$TiCr_3$ (NM)	7.011	2.318
$TiCr_3$ (FM)	6.983	2.390

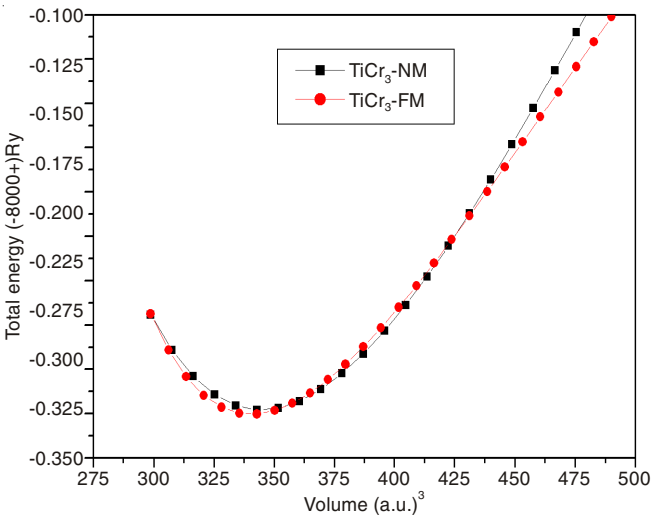

Fig. 1. Total energy *vs.* volume $(a.u)^3$ of $TiCr_3$ (FM) and $TiCr_3$ (NM)

tions to examine the magnetic stability of $TiCr_3$ and $TiCr_3N$. This ferromagnetic calculation shows null magnetic moment for $TiCr_3$ at Ti and Cr sites with a small decrease in lattice constant at ambient volume. It also shows a stable phase of $TiCr_3N$ as a nonmagnetic order. As a consequence of charge transfer between chromium atoms and titanium atom, there is an equal occupation number for both spin directions as tabulated in Table-2.

As can be seen, ferromagnetic calculations gives null local magnetic moments at metals sites (Ti and Cr) and nitrogen sites and hence the ground state of these nitrides is nonmagnetic.

Fig. 2 showed that the $TiCr_3$ compound exhibits the ferromagnetic order from 8.2 (a.u) to 7.4 (a.u). The magnetic transition from ferromagnetic to a null magnetic moment in $TiCr_3$ at a pressure of about -19 Giga Pascal occurs with a small decrease in lattice constant nearly 7.27 (a.u) as shown in Fig. 3.

From the Fig. 3, the pressure above -19 Gpa $TiCr_3$ shows ferromagnetic phase at both spin-polarized and non-spin-polarized calculations and below that pressure both the curves starts to deviate from each other will be the evidence for the separation of ferromagnetic and nonmagnetic phase. The greater lattice constant (8.2172 a.u) offers 9.5756 μB as total magnetic moment per unit cell, where 3.3768 μB at Cr site

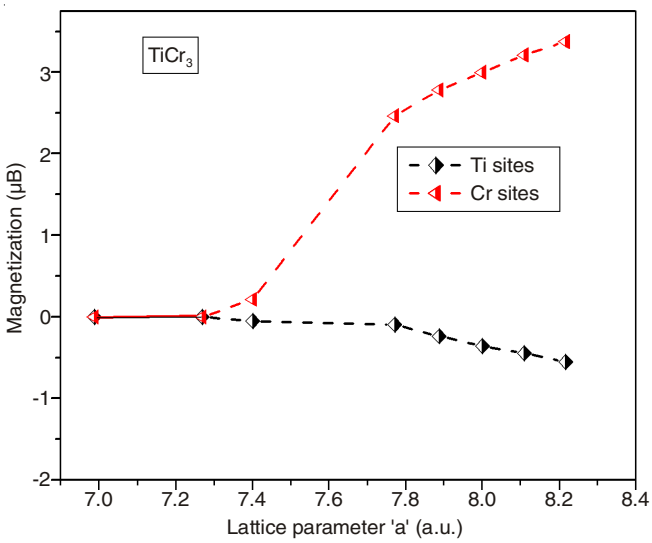

Fig. 2. Magnetization *vs.* lattice parameter of $TiCr_3$

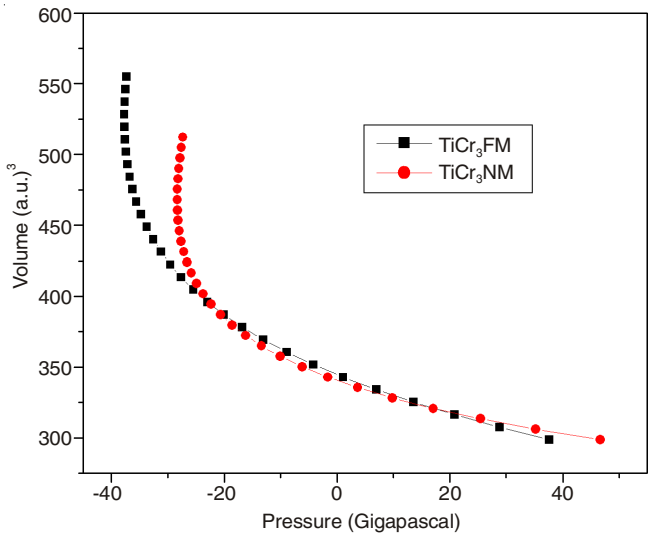

Fig. 3. Pressure *vs.* volume of both $TiCr_3$ (FM) and $TiCr_3$ (NM)

and -0.5547 μB at Ti site. In $TiCr_3N$ compound, the inclusion of nitrogen atom in $TiCr_3$ compound leads to the disappearance of ferromagnetic order.

The total density of states for $TiCr_3$ and partial density of states for $TiCr_3$ and $TiCr_3N$ at ambient pressure has been shown in Figs. 4a-4b and 5a-5f. The total density of state shows the presence of ferromagnetic behaviour in $TiCr_3$ and non-magnetic behaviour in $TiCr_3N$ compound. Fig. 5c and 5f shows the partially unoccupied spin up and spin down d state of Ti and Cr having opposite local magnetic moments. It confirms the ferromagnetic moment for $TiCr_3$ in higher volumes. The $TiCr_3N$

TABLE-2
PRESENTS SOME NUMBER OF STATES OBTAINED FOR $TiCr_3N$ WITH SPIN POLARIZATION AT EQUILIBRIUM VOLUME OF THE COMPOUND

$TiCr_3N$	Ti			Cr			N		
	Spin up	Spin down	Difference	Spin up	Spin down	Difference	Spin up	Spin down	Difference
n_s (electrons/spin)	1.148	1.148	0.000	0.311	0.311	0.000	1.581	1.581	0.000
n_p (electrons/spin)	2.076	2.076	0.000	0.434	0.434	0.000	3.662	3.662	0.000
n_d (electrons/spin)	4.427	4.427	0.000	3.913	3.913	0.000	0.132	0.132	0.000
ΔQ (electrons)		-1.554			0.133			-2.436	
E_F (Rydberg)					0.246				

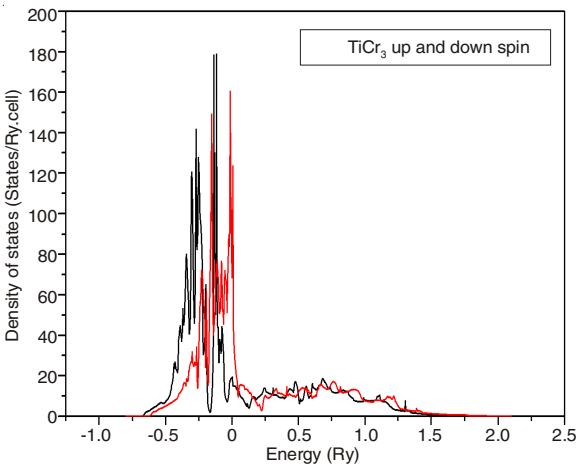

Fig. 4(a). Total density of state of spin up and spin down in $TiCr_3$

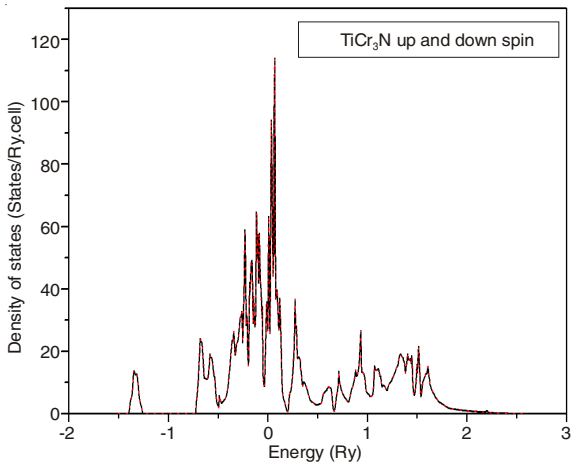

Fig. 4(b). Total density of state of spin up and spin down in $TiCr_3N$

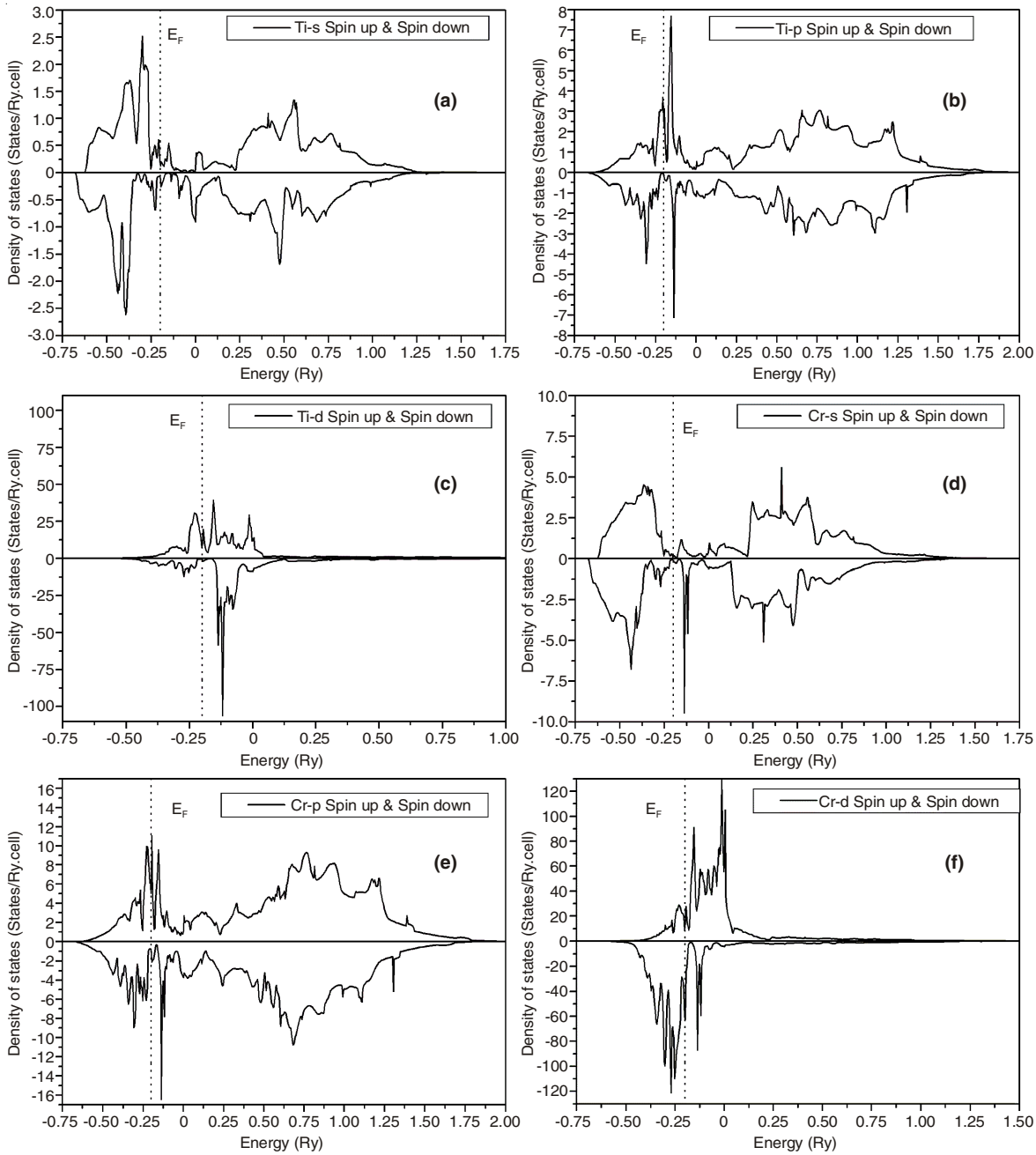

Fig. 5. Projected density of state of spin up and spin down electrons for $TiCr_3$ compound at Ti site (a) Ti-s, (b) Ti-p and (c) Ti-d and at Cr site (d) Cr-s, (e) Cr-p and (f) Cr-d

compound has a null magnetic moment because the density of state in figures (not shown) spin up and spin down of Ti, Cr and N were same that proves the null magnetism.

Finally, it is concluded that there is a magnetic phase transition happens from ferromagnetic phase to nonmagnetic phase for $TiCr_3$ while including nitrogen even at higher volumes investigated through densities of states profiles of $TiCr_3$ and $TiCr_3N$ and presented.

Conclusion

The magnetic structural behaviour of $TiCr_3$ and $TiCr_3N$ has been calculated by using TB-LMTO method within atomic sphere approximation. The structural stability of $TiCr_3$ with magnetic order and nonmagnetic order along with $TiCr_3N$ has been calculated. It is revealed that $TiCr_3$ with the magnetic order is stable when compared with the nonmagnetic order of $TiCr_3$ and $TiCr_3N$ compounds. In addition to structural stability, the magnetic stability of the compounds is also calculated. The $TiCr_3$ shows nonmagnetic order because of equal occupation numbers for both spins at lower volumes and the ferromagnetic order at higher volumes of lattice constant. Further, the calculations have been repeated by including nitrogen atom in $TiCr_3$ compound in which the ferromagnetic behaviour vanishes. The result shows that the structural stability of $TiCr_3N$ is nonmagnetic and it is verified using partial density of states.

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