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ORIGINAL ARTICLE

PRESSURE-INDUCED MAGNETIC TRANSITION IN $TiCO_3$– AN *AB-INITIO* STUDY

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ABSTRACT

The Tight Binding Linear Muffin Tin Orbital method (TB-LMTO) have been used to study the magnetic and electronic structure of Titanium tricobalt ($TiCo_3$)and Titanium tricobaltnitride ($TiCo_3N$).A magnetic phase transition from ferromagnetic phase to nonmagnetic phase under high pressure of 0.197 Mega bar have been calculated. Furthermore a transition from ferromagnetic to nonmagnetic phase in $TiCo_3$ while including nitrogen atom with this compound also predicted. For each compound, the equilibrium lattice constant were attained by reducing the total energy with respect to the cell volume under pressure. Obtained results reveal that the modeled $TiCo_3$ is ferromagnetic (FM) with 1.31 μ_B (Bohr magnetron) as the magnetic moment at Co sites and -1.10μ_B at Ti sites and the total magnetic moment as 2.82 $\mu_B$at equilibrium volume. Hence, $TiCo_3$ attains the stable magnetic order above lattice constant 6.98 Atomic units. It shows a transition to a non-magnetic state below this lattice constant. The transition shows that $TiCo_3$ is ferromagnetic at larger volumes and non-magnetic at lower volumes whereas $TiCo_3$ shows nonmagnetic phase at all volumes with the addition of nitrogen atom. Thus, it shows that inclusion of nitrogen vanishes the ferromagnetic order of $TiCo_3$ even at larger volumes.

Keywords: Magnetic transition, Metal nitrides, Properties, Ferromagnetic, High pressure

1.INTRODUCTION

Titanium based Nitrides are of great important because of its tremendous industrial applications such as Lithium-ion batteries, energy storage, fuel cells and biomedical industries (Linfei Lai et al., 2014; Shanmu Dong et al., 2013; Serro et al., 2009; Pires and Saramago,2009; Koniger et al., 1996; Mezger and Creugers,1992; Kuhnen and Dos Santos,2004; Dos et al., 1997; Kuhnen and Dos,1994. These nitrides offer thehigh wear resistant property to the materials (Kuhnen and Dos,1992). Due to their exceptional physical and chemical properties, it is also used in aeroplanes industries and biomaterials (Toth,1971; Storms,1967).These kind of compounds are chemically stable and shows good corrosion resistance even at room temperature and they are also used as biocompatible layers for orthopedic and dental implants. Finally, their hardness is among the highest next to diamond. It has contributed to the industrial use of titanium nitrides, as good candidates for applications needing high wear resistance(Ohring,1992; Bunshah and Deshpandey). Titanium nitrides doped with transition metal atom displays a wide range of interesting phenomenon of converting the semiconducting materials to magnetic and superconducting compounds (Shein and Ivanovski,2004).Titanium nitride is also used as an electrically conducting barrier. Thus, these compounds have great high tech scientific interest (Dridi et al., 2002). However, Titanium Cobalt alloys are important biomedical materials due to their potential applications in hard tissue replacement(Tetsuya Takahashi et al., 2011). Laser cladding of intermetallic phase $TiCo_3$ and β (i.e. Face Centered Cubic) cobalt provides higher hardness at lower velocities (Hamidreza Alemohammad, et al., 2007).The compounds with transition metal atom also show excellent electrical conductivity, thermal conductivity, high chemical stability, thermal stability, good wear resistance, and corrosion resistance. All these properties make them suitable for many technological applications. C. A. Kuhnen et al studied the electronic structure of compounds FeV_3, VFe_3, V_4N, VFe_3N, and FeV_3N using the LMTO method (Dos Santos et al., 2006).The nitrogen substituted compounds V_4N, FeV_3N and VFe_3N shows nonmagnetic order, when iron is replaced by vanadium atoms destroys the ferromagnetic order

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of theγ'-Fe_4N nitride. Similarly, Magnetic and electronic properties of the two compounds γ'-$AgFe_3N$ and γ'-$AuFe_3N$ have been studied using LMTO calculations and correlated with experimental results (De Figueiredo et al., 1997). Also, LMTO method is engaged to investigate the electronic structure and local magnetic properties of the ferromagnetic iron nitrides $RuFe_3N$,$ZnFe_3N$, $InFe_3N$, Fe_3BN, $PdFe_3N$, $MnFe_3N$, and $SnFe_3N$ (Dos Santos,2007; Dos Santos et al., 2009; Kuhnen and Dos Santos,1994). γ'–Fe_4Nhave been used as model compound substituting the transition metal atoms in place of Fe atom, the electronic properties have been studied using LMTO methods of calculation. In the present work, three Fe atoms are replaced by Co atom and one Fe atom by other transition metal atom Ti to analyze the magnetic properties of those compounds with and without nitrogen. The investigated structural properties of XFe_3N cubic ternary iron based nitrides reveals that in the cases of $ScFe_3N$, $CoFe_3N$, $NiFe_3N$, $CuFe_3N$ and $ZnFe_3N$, the equilibrium configurations corresponds to the cubic structure with space group Pm-3m.

This first principle ab-initio theoretical method is an effort to get a clear understanding of the electronic and magnetic structure of $TiCo_3$ and $TiCo_3N$ compounds. The interest in this substitution arises because of the recent applications and need promising features of this class of materials.

2.METHOD OF CALCULATION

The electronic and magnetic structure of $TiCo_3$ and $TiCo_3N$ compounds have been studied using self-consistent TB-LMTO method. The $TiCo_3N$ have the perovskite structure as $CaTiO_3$ –type structure and $TiCo_3$ compound have the face-centered cubic structure as Au_3Cu type structure as shown in figures 1(a) and 1(b) respectively. The software used to draw figure 1a and 1b is XcrySDen and other figures is Origin. Both compounds are crystallized with space group Pm-3m (space group no: 221) (Gil Rebaza et al., ,2012). In order to find the phase stability of the compounds, the total energies have been calculated for these compounds and fitted with Birch Murnaghan equation of state (Brich,1978).

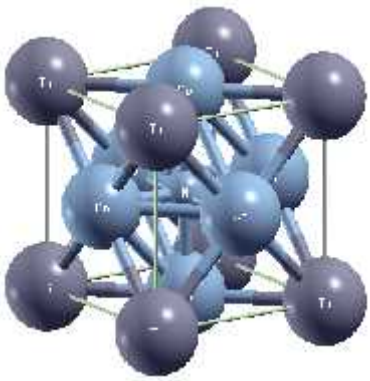

Fig. 1a Atomic Structure of $TiCo_3N$

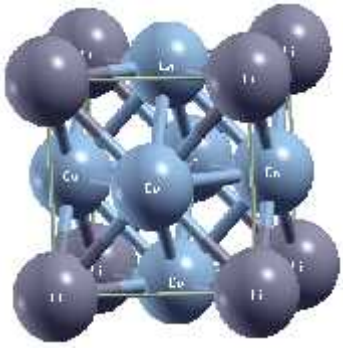

Fig. 1b Atomic Structure of $TiCo_3$

Band structure calculations may be referred as linear methods were introduced by O. K. Anderson in 1971, which are later derived as many efficient computational patterns. One of these linear methods that solve self-consistent electronic structure problem in an extremely effective way is the Linear Muffin Tin Orbital (LMTO) method(Skriver et al., 1975; Andersen,1975; Harrison,1980). Using this method various calculations for infinite crystals and ground state properties of real materials may be estimated. The simplest and most widely used one-electron Hamiltonian is that tight-binding (TB) method with minimal base and in its two-center approximation has been necessary for self-consistent density functional calculations.

The total energy calculations were performed to obtain the ground state properties of the compounds. Muffin tin approximation has been employed to the crystal potential with overlapping Wigner-Seitz spheres. A spin polarized LMTO calculation have been performed using Von Barth and Hedin Parameterization (Von Barth,1972) exchange-correlation. The whole part of Brillouin zone consists of reciprocal space sum with 216 k-points. The self-consistent calculations have been carried out until energy convergence on a scale better than 0.1mRy. The Densities of states (DOS) have been calculated as a sum of delta function for 6 x 6 x 6 mesh points. In the present work, 3d and 4s orbitals of Ti, 3d and 4s orbitals of Co and 2s, 2p orbitals of N have been treated as valence states.

3.RESULTS AND DISCUSSION

The equilibrium volume of $TiCo_3$ and $TiCo_3N$ ordered compounds have been obtained using total energy calculations. The calculated total energy versus volume for $TiCo_3$ in both ferromagnetic (FM) and nonmagnetic (NM) states as shown in figure 2 and for $TiCo_3N$ in figure 3.

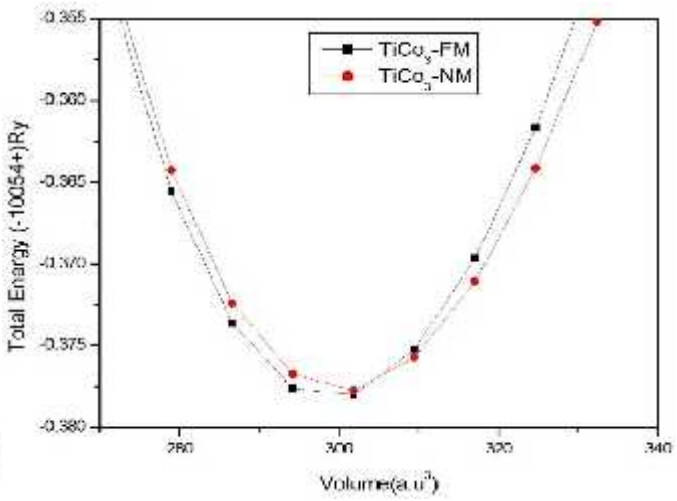

Fig. 2 Total energy with volume in ferromagnetic and non-magnetic states of $TiCo_3$

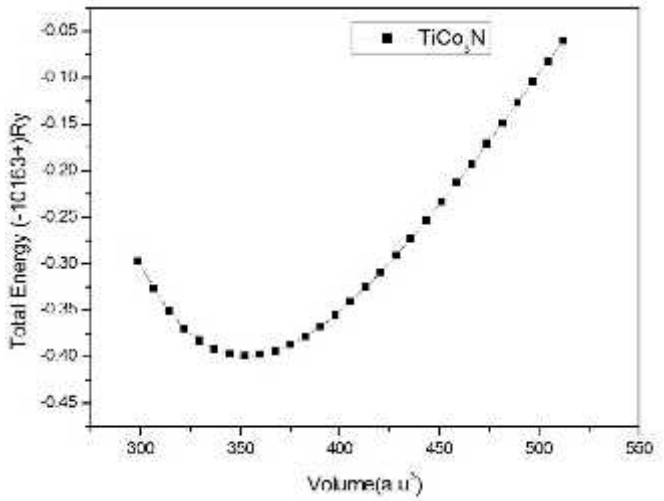

Fig. 3 Variation of total energy with the volume of $TiCo_3N$ in the nonmagnetic state

The figure 2 clearly shows that ferromagnetic state (FM) of $TiCo_3$is more stable than a nonmagnetic phase. The FM calculation of $TiCo_3N$ shows null magnetic moment at Ti, Co and N sites and the nonmagnetic(NM) calculation of the compound has been analyzed to obtain the equilibrium volume 352.494 cubic atomic unit $(a.u)^3$ as shown in figure 3. The binding curves in figures 2 and 3 were obtained through an analytical fitting of the calculated total energies to a fourth-degree polynomial. The corresponding equilibrium lattice constant and bulk moduli are shown in table 1.

Table 1. Theoretical parameters of $TiCo_3$ and the $TiCo_3N$ compounds (Equilibrium lattice constant *a* (in a.u) and bulk modulus B (in Giga Pascal))

Compound & type of calculation	Bulk Modulus B (Gpa)	Lattice Constant *a* (a.u)
$TiCo_3$ –NM	251.800	6.686
$TiCo_3$ –FM	232.330	6.697
$TiCo_3N$ –NM	277.890	7.064

From the table, it is clear that the inclusion of nitrogen into $TiCo_3$ expands the lattice constant around 5.65% and the bulk modulus is also greater in the case of $TiCo_3N$. Regarding the magnetic moment, $TiCo_3$compound found to have some magnetic moment and $TiCo_3N$ have a null magnetic moment because of the arrangement of atoms in the lattice. The inclusion of the nitrogen atom at body centered cubic position leads to Co-N distances shorter than the Ti-N distances. Thus, it is proved that the interaction possibly occurs between Co-N than Ti-N. The changes in the electronic structure can be easily understood with the calculated densities of states (DOS) at theoretical equilibrium volumes for both compounds. The calculated s, p and d densities of states for both spin directions at Ti and Co sites for $TiCo_3$ are shown in figure 4 and 5.

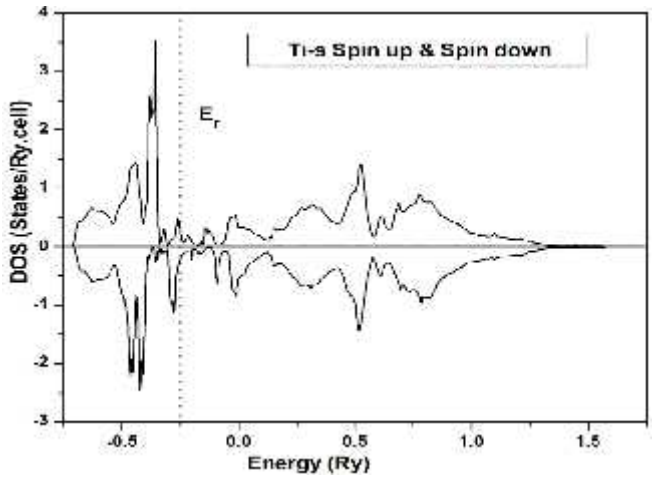

Fig.4a the s-projected densities of states for a spin up and spin down electrons at Ti sites for $TiCo_3$

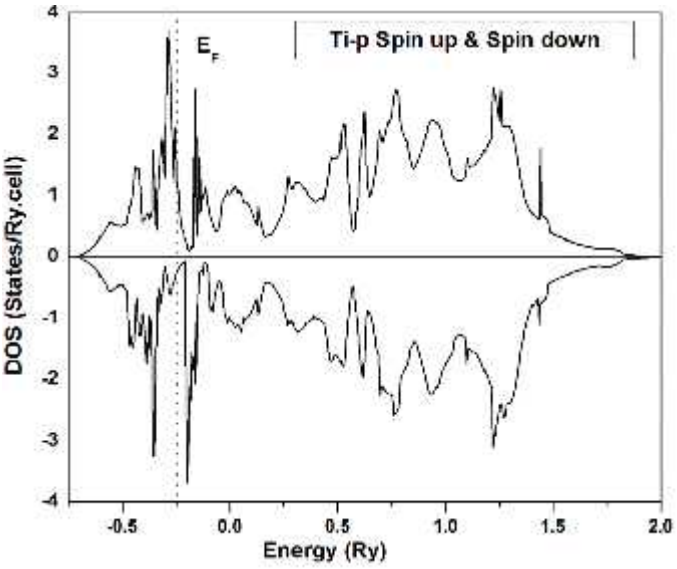

Fig. 4bThep-projected densities of states for spin-up and spin-down electrons at Ti sites for $TiCo_3$

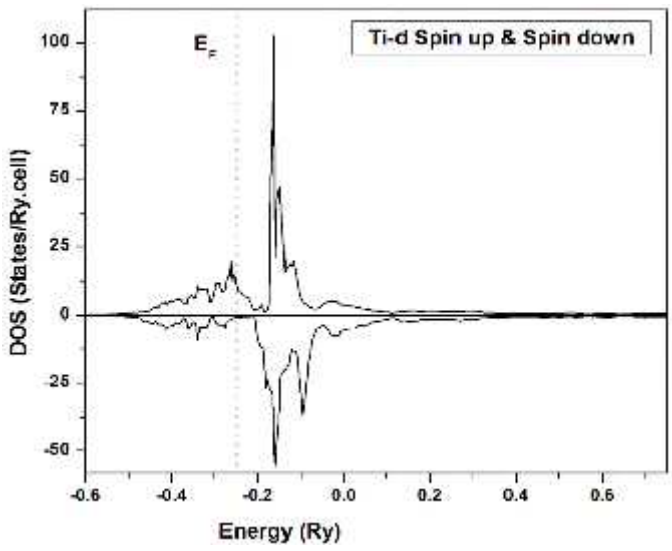

Fig. 4cthe d-projected densities of states for spin-up electrons and spin-down at Ti sites for $TiCo_3$

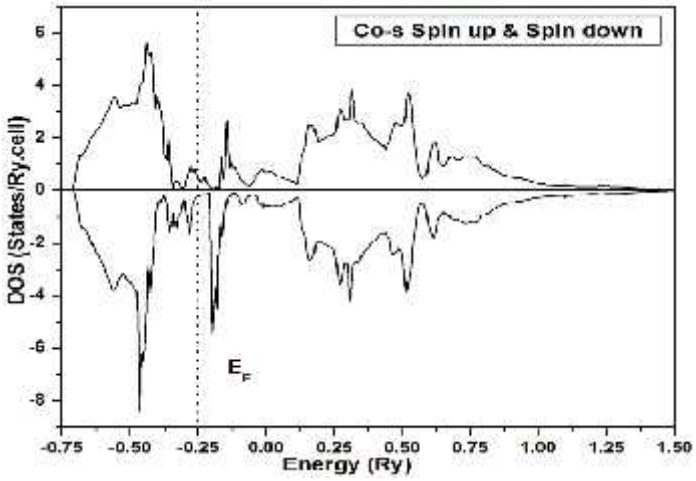

Fig. 5a the s-projected densities of states for spin-up and spin-down electrons at Co sites for $TiCo_3$

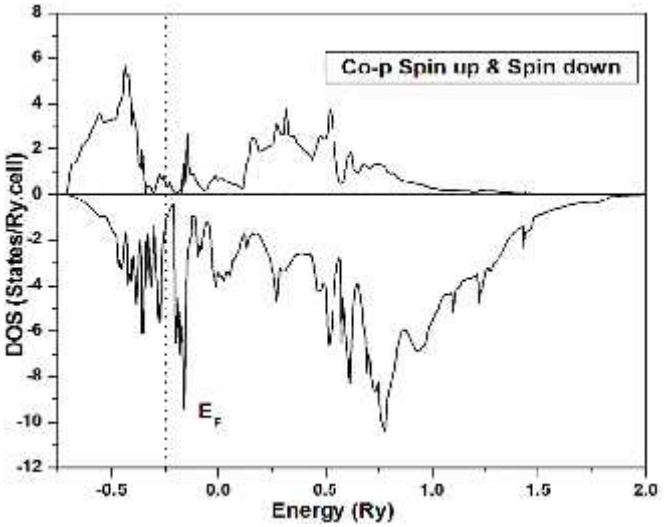

Fig. 5bthep-projected densities of states for a spin up and spin down electrons at Co sites for $TiCo_3$

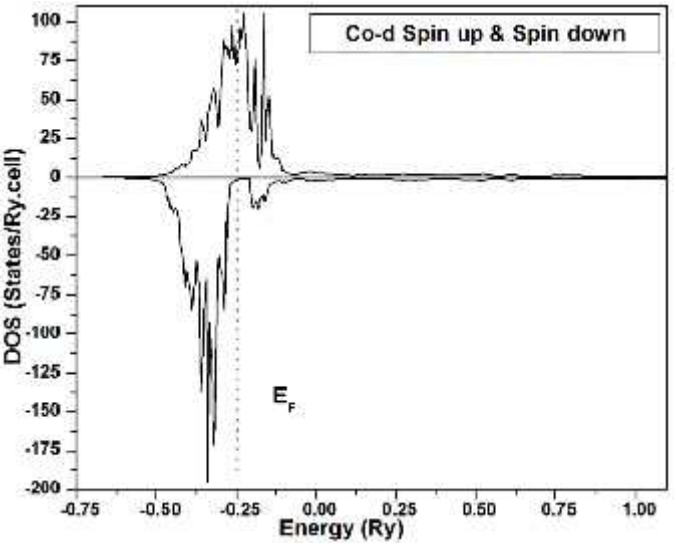

Fig. 5cthe d-projected densities of states for spin-up and spin-down electrons at Co sites for $TiCo_3$

The interaction between Co and Ti atoms are reflected in the pronounced peaks in the DOS. At Ti sites, the d-DOS may be pronounced than s and p states. From the projected DOS structures for figure 4 and 5, it is clear that for both sites the self-consistent fields felt by the spin up and spin down electrons are different. For Co sites, the spin down d states are unoccupied provides net magnetic moment (it is shown in figure 5c). Since the $TiCo_3N$ nitride is nonmagnetic (Figure 6), the potentials felt by spin up and spin down electrons become equal and electronic state exhibits the same DOS for up and down spin.

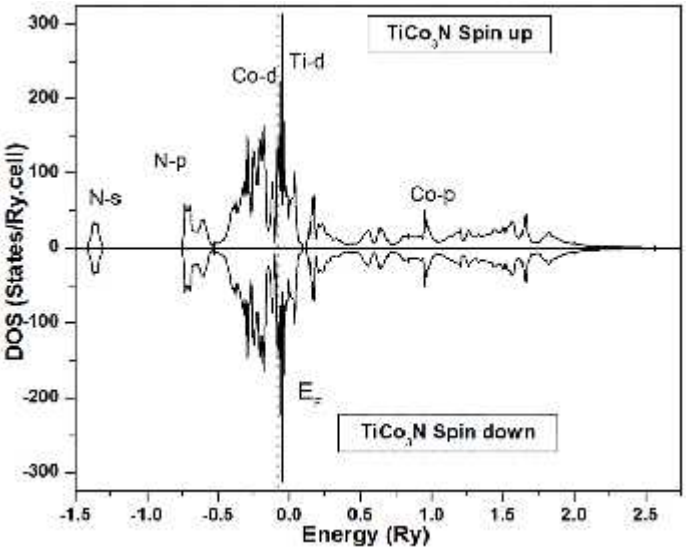

Fig. 6 Overall DOS of $TiCo_3N$ for Spin up and spin down states

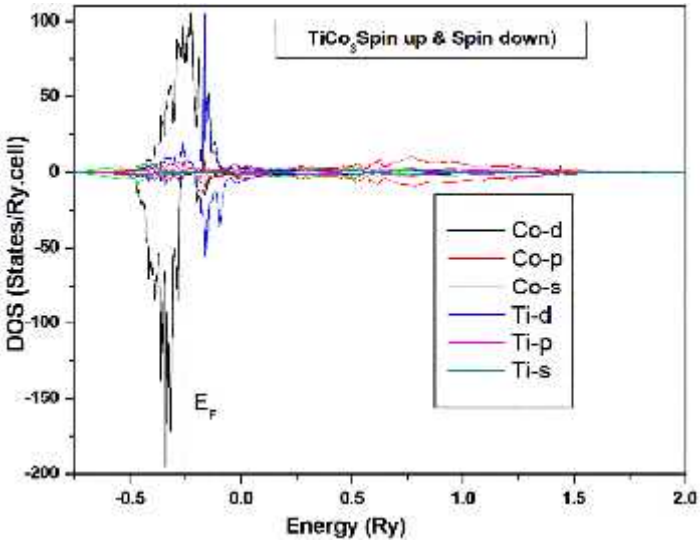

Fig. 7 The s, p, and d- projected densities of states for $TiCo_3$

From the figure.7, there found the negligible contribution of s band for the magnetic moment whereas slight asymmetric nature of p state below the Fermi energy level shows that the contribution of p orbital is less. The great asymmetry in up and down spin of d-DOS representing that overall magnetic moment of $TiCo_3$ has been given by d electrons. The vertical dotted line at -0.25 Ry denotes Fermi energy. The population of the spin down d states at Co sites comes from an inversion of spin up into spin down d electrons and a small charge transfer from N sites to Co sites that occupy spin down d states. The interactions between Co and N atoms are stronger than the interactions between Ti and N atoms. From total energy calculations, it has been obtained that $TiCo_3$ is ferromagnetic. Analyzing the magnetic behavior of $TiCo_3$, it undergoes a magnetic transition from ferromagnetic to non-magnetic states for lattice constants below 6.98 a.u.

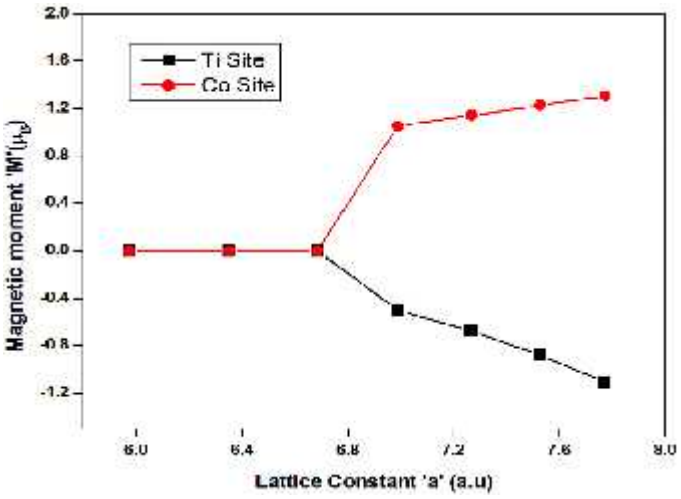

Fig.8 Variation of magnetic moment for $TiCo_3$ as a function of lattice constant at Ti and Co sites

Figure 8 shows the behavior of magnetic moments at Co sites as a function of lattice spacing. In this figure, the magnetic moment increases smoothly for higher volume (negative pressures) but for lattice constants below the equilibrium volume in the range from 6.9 a.u to 6.7 a.u there is a great slope in the magnetic moment versus lattice constant curve(figure 8), that is, the magnetic moment decreases substantially. In this range of lattice constant, the magnetic moment decreases slowly and continuously goes to zero which predicts a transition to a non-magnetic state at lattice constant of 6.536a.u shown in figure 9. This magnetic transition happens because of magnetic collapse due to the expansion of band in transition metal atoms under pressure. There is a decrease in the magnetic moment while increasing pressure (lower volumes) at pressure 0.197 Mega bar the transition occurs from ferromagnetic to nonmagnetic state. Hence, the $TiCo_3$ is ferromagnetic at larger volumes and non-magnetic at lower volumes. Figure 10 contains the relation connecting reduced volume and pressure of $TiCo_3$ and $TiCo_3N$. Reduced volume decreases with increase in pressure.

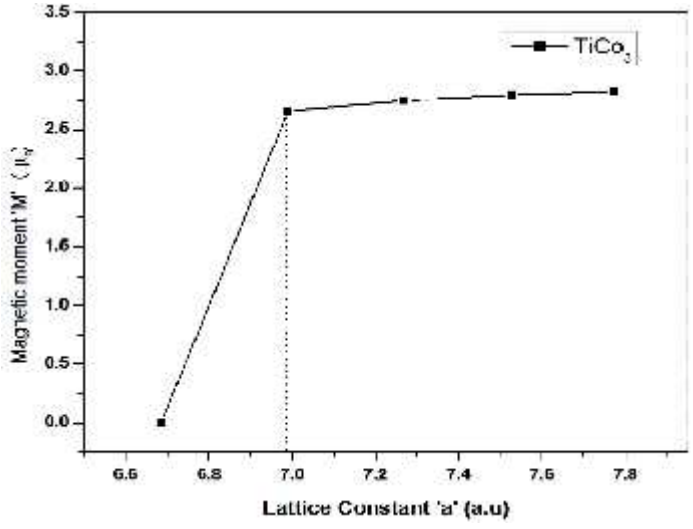

Fig.9Magnetic moment versus lattice constant for $TiCo_3$

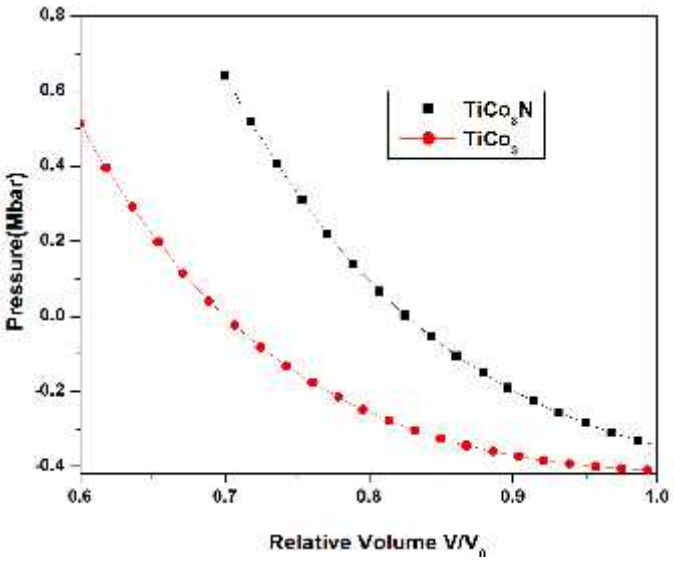

Fig. 10Pressure in Mega bar versus relative volume of $TiCo_3$ and $TiCo_3N$

4.CONCLUSION

The electronic structure, ground state and magnetic properties of compounds $TiCo_3$ and $TiCo_3N$ have been studied using TB-LMTO method. The equilibrium lattice constant for the compounds has been estimated by calculating total energies. For the $TiCo_3N$ ferromagnetic calculations give null magnetic moment at all sites and the stable phase is non-magnetic. From DOS profiles of the $TiCo_3N$compound, the spin-down d-states at Co sites which come from an inversion of spin-up into spin-down d-electrons and a small charge transfer from N sites to Co sites that occupied spin-down d-states offers null magnetism. Also, the stable crystallographic phase of $TiCo_3$ is ferromagnetic. An interesting feature regarding the ferromagnetic calculations of $TiCo_3$ predicts a magnetic transition from ferromagnetic phase to a non-magnetic phase at very low volumes with a minor variance in the critical lattice spacing. Regarding the bulk modulus, $TiCo_3N$ has the higher bulk modulus in accordance with the fact that when Ti and Co atoms occupy the face-centered positions or when occupying the corner positions, the nitrogen interacts stronger with metals at face-centered positions with a very small interaction with metals at corner positions. The nitrogen–metal interactions contribute for the high value of bulk modulus of $TiCo_3N$ nitride which is comparatively same as other transition metals V, Cr, Mn and Fe (Sathana et al., 2014; Sathana et al., 2017). Similar to the other transition metals Cobalt also have low bulk modulus for $TiCo_3$ compound.

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