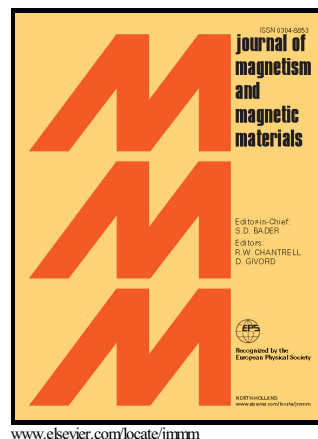


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( $\text{T}=\text{Fe}$ ,  $\text{Co}$  and  $\text{Ni}$ ) by Hybrid Functional Theory

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## Structural and Magnetic Properties of $\text{TiTF}_3$ (T = Fe, Co and Ni) by Hybrid Functional Theory

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### Abstract

DFT studies are performed to investigate the structural, mechanical and magneto-electronic properties of the  $\text{TiTF}_3$  (T = Fe, Co and Ni) perovskites for the first time using GGA, GGA+U and hybrid density functional theory (HF). Our calculations show that HF give better results than GGA and GGA+U and more consistent with the experiments. The comparison of the lattice constants calculated by HF with experiments shows a maximum underestimation less than 0.2 %. The chemical bonding between different ions in these compounds is explained on the bases of electronic clouds, which reveals that in  $\text{TiFeF}_3$ , Fe has more ionic character with F than the rest. The mechanical properties explain the hardness of these compounds and show that  $\text{TiFeF}_3$  is more ductile. Spin-dependent electronic band profiles show that  $\text{TiFeF}_3$  and  $\text{TiCoF}_3$  are metallic, whereas  $\text{TiNiF}_3$  is pseudo direct wide bandgap semiconductor. The stable magnetic phase optimizations and the calculated magnetic susceptibility confirm that  $\text{TiFeF}_3$  and  $\text{TiNiF}_3$  are ferromagnetic whereas  $\text{TiCoF}_3$  is anti-ferromagnetic material.

**Keywords:** Fluoride perovskites; elastic properties; electronic band structure; ferromagnetism; ab-initio calculations

## 1. Introduction

Very recently mixed-halide organic/inorganic hybrid perovskites came to the fore as a result of their high performance in converting solar energy into electrical energy with efficiency more than 20% architectures under full-sun light [1, 2]. The interesting physical and structural properties make them significant candidates for photovoltaic cells for example perovskite structured semiconductor ( $\text{CH}_3\text{NH}_3\text{PbI}_3$ ) type material has high charge carrier mobilities which is important because of high charge carrier lifetimes [3] ( $\text{CH}_3\text{NH}_3\text{SnI}_3$ ) and  $\text{CH}_3\text{NH}_3\text{SnI}_{3-x}\text{Br}_x$  perovskites are also promising candidates for photovoltaic cells [4]. Transition metals (T) based perovskite halides have attracted enormous attention of materials scientists because of their technological applications in magnetoresistivity, piezoelectricity, thermoelectricity, ferroelectricity, high temperature superconductivity (HTS), fuel cells, sensors, light-emitting diodes (LEDs) and in hybrid solar cells [5-8].

Thallium based transition metal fluorides  $\text{TlTF}_3$  (T = Fe, Co, and Ni) have cubic structure with space group  $\text{Pm}\bar{3}\text{m}$  (no. 221) and lattice constants of these material are 4.188 Å, 4.138 Å and 4.10 Å respectively [5, 9-14]. Rudoff et al. [12] synthesized  $\text{TlCoF}_3$  by heating mixtures of two binaries  $\text{TlF}$  and  $\text{CoF}_2$  and reported the cubic structure of the compound. Testardi et al. [14] synthesized  $\text{TlFeF}_3$  by the reaction of molten  $\text{TlF}$  and  $\text{FeF}_2$  in graphite or platinum crucible under a purified helium atmosphere and reported that the structural and magnetic properties are similar to  $\text{RbFeF}_3$  which is a ferromagnetic cubic perovskites. Kohn et al. [15] synthesized  $\text{TlNiF}_3$  by dissolving equimolar mixture of  $\text{TlOH}$  and  $\text{Ni}(\text{OH})_2$  in  $\text{HF}$  and reported the ferrimagnetic nature of compound below 150 K. Rayan et al. [13] reported the anti-ferromagnetic nature of  $\text{TlCoF}_3$  compound,  $\text{TlFeF}_3$  is a ferromagnetic material [14], while  $\text{TlNiF}_3$  compound is transparent with yellow color and ferrimagnetic in nature [15].

Though  $\text{TlFeF}_3$ ,  $\text{TlCoF}_3$  and  $\text{TlNiF}_3$  compounds are experimentally explained but no theoretical evidence available to interpret their experimental nature, we investigate different properties of these compounds like structural, chemical bonding and stability, mechanical, electronic and magnetic properties by using different exchange-correlation potentials like GGA, GGA+U and hybrid density functional theory (HF) based on DFT. Furthermore BoltzTraP package is utilized to calculate the magnetic susceptibilities and heat capacities versus temperature and are discussed in details.

## 2. Computational Details

Structural, mechanical and magneto-electronic properties of the thallium based perovskites  $\text{TlTF}_3$  ( $T = \text{Fe, Co and Ni}$ ) are investigated using the full potential linearized augmented plane-waves (FP-LAPW) method with the GGA [16, 17], GGA+U [18-20] and hybrid density functional theory [21] are used to solve the Kohn-Sham equations [22]. The three independent elastic coefficients are calculated using the method developed by Charpin as implemented it in the WIEN2k package [23].

Furthermore to study the magnetic properties of these compounds in detail BoltzTraP code is utilized [24] based on Boltzmann's equations. Details of the FP-LAPW method, formulas and the WIEN2k package used in the present calculations can be found in Ref. [23].

To ensure well converged and accurate results by GGA+U an approximated correction value of Hubbard potential ( $U$ ) for the self-interaction correction (SIC) is chose after examining and testing several values of  $U$  in order to adjust the T-3d orbitals level in the density of states. In order to get better results the  $U_{eff}$  is eventually optimized to 2 eV. For the calculations of HF we use the correct exchange potential  $\alpha = 0.45$  eV. For all calculations 2300 k-points and  $\text{RMT-K}_{\text{max}} = 8.00$  basis functions are used.

### 3. Results and Discussion

#### 3.1. Structural Properties

The structure of thallium based transition metal fluorides  $\text{TlTF}_3$  ( $T = \text{Fe, Co and Ni}$ ) are studied using different correlation potential like GGA, GGA+U and HF in the frame work of DFT. To calculate the relax ground state properties, optimizations are performed for each unit cell and the structural parameters are evaluated by using the fitted Birch-Murnaghan equation of state [25]. The lattice constants ( $a_0$ ) and ground state energies ( $E_0$ ) for these compounds are presented in Table 1. All the techniques, GGA, GGA+U and HF underestimated the lattice constants due to the fact of exchange correlation of electrons. In  $\text{TlFeF}_3$  the lattice constant is 1.05 % underestimated by GGA, 0.90 % by GGA+U and 0.19% by HF, in case of  $\text{TlCoF}_3$  the lattice constant is 0.94% underestimated by the GGA, 0.86 % by GGA+U and 0.19% by HF, and for  $\text{TlNiF}_3$  its lattice constant is 0.6% underestimated by GGA, 0.48% by GGA+U and 0% by HF [9, 12, 15]. From the calculated data it is clear that HF is a good approach to calculate the lattice constants of the fluorides. The data is also compared with the analytical reported work on  $\text{TlFeF}_3$  and  $\text{TlCoF}_3$  and found in good agreement [5, 9, 10]. As the lattice constant of  $\text{TlNiF}_3$  is not reported analytically so we also calculate the lattice constant analytically using ionic radii method [26] and presented in Table 1. Fig. 1 shows the comparison of the calculated lattice constants by GGA, GGA+U and HF versus experimental and analytical lattice constants. From the plot it is clear that HF is much better than GGA and GGA+U because lattice constants calculated on this approach are comparable with experimental results. This means that HF properly treat these strongly correlated system (d state of Fe, Co and Ni), which shows the reliability of our work.

Bond lengths plays important role to investigate the perovskite structure. The calculated bond lengths of  $\text{TlTF}_3$  ( $T = \text{Fe, Co and Ni}$ ) are presented in Table 1 are compared with the

experiments and found that the HF results are much consistent. The calculated bond lengths between T – F (Fe, Co and Ni) are 2.090 Å, 2.065 Å and 2.050 Å respectively, where the experimental reported value for Co – F is 2.069 Å [12]. Average bond lengths between different atoms in these fluorides are used to calculate the tolerance factor (t) of a perovskite, and the crystal structure of the compound can be predicted [26];

$$t = 0.707 \frac{\langle Tl - F \rangle}{\langle T - F \rangle} \quad (1)$$

where  $\langle Tl - F \rangle$  is the average bond length between Tl and F, whereas  $\langle T - F \rangle$  is the average bond lengths between Fe, Co and Ni with F. The Tolerance factor (t) calculated by Eq. 1 are presented in Table 1. It can be obvious from the table that the calculated tolerance factors for  $TlFeF_3$  is 0.995 for  $TlCoF_3$  is 0.993 and for  $TlNiF_3$  0.999 lies in the range 0.93 - 1.04 [26] confirm the cubic structure of these compounds. Tolerance factor for  $TlNiF_3$  is also calculated analytically using ionic radii method [10], which also confirms the cubic phase of these compounds.

Electron charge density explains the nature of chemical bonding in materials, where chemical bond occurs when one or more electrons simultaneously attracted the two nuclei. Charge density of  $TlTF_3$  (T = Fe, Co and Ni) for (100) and (110) planes for both spin states are shown in Fig. 2. For spin up states Fig. 2 (a, c) electron density distribution (100) and (110) planes show overlapping of the electron density between T and F and reveal that the bond nature between T and F is covalent for all the three compounds whereas between Tl and T (T = Fe, Co and) is ionic. In case of spin down Fig. 2 (b, d) the shape of T ions shifts from almost spherical to dumbbell, which shows polarization and ionic interactions of transition metal fluorides with F. In case of  $TlFeF_3$  for (110) plane Fig. 2(d) in spin down state there is no overlapping of electron charge density of Fe and F and the shape of Fe is much dumbbell than Co and Ni, hence in

TlFeF<sub>3</sub> Fe have stronger ionic interaction with F than the other compounds and very weak covalent interaction. Hence our calculations show that in TlFeF<sub>3</sub> the ionic character is stronger as compared to TlCoF<sub>3</sub> and TlNiF<sub>3</sub>.

Cohesive energy of a material is the energy to break all the bonds associated with its constitute atoms. Cohesive energy is important, not only because it explores the energetic quality of a system, but also because of the range of densities tested, namely infinite and finite corresponding to the solid and atomic systems respectively. To calculate cohesive energy ( $E_{coh}$ ) we used the Dmitrii et al. [27] empirical formula;

$$E_{coh} = E_{total} - (E_{Ti} + E_T + 3E_F) \quad (2)$$

in Eq. (2)  $E_{coh}$  is the cohesive energy the compound,  $E_{total}$  is the total energy of the crystal that is calculated by HF, while  $E_{Ti}$ ,  $E_T$  and  $E_F$  are the ground state energies of the free atoms. The calculated cohesive energies of the compounds are given in Table 1. From the table it is clear that the cohesive energy for TlCoF<sub>3</sub> is -4.62 Ry, for TlFeF<sub>3</sub> is -1.35 Ry and for is -1.99 Ry respectively. As the cohesive energy of TlCoF<sub>3</sub> is much greater than TlNiF<sub>3</sub> and TlFeF<sub>3</sub>, hence it is more stable than the rest compounds.

### 3.2 Mechanical Properties

Mechanical properties of a material tell us about the behavior of solid and are of great interest in various fields of applications. The elastic constants ( $C_{ij}$ ) are important material parameters. We have calculated the elastic constants  $C_{ij}$  (GPa) ( $C_{ij} = C_{11}, C_{12}, C_{44}$ ) in Voigt notation which are derived from the change in the internal energy under deformation and other parameters such as bulk modulus (B), shear modulus ( $G_H$ ), tetragonal shear ( $G'$ ), Young's modules (Y) and Poisson's ratio ( $\nu$ ) for TlTF<sub>3</sub> (T = Fe, Co and Ni) using DFT cubic elastic package [23, 28]. For the investigation of above physical quantities of cubic structure, three

independent constants are very important  $C_{11}$ ,  $C_{12}$  and  $C_{44}$ . The Stability of cubic structure can be guessed by the well known spinodal shear and Born criteria [28-32]

$$C_{11} + 2C_{12} > 0; C_{44} > 0; C_{11} - C_{12} > 0 \quad (3)$$

The calculated different physical quantities like bulk modulus (B), Voigt shear modulus ( $G_V$ ), Reuss shear modulus ( $G_R$ ), shear modulus ( $G_H$ ), Young's modulus (Y), Poisson's ratio ( $\nu$ ), tetragonal Shear (C'), Cauchy pressure (C''), Pugh's ductility index (B/ $G_H$ ), plasticity (B/ $C_{44}$ ), mass density ( $\rho$ ), anisotropic factor (A), longitudinal velocities ( $v_l$ ), transverse velocities ( $v_T$ ) and Debye temperature ( $\theta_D$ ) of  $TiTF_3$  (T = Fe, Co and Ni) by formulae [31, 32]. The stability criteria Eq. (3) for cubic structure are satisfied. The other parameter like elastic anisotropic factor (A), by which we measure the anisotropy of the elastic wave velocity in a crystal ( $A = 1$  for an isotropic material. It also tells more about the structural stability and it is correlated with the possibility of inducing micro cracks in the materials. The calculated elastic anisotropic factor (A) for  $TiCoF_3$  is greater than 1 while for  $TiNiF_3$  is less than 1 which indicates that these compounds are elastically anisotropic, while  $A \approx 1$  for  $TiFeF_3$  is elastically isotropic. The material behaves in a ductile manner if Pugh =  $B/G_H > 1.75$  [28, 31] from Table 2 we see that B/ $G_H$  ratio is greater than 1.75 for all the three compounds,  $TiFeF_3$  is the most ductile material than the rest of the compounds. The bond nature of cubic compounds is explained with respect to their Cauchy pressure (C''). Compounds having more positive Cauchy pressure tend to form metallic bonds [31], Cauchy pressure (C'') for  $TiTF_3$  (T = Fe, Co and Ni) are 30.12 GPa, 31.50 GPa and 15.67 GPa respectively. It can be seen from Table 2 that  $TiFeF_3$  has highest positive Cauchy pressure resulting strong metallic bonding than the others. The Young's modulus (Y) gives information about stiffness of the solids when the value of Y is large then stiffer is the materials having covalent bond. Young's modulus (Y) for  $TiTF_3$  (T = Fe, Co and Ni) are 62.40 GPa, 54.82 GPa



and 94.86 GPa respectively. The value of  $Y$  is larger of  $\text{TiNiF}_3$  as compared to  $\text{TiCoF}_3$  and  $\text{TiFeF}_3$  therefore  $\text{TiNiF}_3$  has high covalency. The hardness of the material does not depend only on Young's modulus but it has strong dependence upon shear modulus and the value of Poisson's ratio. Covalent materials generally have a high shear modulus. The value of Poisson's ratio  $\nu \approx 0.1$  for covalent materials and  $\nu \approx 0.33$  for metallic, if a material have highly directional bonds, then shear modulus increases and gives a low Poisson ratio. If a material has short covalent bonds atomic dislocations that lead to plastic deformation are less likely to occur than in materials with longer delocalized bonds. If a material contains many delocalized bonds, it is likely to be soft [31]. The same case is obtained for  $\text{TiFeF}_3$  which possesses highest value of Poisson's ratio and lowest value of Young's and shear moduli which shows that  $\text{TiFeF}_3$  is soft (ductile) due to strong metallic bonding. While for  $\text{TiNiF}_3$  the lowest value of Poisson's ratio and highest value of Young's and shear modulus reveals that this compound might has the presence of short directional covalent bond along with metallic nature.

Plasticity is the ratio of bulk modulus  $B$  and  $C_{44}$  [31] this ratio is highest for  $\text{TiFeF}_3$  and lowest for  $\text{TiNiF}_3$ . This confirms that  $\text{TiFeF}_3$  contains delocalized bonds and may possess lubricating properties. For covalent and ionic materials  $G_H/B = 1.1$  and  $G_H/B = 0.6$  [33] respectively. In our calculations the  $G_H/B$  ratio for  $\text{TiFeF}_3$ ,  $\text{TiCoF}_3$  and  $\text{TiNiF}_3$  are 0.31, 0.32 and 0.47 respectively, indicating that these compounds have weak ionic bonds also discussed and shown in electron charge density plot Fig. 2.

Debye temperature ( $\theta_D$ ) is an important parameter to know many physical properties such as specific heat and other thermal properties, it also defines a division line between quantum mechanical and classical behavior of phonons. The calculated transverse and longitudinal sound velocities are presented in the Table 2, from the table it is clear that  $\text{TiNiF}_3$  have high sound

velocities than the other two compounds, as Debye temperature ( $\theta_D$ ) is directly proportional to the average sound velocity therefore  $\text{TiNiF}_3$  possesses high Debye temperature ( $\theta_D$ ) than the other two compounds shown in the Table 2.

### 3.3 Electronic Properties

Electronic properties are associated with bandgap between the top of the valance band and the bottom of the conduction band. Therefore to investigate the electronic properties of  $\text{TiTF}_3$  ( $T = \text{Fe, Co and Ni}$ ) we used HF spin-dependent self consistent field calculations and are plotted in Fig. 3. It is obvious from the figure that  $\text{TiCoF}_3$  is an indirect band of 3.8 eV exists at M-X symmetry points of Brillouin zone for spin up state and in the spin down state the valance band cross the Fermi level ( $E_F$ ). The compound show semiconductor behavior in spin up while metallic behavior in spin down state. This dual behavior is called half metallicity. Half metals are not physically exist therefore the compound is either semiconductor or metal. To clarify this we perform double cell calculations shown in Fig. 4, from the plot it is clear that the densities of the valance and conduction bands overlapped around the Fermi level ( $E_F$ ) shows that the compound is metallic. For  $\text{TiFeF}_3$  conduction band cross the Fermi level ( $E_F$ ) in spin up as well as in spin down state the valance and conduction bands are covered by the densities hence  $\text{TiFeF}_3$  is metallic in nature. Similarly for  $\text{TiNiF}_3$  a pseudo direct bandgap of 4.0 eV exist in case of spin up state and the bandgap of 3.6 eV for spin down at X symmetry point shown in Fig. 3, this shows that  $\text{TiNiF}_3$  is pseudo direct wide bandgap semiconductor. The difference in the band gap energies in spin up and spin down states are due to the electrons polarization.

### 3.4 Magnetic Properties

To investigate the ground state magnetic phase of  $\text{TiTF}_3$  ( $T = \text{Fe, Co and Ni}$ ) perovskites we optimized the double cell of these compounds ferromagnetic, anti-ferromagnetic and

paramagnetic phases. The energy difference  $\Delta E = E_{\text{FM}} - E_{\text{AFM}}$  for  $\text{TiFeF}_3$ ,  $\text{TiCoF}_3$  and  $\text{TiNiF}_3$  per unit cells are given in Table 3. For  $\text{TiFeF}_3$  and  $\text{TiNiF}_3$  change in energy  $\Delta E$  is negative which shows that these compounds are stable in ferromagnetic phase, while change in energy  $\Delta E$  is positive for  $\text{TiCoF}_3$  which reveals that it is stable in anti-ferromagnetic state, our calculated results are consistent with the experiments [12-15, 33]. To explore the origin of magnetism in these compounds the spin magnetic moments of the magnetic atoms T (T = Fe, Co and Ni) which have main contribution; and the total spin magnetic moments per unit cell are calculated and presented in Table 3. The effective magnetic moment ( $M_{\text{eff}}$ ) of  $\text{TiCoF}_3$  per unit cell is  $3.002 \mu_B$  which is consistent to the experiment [13]. Similarly the effective magnetic moments for  $\text{TiFeF}_3$  and for  $\text{TiNiF}_3$  are  $4.148 \mu_B$  and  $2.001 \mu_B$  respectively. As  $\text{TiCoF}_3$  is AFM to confirm we perform double cell AFM calculation for the compound and the spin dependent DOS plot is shown in Fig. 4. It is obvious from the figure that the densities are symmetric (mirror reflection) about the arbitrary axis and effective magnetic moment ( $M_{\text{eff}}$ ) cancel each other, results zero net magnetic moment which confirmation the AFM nature of  $\text{TiCoF}_3$  and agreement with experiments [13].

Magnetic susceptibility ( $\chi$ ) and temperature are inversely related to each other by the Curie Weiss law [34];

$$\chi = \frac{C}{T \pm T_\theta} \quad (4)$$

where C is Curie constant,  $T_\theta$  is the Weiss constants and is different for different material, T is temperature in Kelvin. This law is valid for paramagnet material but at low temperature it can also be applied to ferromagnetic and anti-ferromagnetic materials. For paramagnetic material  $T_\theta = 0$ , for ferromagnetic material  $T_\theta > 0$  and for anti-ferromagnetic material  $T_\theta < 0$ . We also

calculate the magnetic properties of these compounds using BoltzTraP code [24], magnetic susceptibility ( $\chi$ ) versus temperature  $T$  (K) is plotted in Fig. 5. It is clear from the plot that the rise in temperature, thermal agitation destroying the alignment of the magnetic moments that's why the magnetic susceptibility decreases with the increase in temperature. The magnetic susceptibilities are different because of the different transition metals  $T$  (Fe, Co and Ni) in these compounds in which Fe and Ni ordered ferromagnetically whereas Co anti-ferromagnetically. The magnetic susceptibility  $\chi$  is negligibly small for  $\text{TiCoF}_3$  shows that it is an anti-ferromagnetic compound. The  $\text{TiFeF}_3$  and  $\text{TiNiF}_3$  magnetic susceptibility ( $\chi$ ) decrease abruptly with the increase in temperature and then decrease with a minimum proportion at which magnetic phase transition occurs from ferromagnetic to paramagnetic called Curie temperature ( $T_C$ ). From Table 3 the calculated  $T_C$  for  $\text{TiFeF}_3$  and  $\text{TiNiF}_3$  are 120 K and 127 K respectively. As the experimental  $T_C$  for  $\text{TiNiF}_3$  is 129 K [33] which show that our results are logical and reliable. The calculated Neel's temperature ( $T_N$ ) for  $\text{TiCoF}_3$  is 20 K in the cubic structure, Julliard et al. [35] reported the magnetic transition temperature  $T_N = 94$  K for hexagonal structure of  $\text{TiCoF}_3$ ; this difference is due to the fact of the change in the structure. In the inverse magnetic susceptibility ( $1/\chi$ ) versus temperature ( $T$ ) plot Fig. 5 tell us about the alignment of the magnetic domains. The x intercept give us Weiss constant ( $T_\theta$ ), in case of  $\text{TiCoF}_3$  Weiss constant  $T_\theta < 0$  which confirm the anti-ferromagnetic nature of the compound while in case of  $\text{TiFeF}_3$  and  $\text{TiNiF}_3$  the x intercept  $T_c > 0$  which confirm the ferromagnetic nature of these compounds.

### 3.4 Heat Capacity

Specific heat capacity is the amount of heat requires to changes the temperature of the unit substance through one degree Kelvin. In specific heat we take heat capacity at constant pressure ( $C_P$ ) or at constant volume ( $C_V$ ). As the lattice of atoms or molecule of the crystal are in

continues vibration which is called phonon, so in the result wave is produce which is called sound wave. At lower temperature heat capacity obeys Einstein's and Debye's models. We performed calculation using BoltzTraP code [24] and the heat capacity at constant pressure versus temperature is plotted in Fig. 6 for all the three compounds. From Fig. 5 it is clear that heat capacity ( $C_p$ ) is approximately zero in the temperature range of 0 K to 220 K for all these compounds, after that when we go from 220 K to 240 K slightly increase in the heat capacity of  $\text{TiFeF}_3$  and  $\text{TiNiF}_3$  while for  $\text{TiCoF}_3$   $C_p$  is still negligible, heat capacity increase abruptly with increase in the temperature range from 240 K to 300 K. This change in heat capacity is more rapid in  $\text{TiNiF}_3$  than  $\text{TiCoF}_3$  and  $\text{TiFeF}_3$ . Figure also clarify that  $\text{TiCoF}_3$  have smaller heat capacity than the other two compounds. Our calculated heat capacity versus temperature plots for all compounds follow same trend as the experimental reported in different literature [36], which is in good agreement with the experimentally as well as theoretically plot for heat capacity ( $C_p$ ) versus temperature (T) for diamond as reported in Ref. [36].

#### 4. Conclusions

In short structural, mechanical and magneto-electronic properties of  $\text{TiTF}_3$  (T = Fe, Co and Ni) are investigated for the first time using GGA, GGA+U and HF (PBE-sol) based on DFT. Our calculations show that the results of HF are much consistent with the available experimental data as compared to GGA and GGA+U. Tolerance factor are calculated on the basis bond lengths which confirm that these compounds are stable in the cubic structure. The electronic charge densities explain the chemical bonding in the compounds. The bond between Fe and F in  $\text{TiFeF}_3$  is nearly ionic and converting to strong covalent between Co and Ni with F in  $\text{TiCoF}_3$  and  $\text{TiNiF}_3$ . Cohesive energies show that  $\text{TiCoF}_3$  is more stable than  $\text{TiFeF}_3$  and  $\text{TiNiF}_3$ . Mechanical properties explain the elastic properties of these compounds and show that  $\text{TiFeF}_3$  is much

ductile than the rest compounds. The spin-dependent electronic band structures show that  $\text{TiFeF}_3$  and  $\text{TiCoF}_3$  are metallic while  $\text{TiNiF}_3$  is a pseudo direct wide bandgap semiconductor. The magnetic phase stability are calculated which are well consistent with experimental results. The Neel's temperature and Curie's temperature are also calculated for the relative compounds.

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**Figure Captions**

**Fig. 1** Comparison of the calculated lattice constants with the experimental and analytical results of  $\text{TlTF}_3$  ( $T = \text{Fe, Co and Ni}$ ).

**Fig. 2** Spin-dependent electron charge densities in (100) and (110) planes of  $\text{TlTF}_3$  ( $T = \text{Fe, Co and Ni}$ ).

**Fig. 3** Spin-dependent electronic band structures of  $\text{TlTF}_3$  ( $T = \text{Fe, Co and Ni}$ )

**Fig. 4** Double cell AFM total density of states of  $\text{TlCoF}_3$

**Fig. 5** Magnetic susceptibility ( $\chi$ ) and inverse of magnetic susceptibility ( $\chi^{-1}$ ) plots against temperature of  $\text{TlTF}_3$  ( $T = \text{Fe, Co and Ni}$ )

**Fig. 6** Specific heat capacity ( $C_p$ ) ( $\text{J.mol}^{-1}.\text{K}^{-1}$ ) versus temperature  $T$  (K) of  $\text{TlTF}_3$  ( $T = \text{Fe, Co and Ni}$ )

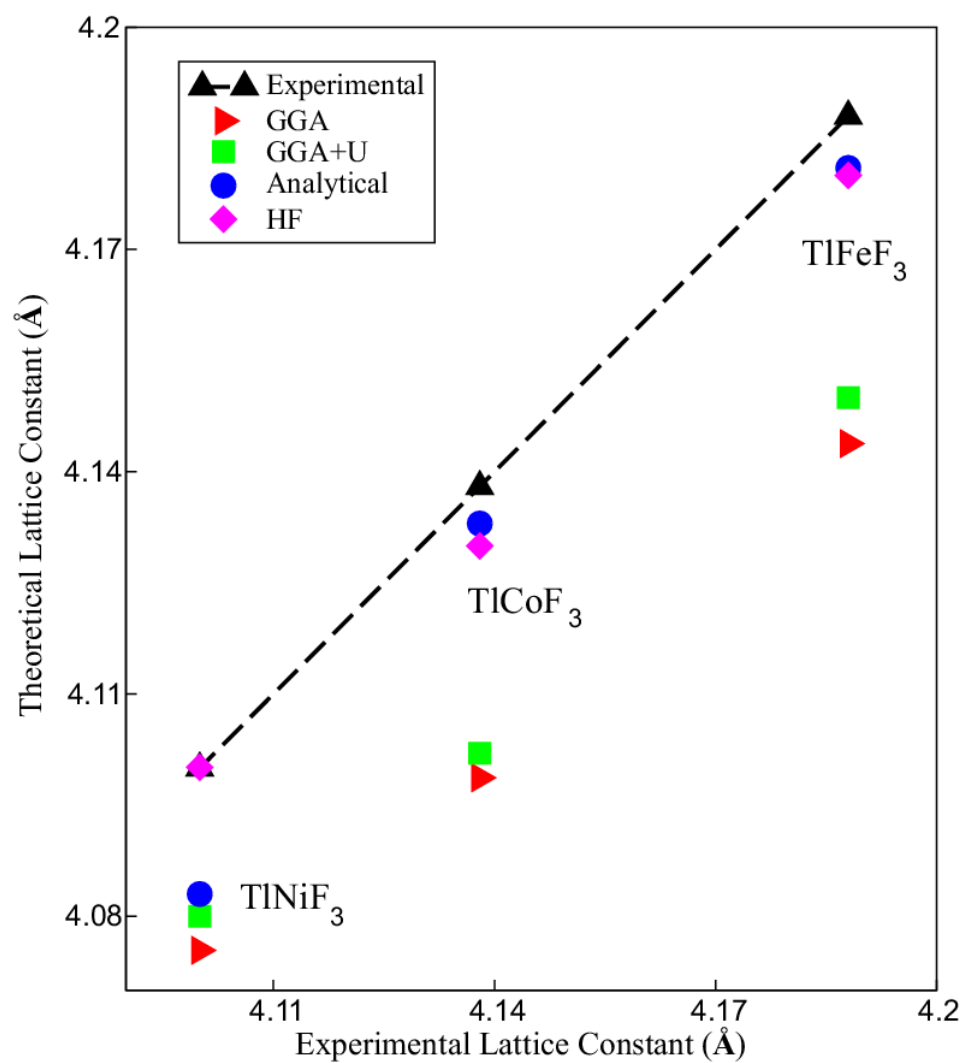


Fig. 1

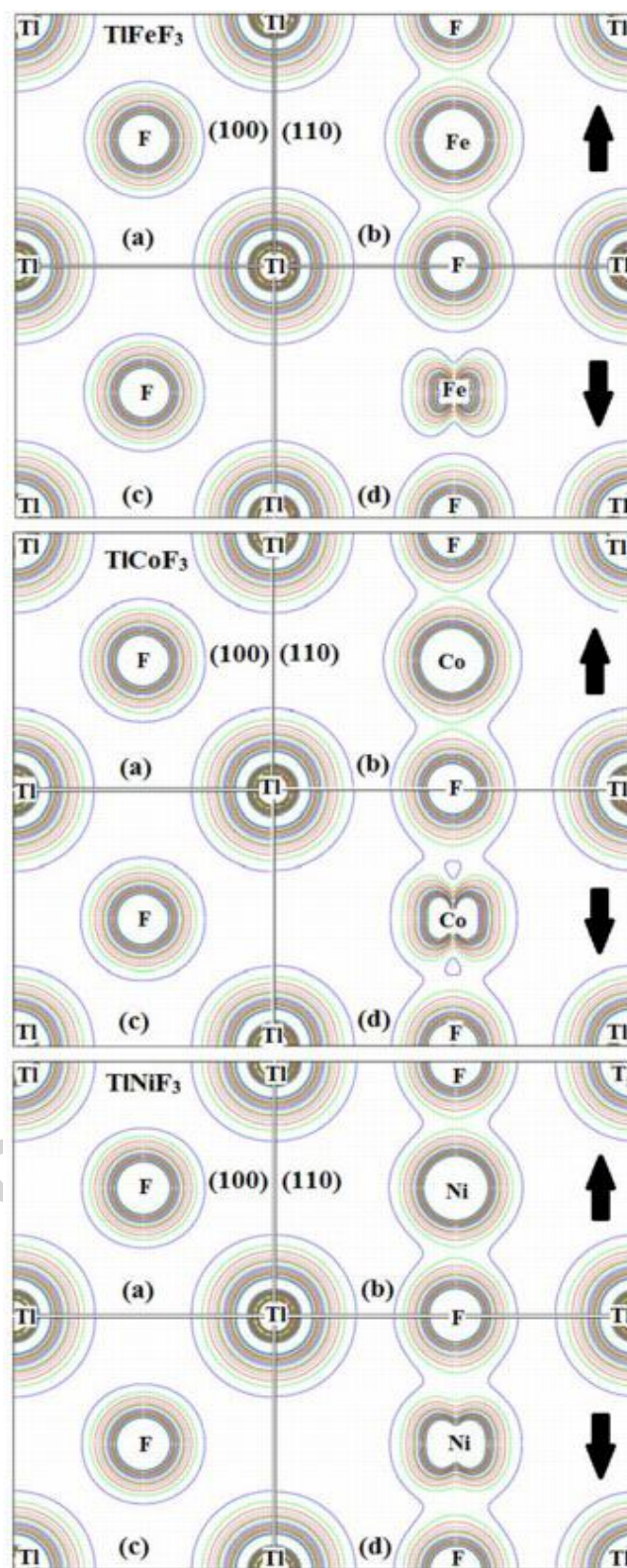


Fig. 2

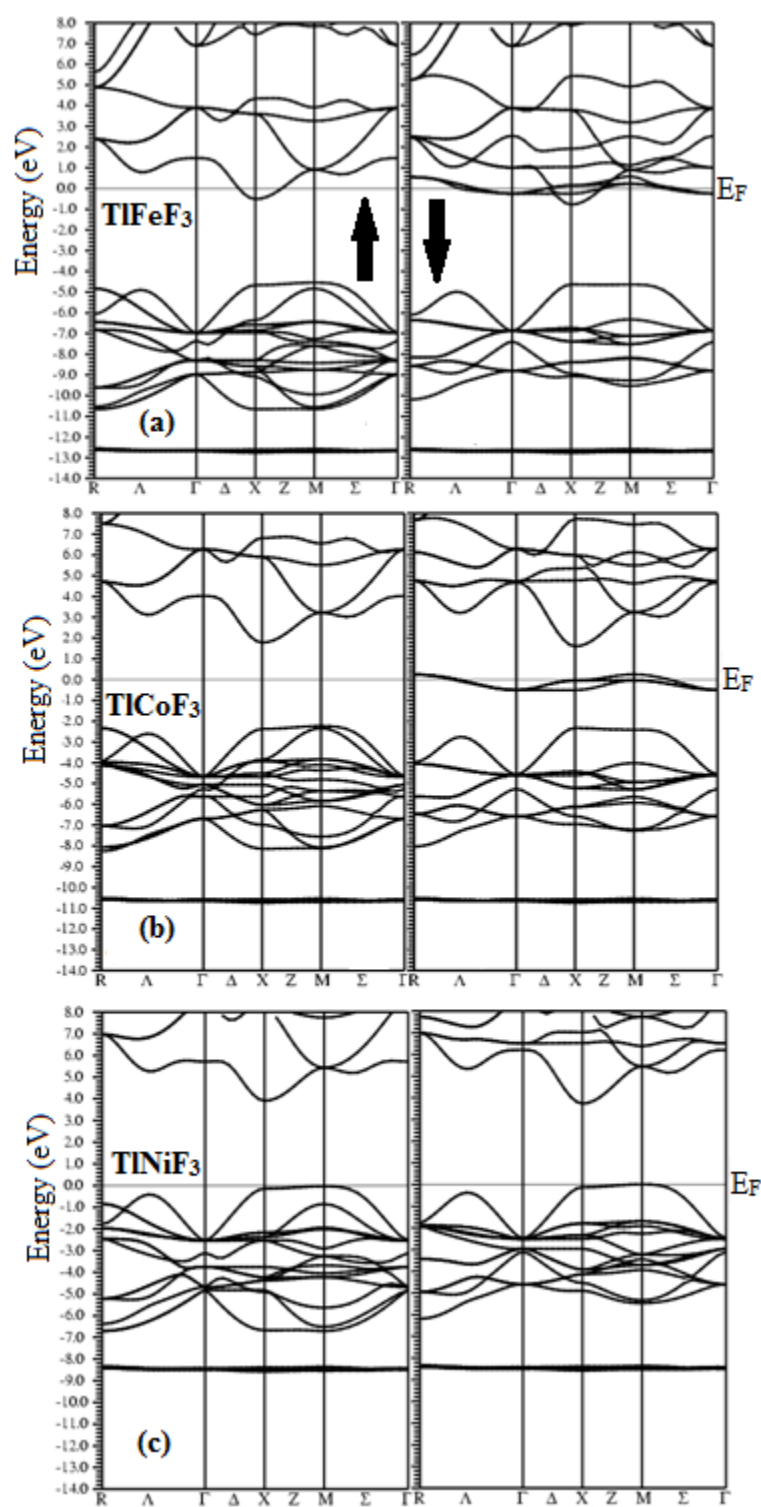
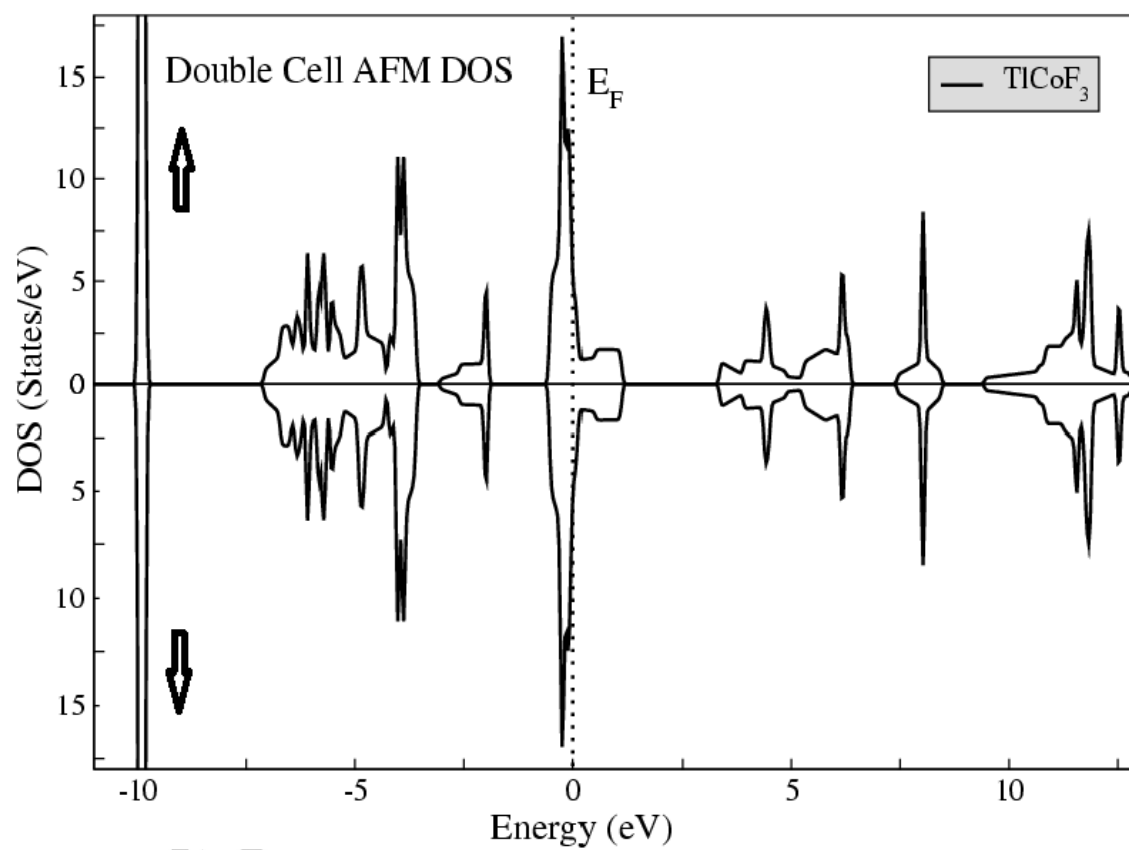


Fig. 3

**Fig. 4**

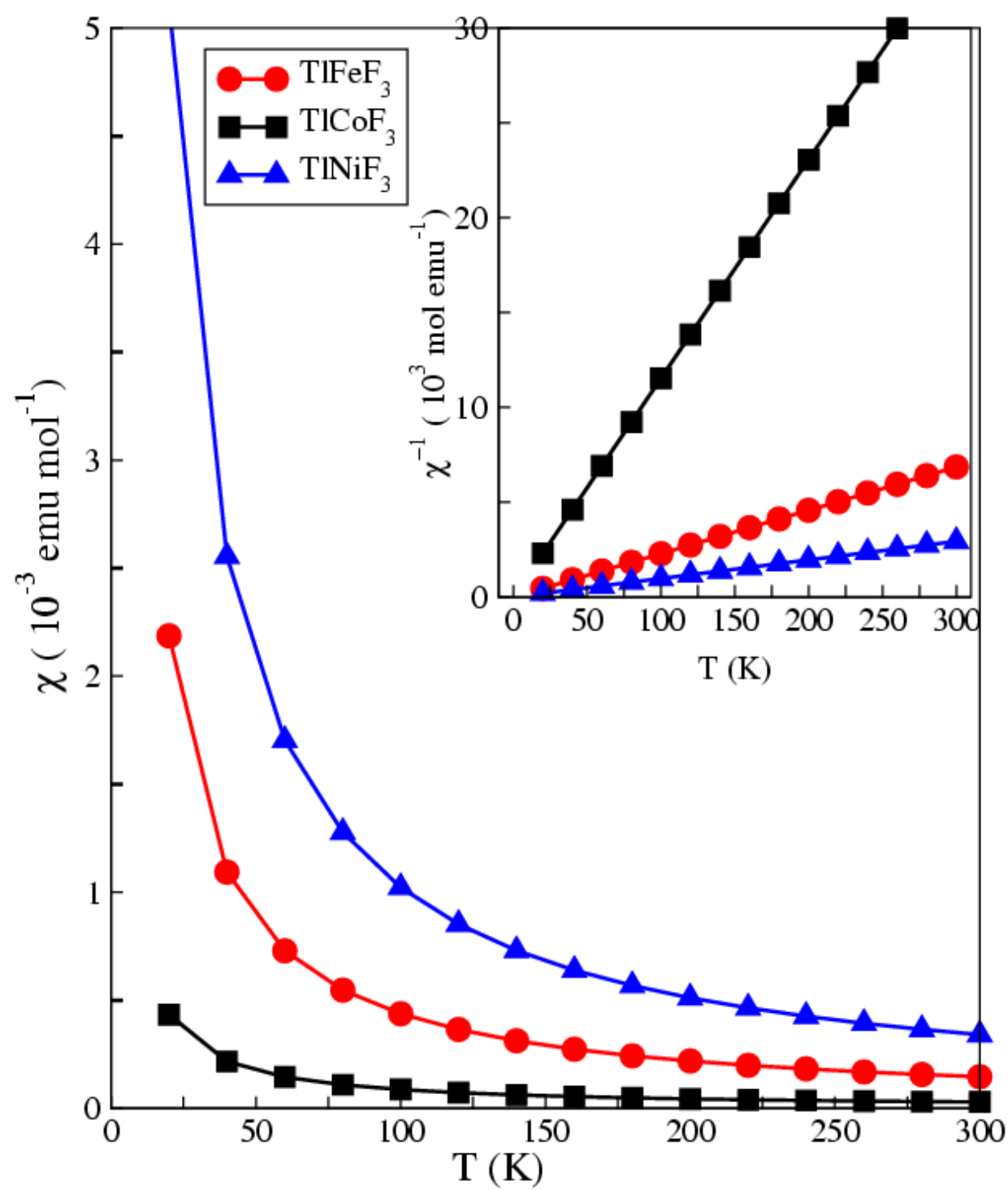


Fig. 5

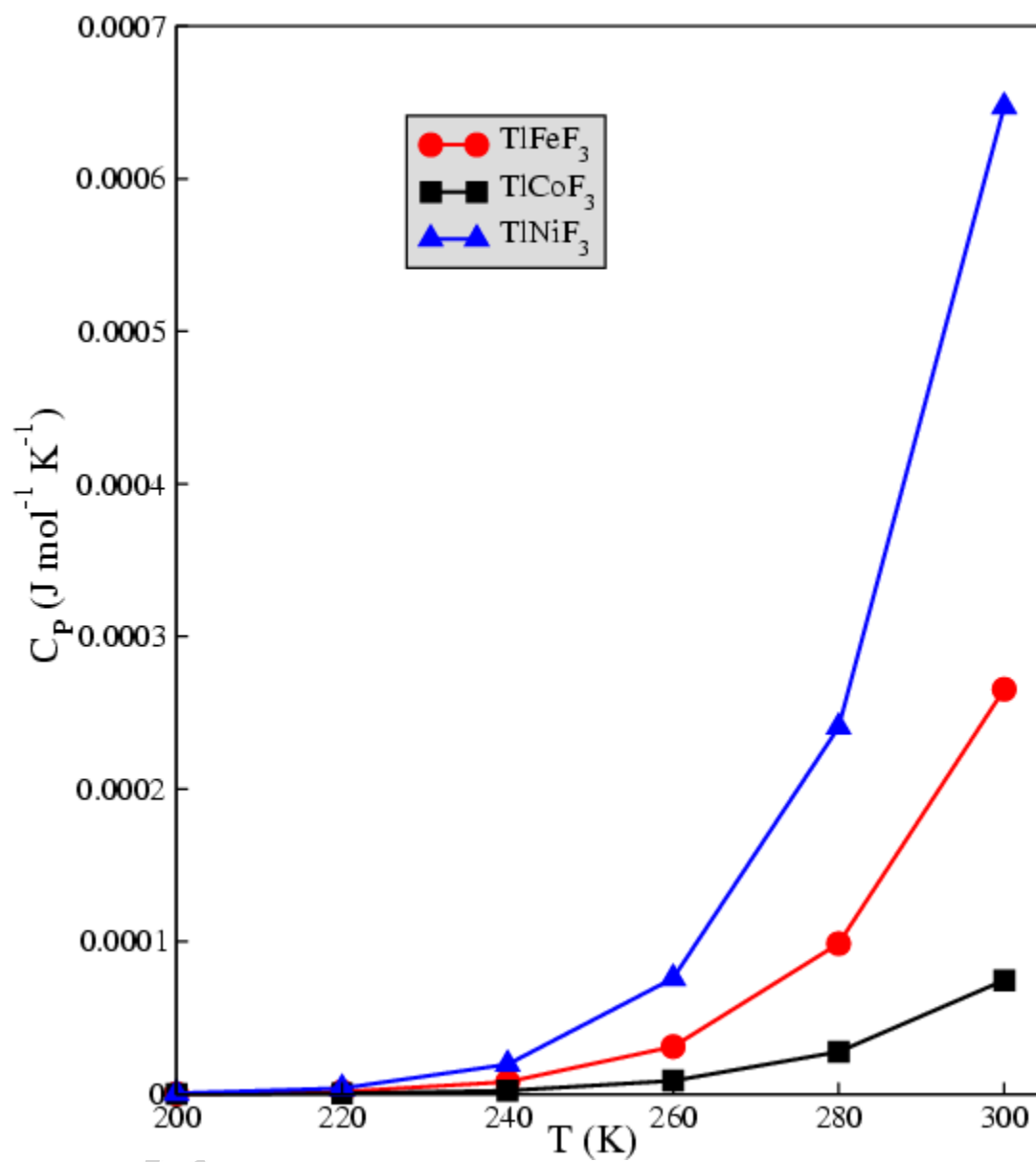


Fig. 6



**Table 1** Calculated analytical and experimental lattice constants ( $a_0$ ), ground state energies ( $E_0$ ), tolerance factor (t), cohesive energies ( $E_{\text{coh}}$ ) and bond lengths between different atoms in  $\text{TlTF}_3$  (T = Fe, Co and Ni)

Compounds	Present Work			Experimental	Analytical Ionic radii method
	HF	GGA+U	GGA		
<b>TlFeF<sub>3</sub></b>					
a <sub>0</sub> (Å)	4.18	4.15	4.144	4.188 <sup>a</sup>	3.899 <sup>a</sup> , 4.181 <sup>b</sup> , 4.14 <sup>c</sup>
E <sub>o</sub> (Ry)	-43707.222				
Tolerance factor (t)	0.993				1.022 <sup>c</sup> , 0.948 <sup>b</sup>
E <sub>coh</sub> (Ry)	-1.35				
Bond Lengths					
Tl — F (Å)	2.956	2.934	2.93		
Fe — F (Å)	2.090	2.075	2.07		
<b>TlCoF<sub>3</sub></b>					
a <sub>0</sub> (Å)	4.13	4.102	4.099	4.138 <sup>d</sup>	3.863 <sup>a</sup> , 4.133 <sup>b</sup> , 4.1 <sup>c</sup>
E <sub>o</sub> (Ry)	-43949.103				
Tolerance factor (t)	0.995				1.04 <sup>c</sup> , 0.967 <sup>b</sup>
E <sub>coh</sub> (Ry)	-4.62				
Bond Lengths					
Tl — F (Å)	2.920	2.901	2.90		
Co — F (Å)	2.065	2.051	2.05	2.069 <sup>d</sup>	
<b>TlNiF<sub>3</sub></b>					
a <sub>0</sub> (Å)	4.10	4.08	4.075	4.10 <sup>e</sup>	4.066
E <sub>o</sub> (Ry)	-44203.692				
Tolerance factor (t)	0.989				
E <sub>coh</sub> (Ry)	-1.99				
Bond Lengths					
Tl — F (Å)	2.899	2.885	2.88		
Ni — F (Å)	2.050	2.040	2.04		
[9] <sup>a</sup> , [5] <sup>b</sup> , [10] <sup>c</sup> , [12] <sup>d</sup> , [15] <sup>e</sup>					

**Table 2** Calculated mechanical properties like elastic constants  $C_{11}$ ,  $C_{12}$ ,  $C_{44}$ , bulk modulus ( $B$ ), Voigt shear modulus ( $G_V$ ), Reuss shear modulus( $G_R$ ), shear modulus( $G_H$ ), young modulus ( $Y$ ), Poisson's ratio ( $\nu$ ), anisotropic factor ( $A$ ), Tetragonal Shear ( $C'$ ), Cauchy pressure ( $C''$ ), paugh ( $B/G_H$ ), plasticity ( $B/C_{44}$ ), mass density ( $\rho$ ), longitudinal velocities ( $v_L$ ), transverse velocities ( $v_T$ ) and Debye temperature ( $\theta_D$ ) of  $TiTF_3$  ( $T = Fe, Co$  and  $Ni$ ).

Parameters	TiFeF <sub>3</sub>	TiCoF <sub>3</sub>	TiNiF <sub>3</sub>
$C_{11}$ (GPa)	91.23	88.77	132.36
$C_{12}$ (GPa)	52.03	58.63	48.95
$C_{44}$ (GPa)	20.54	28.51	33.28
$B$ (GPa)	65.10	68.68	76.76
$G_V$ (GPa)	20.16	23.13	36.65
$G_R$ (GPa)	20.15	21.01	36.21
$G_H$ (GPa)	20.16	22.07	36.43
$Y$ (GPa)	54.82	62.40	94.86
$\nu$	0.36	0.35	0.30
$A$	1.05	1.89	0.80
$C'$ (GPa)	19.60	15.07	41.70
$C''$ (GPa)	31.50	30.12	15.67
$B/G_H$	3.20	3.11	2.11
$B/C_{44}$	3.17	2.41	2.31
$\rho$ (g/cm <sup>3</sup> )	7.17	7.50	7.71
$v_L$ (m/s)	3581.66	3615.30	4031.33
$v_T$ (m/s)	1676.80	1714.72	2173.43
$v_M$ (m/s)	1890.51	1930.46	2425.50
$\theta_D$ (K)	134.51	139.01	176.20

**Table 3** Calculated and available experimental magnetic parameters, magnetic energies ( $\Delta E = E_{\text{FM}} - E_{\text{AFM}}$ ), total magnetic moment  $M_{\text{eff}}$  ( $\mu_{\text{B}}$ ) per unit cell, magnetic moments of T ( $M_{\text{Fe/Co/Ni}}$ ), Weiss constant ( $T_0$ ), Curie/ Neel temperature ( $T_{\text{C}}/T_{\text{N}}$ ) of  $\text{TiTF}_3$  (T = Fe, Co and Ni).

Magnetic Parameters	$\text{TiFeF}_3$	$\text{TiCoF}_3$	$\text{TiNiF}_3$
$\Delta E$ (Ry)	-0.260	+0.073	-0.046
Exp.	FM <sup>a</sup>	AFM <sup>b, c</sup>	FM <sup>d, e</sup>
$M_{\text{eff}}$ ( $\mu_{\text{B}}$ )	4.148	3.002	2.001
Exp.	-----	2.78 <sup>d</sup>	-----
$M_{\text{Fe/Co/Ni}}$ ( $\mu_{\text{B}}$ )	3.948	2.782	1.894
$T_{\text{C}}/T_{\text{N}}$ (K)	120	20	127
Exp.	-----	-----	129 <sup>e</sup>
[14] <sup>a</sup> , [12] <sup>b</sup> , [13] <sup>c</sup> , [15] <sup>d</sup> , [33] <sup>e</sup>			

### RESEARCH HIGHLIGHTS

- $\text{TiTF}_3$  (T = Fe, Co and Ni) perovskites are investigated theoretically by hybrid density functional theory.
- Mechanical properties explain the hardness of these compounds and show that  $\text{TiFeF}_3$  is more ductile.
- The bandgap calculations show that  $\text{TiFeF}_3$  and  $\text{TiCoF}_3$  are metallic, whereas  $\text{TiNiF}_3$  is a wide bandgap semiconductor.
- Magnetic optimizations and magnetic susceptibility confirm that  $\text{TiFeF}_3$  and  $\text{TiNiF}_3$  are ferromagnetic whereas  $\text{TiCoF}_3$  is anti-ferromagnetic material.