

Effects of anion-ligands replacement on the Structural, Electronic and Magnetic properties of ThCo_2X_2 ($\text{X} = \text{Si}, \text{Ge}$)

Abdul Ahad Khan^a, Zeshan Zada^b, Ali H. Reshak^{c,d,*}, Jehan Akbar^e,
Muhammad Saqib^f, Muhammad Azhar Naeem^g, Muhammad Ismail^h, Sabeen Zada^h,
G. Murtaza^{b,i}, Amel Laref^j, Muhammad M. Ramli^d

^a Department of Physics, University of the Peshawar, KP, Pakistan

^b Material Modelling Lab, Department of Physics, Islamia College Peshawar, KP, Pakistan

^c Physics Department, College of Science, University of Basrah, Basrah post code 61004, Iraq

^d Center of Excellence Geopolymer and Green Technology (CEGeoGTech), University Malaysia Perlis, 01007 Kangar, Perlis, Malaysia

^e Department of Physics, Hazara University, KPK, Pakistan

^f Department of Electrical and Computer Engineering, COMSATS University Islamabad, Abbottabad Campus, KPK, Pakistan

^g Department of electrical engineering, University of the Punjab, Lahore, Pakistan

^h Department of Chemistry, Women University Swabi, KP, Pakistan

ⁱ Department of Mathematics & Natural sciences, Prince Mohammad Bin Fahd University, P. O. Box 1664, Alkhorbar 31952, Kingdom of Saudi Arabia

^j Department of Physics and Astronomy, College of Science, King Saud University, Riyadh, 11451, Kingdom of Saudi Arabia

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ABSTRACT

Our study reveals first principles investigation of structural, electronic and magnetic properties of ThCo_2X_2 ($\text{X} = \text{Si}, \text{Ge}$) compound, by application of full-potential linearized augmented plane wave (FP-LAPW). The calculations for the structural determination of thorium compounds are obtained with the PBE-GGA potential to achieve theoretical reliability with available experimental results, while for the improvement of electronic and magnetic properties the GGA+U method is used. The compounds are optimized in a stable ferromagnetic phase which is more suitable for the examination of the magnetic properties as compared to paramagnetic and anti-ferromagnetic phases. The two potentials namely (PBE-GGA and GGA+U) are used to compute the band structures and density of state (DOS). The plotted band structures together with (DOS) through both spin channels declare full metallic character in the thorium based ThCo_2X_2 compound. A strong hybridization among Co-d and ($\text{X} = \text{Si}, \text{Ge}$)-p states in the valence band with Th-f state lies in the conduction band. Also, the achieved total magnetic moment for the ThCo_2Ge_2 compound affirms stronger ferromagnetism than the ThCo_2Si_2 compound.

1. Introduction

From the last few decades, the enthusiasm towards the search of materials with intermetallic phases have been growing because of their mysterious properties and different broad range logical and innovative applications like shape memory alloys, in jewellery and dentistry [1,2] computer read along with their utilization as “colossal-magneto-resistive (CMR)” or else “giant-magneto-resistive

* Corresponding author.

E-mail address: maalidph@yahoo.co.uk (A.H. Reshak).

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(GMR)” materials. The mechanism behind magneto-resistance within metallic thin films for achieving advance technology is by altering and adjusting resistivity due to the external presence of magnetic field [3]. So far, majority of the applications has been obtained of GMR as spin filters, spin valves together with magnetic field sensors [4,5] where the most important component is GMR which are usefully utilized to read-heads in the hard disk drives, in various biosensors, recent micro-electro-mechanical (M-E-M-S) systems. These intermetallic compounds have their particular electronic structure which further building them liable for various innovative properties at quantum level.

Generally, Intermetallic phases with formula AM_2X_2 (where A belongs to rare or alkaline-earth metals, M belongs to d-block metals; while X belongs to Group 13-15 elements) lies in two pervasive structure types, with space groups namely $ThCr_2Si_2$ (I4/mmm) and $CaAl_2Si_2$ (P3m1) respectively. The later one particularly has been used for the investigation of various physical properties among intermetallic zintl phase compounds in recent studies [6–10].

So far, the ternary compounds like thorium $AnCo_2X_2$ ($An = \text{Thorium}$; $X = \text{Silicon, Germanium}$) and lanthanide compounds $LnCo_2X_2$ have been investigated with body centered tetragonal crystalline shape. The space group of the compounds having structure like $AnCo_2X_2$ is I4/mmm, with two formula units per tetragonal cell. The name given to the structure is due the very light thorium compound of the series. For the first time ThM_2X_2 compounds ($M=3d$ transition element) were prepared and studied experimentally by Sikirica and Ban [11,12]. The study of uranium compounds UCo_2Si_2 and UCo_2Ge_2 were made much later than the study of iso-structural thorium compounds, were found to order anti-ferromagnetically with the AF-I (+ -, + -) structure, for the temperature below T_n of $85K^0$ and $175K^0$, respectively, as confirm in numerous subsequent investigations [13,14]. The study of the Neutron-diffraction shows that the magnetic order of the uranium moments only, aligned themselves along the tetragonal axis that are perpendicular to the ferromagnetic basal planes which are stacked accordingly (+ -, + -) to the AF-I series. For the iso-structural lanthanides heavy compounds like $LnCo_2X_2$ similar magnetic structure was observed, with the similar order of magnetic moments for the lanthanide only.

Two researchers Omejec and Ban experimentally investigated paramagnetic properties of thorium compounds like $ThCo_2Si_2$ and $ThCo_2Ge_2$ [15], and published in 1971. They measure the magnetic susceptibility of all the ThM_2X_2 compounds by using an apparatus called Faraday apparatus (self-constructed) within the temperature range of 100–570K⁰. Furthermore, on comparing the results of inverse susceptibility and Curie–Weiss law, they were be able to find out “a kind of magnetic feature, the numerical values for Curie and Neel temperatures and the magnetization for transition-metal atoms”. They also reported that anti-ferromagnetic (AF) order in $ThCr_2X_2$ and $ThNi_2X_2$, indicate “highly negative” Neel temperatures, and “moderately negative” in $ThFe_2Si_2$. The ferromagnetic ordering in the thorium compounds i.e. $ThCo_2X_2$, $ThFe_2Ge_2$, $ThMn_2X_2$ and $ThCu_2Ge_2$, shows positive Curie temperatures, and on diamagnetism in $ThCu_2Si_2$. compound The thorium has no magnetic dipole moment, therefore the due to ordering there is the magnetic moments which is due to the 3d-transition elements. The study of Omejec and Ban [15] should be considered with intensive carefulness. The magnetic dipole moment was discussed by them may be the effective para-magnetic moment (μ_{eff}), and the “mathematical values of Curie and Neel temperature” maybe the representation of para-magnetic Curie temperature (θ). For the lowest measuring temperature about 100K, they cannot point out the Positive values of the latter for magnetic ordering. Moreover, the magnetic ordering for the compounds $ThCo_2Ge_2$ and $ThCo_2Si_2$, proposed by Omejec and Ban is ferromagnetic in nature, as determined by them from the measured para-magnetic Curie temperatures, $\theta=14K$ and $54K$, respectively [15]. The effective para-magnetic moments were observed by them is $\mu_{eff} = 1.42$ and $3.82mB/Co$ atom, respectively.

A number of researchers have attempted to study up to some extent the physical properties of $ThCo_2X_2$ ($X=Si, Ge$) compounds experimentally, however, the lack of theoretical studies was untouched by using DFT. In the present work, our attention is focused on the improvement of structural, electronic and magnetic properties to cover the shortage of theoretical information about $ThCo_2X_2$ compounds by using FP-APW method.

2. Computational method

Our DFT calculations for $ThCo_2X_2$ ($X = Si, Ge$) compounds based on FP-LAPW method, using Wien-2k code [16]. The Muffin-tin sphere radii (RMT) were selected in such a way that the atoms do not overlaps with the values 2.5a.u. for Th, 2.41 and 2.08a.u for Co and 1.78a.u and 1.98a.u. for Si and Ge respectively. The convergence for the basis set was controlled by a cut off parameter $RMT \cdot K_{max} = 7$, which shows the separation of valence and core states, where RMT is the smallest radius of the Muffin tin and K_{max} is the highest value of the reciprocal lattice constant that can be used in plane wave expansion. This strategy depends on the fact that the entire crystal is partitioned into non-overlapping muffin-tin (Mu-T) spheres separated by an interstitial region. At this point, a simple basis set function is picked and expanded in support of spherical harmonic functions within MT spheres, and simple plane waves are utilized in the interstitial region as well. In the Fourier expansion of the charge density the magnitude of the largest vector (G_{max}) is 12 atom unit (au)⁻¹ [28–31]. For the self-consistency-cycle we use energy convergence as 0.0001Ry and charge convergence as 0.001e. In our calculations we have not taken into account the effect of spin orbit coupling. For the integration of Brillouin zone (BZ), the tetrahedron method [17] with 195 special k-points in the irreducible wedge (1000 k-points in the full BZ) was consider to obtained the charge density in each self-consistency step. The structural properties of the compound $ThCo_2X_2$ ($X = Si, Ge$) are calculated with exchange and correlation potentials (GGA+U, GGA- PBE and LDA) [18–21] which is implemented in Wien-2k code. For both the compounds the used value in this study is $U=6eV$ which is reasonably good approximation to deal with Co atom d-states, as reported in past published work [33]. For the electronic and magnetic properties of $ThCo_2X_2$ ($X = Si, Ge$) compounds GGA-PBE and GGA+U potentials were employed.

3. Results and discussion

3.1. Structural properties

The thorium based ternary intermetallic systems with general formula ThCo_2X_2 ($\text{X} = \text{Si}, \text{Ge}$) has been crystallized in tetragonal lattice structure having space group (14/mmm #139). The site positions for Th are the Wyckoff position 2(a) [15], and for Co is 4(d) while for ($\text{X} = \text{Si}, \text{Ge}$) is 4(e) as shown in Fig. 1.

The compound's structure behaviour is determined by calculating the atomic lattice positions and cell dimensions. From optimization it has cleared that suitable phase for ThCo_2X_2 ($\text{X} = \text{Si}, \text{Ge}$) is ferromagnetic phase. While from the experimental available data up to our literature survey it has been cleared that the suitable phase for these compounds exist in FM phase [15,26].

For the optimization of unit cell and finding of ground state energy we calculated the total energy for different volumes in the neighbourhood of the experimental volume. To obtain the ground state properties of the compound, we determined the total energy and draw it against volume and hence fit it to the empirical Murnaghan's equation of state [22]. The calculated total energy of the state for both the compounds ThCo_2Si_2 and ThCo_2Ge_2 as a function of volume in (PM, FM and AFM) phases is plotted in Fig. 2.

Relative energies of PM, FM and AFM phases are given in Table 1. By using these energies one can find total or absolute energy of both these compounds by the known relation FM-PM:

$$\begin{aligned} \text{Fm-Nm} &= -59,807.473 + 59,807.469 = -0.004 (\text{for } \text{ThCo}_2\text{Si}_2) \\ \text{Fm-Nm} &= -67,043.683 + 67,043.569 = -0.114 (\text{for } \text{ThCo}_2\text{Ge}_2) \end{aligned}$$

However, the only mentioned energy of (PM phase) is noted for both compounds, the rest of the other parameters are determined by using PBE-GGA approximations and are obtained in ferromagnetic phase like in our previous published work [31].

Moreover, both compounds stabilize in the FM phase. The calculated values of lattice parameters (a and c (Å)), ground state energy, unit cell volume (V_0), bulk modulus (B_0), and derivative bulk modulus (B'_0) from structural optimization for both compounds are present in Table. 1.

It is observed that the lattice constants (a and c (Å)) and unit cell volume (V_0) increases while computing through (PM, FM and AFM) phases as we replace the Si Anion by Ge. This enhancement actually caused by the fact that the increment in atomic size of the anions from Si to Ge element. Finally, the B (GPa) which explain the materials compressibility, a clear decreasing trend in calculated values from Si to Ge define ThCo_2Ge_2 more compressible as compare to ThCo_2Si_2 compound. The theoretical calculated results can be verified by experiment; still, we have only experimental lattice constants about thorium compounds that we compare with our results. Thus, our reported values are good in alignment with the available experimental findings [26, 11, 12].

The stability of the structural cell is confirmed by calculating the cohesive energy, using the cohesive energy formula [23].

$$E_{coh} = \frac{E_{\text{ThCo}_2\text{X}_2} - aE_{\text{Th}}^{tot} - bE_{\text{Co}}^{tot} - cE_{\text{X}}^{tot}}{a + b + c}$$

Where, $E_{\text{ThCo}_2\text{X}_2}$, aE_{Th}^{tot} , bE_{Co}^{tot} \wedge cE_{X}^{tot} are total energy of ThCo_2X_2 ($\text{X} = \text{Si}$ or Ge) unit cell, isolated Th, Co and Si/Ge atoms, respectively. The indexes a , b and c represent the number of each atom in the cell. The obtained cohesive energy of tetragonal ThCo_2X_2 ($\text{X} = \text{Si}$ or Ge) is 4.95 eV/atom.

3.2. Electronic and magnetic properties

The electronic band structure and density of state play a vital role in determining the crystal structure [24, 25]. For the clear

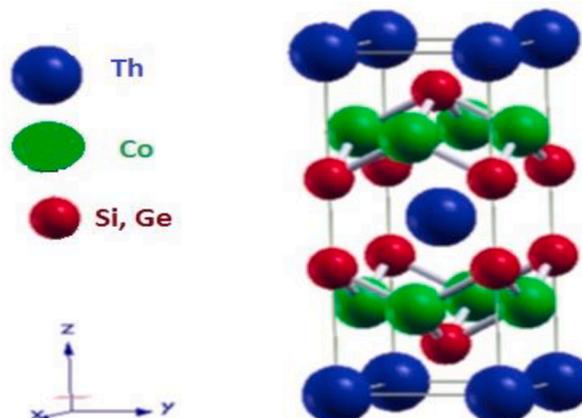


Fig. 1. Unit cell of tetragonal ThCo_2X_2 ($\text{X} = \text{Si}, \text{Ge}$) compound structure. Blue sphere represents Th, Green Sphere shows Co and red one is for X.

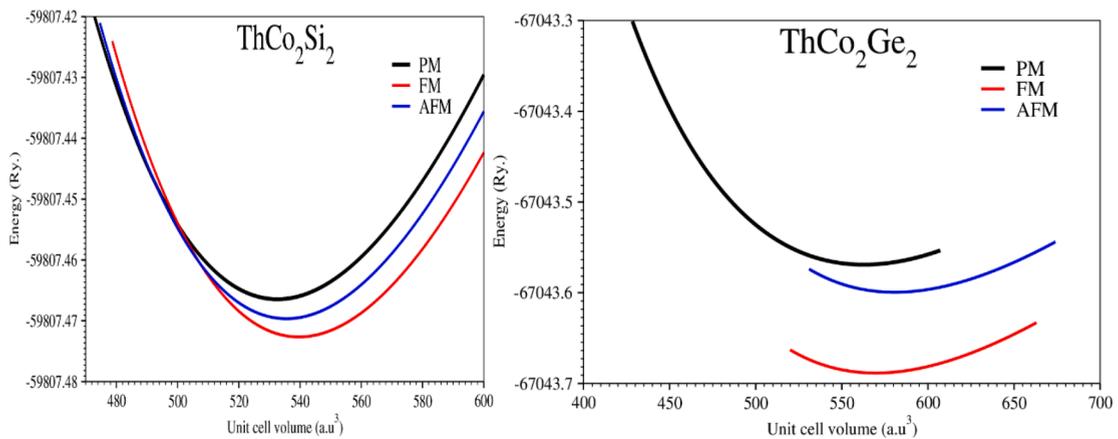


Fig. 2. Optimization plots showing energy versus volume of ThCo_2Si_2 and ThCo_2Ge_2 compounds for PM, FM and AFM.

Table 1

Calculated unit cell parameters of ThCo_2X_2 ($\text{X} = \text{Si, Ge}$) compound in (PM, FM and AFM) phases along with other available data.

Compounds	Lattice constant (Å) ^a	$V_0(\text{a.u.})^3$	B(GPa)	B_p	$E_0(\text{Ry})$			
						PM	FM	AFM
$\text{ThCo}_2\text{Si}_2(\text{PBE-GGA})$	4.013	9.751	537.5986	161.5	5.0	-59807.469	-59807.473	-59807.47
	Exp ^{a,c}	4.015 ^a	9.756 ^a					
		4.015 ± 0.003 ^c	9.760 ± 0.005 ^c					
$\text{ThCo}_2\text{Ge}_2(\text{PBE-GGA})$	4.101	9.921	569.7071	143.158	5.0	-67043.569	-67043.683	-67043.60
	Exp ^{a,b}	4.103 ^a	9.929 ^a					
		4.109 ± 0.002 ^b	9.934 ± 0.004 ^b					

^a Ref. [26]

^b Ref. [11]

^c Ref. [12],

understanding of bonding character of a compound, the total density of state (TDOS) and partial densities of states (PDOS) are very necessary to examine. We have calculated the total and partial density of state by two different exchange and correlation potentials PBE-GGA and GGA+U in the energy range between -6eV and 6eV. Fig. 3(a,b). Represent the TDOS and PDOS of the thorium compounds ThCo_2Si_2 and ThCo_2Ge_2 for both the spins up and down channels.

Both compounds show full metallic nature on the grounds that the appeared total and partial (p, d, f) states crossing the Fermi-level dominantly in both spin channels. Therefore, from Fig. 3(a, b) we can say that the orbital contributions in both compounds are quite similar. Further, clarification from the total DOS is clearly observe where the active progress at (EF) mostly arises from Co-d state. Furthermore, there is a strong hybridization among Co-d and (X= Si, Ge)-p states in the valence band with Th-f state lies in the conduction band. These states are the responsible factor towards the materials with metallic properties.

The major appearance and contribution of Co-d state at the Fermi level along with the dominant spread from high toward low energy (-1.5 to -4.5eV (GGA-PBE) and -2.5 to -5eV (GGA+U)) for ThCo_2Si_2 and (0 to -3.5eV (GGA-PBE) and -3.6 to -5.5eV (GGA+U)) for ThCo_2Ge_2 in the valence band region. This shifting toward further lower in energy of d-state for both compounds are actually due to the use of (GGA+U) potential which treats localized d-shell electrons of the Co atom. Further the disappearance of the Co-d state from both channels at further lower in energy by using (GGA-PBE) while shifting towards higher in energy of the same Co-d state through down spin by utilizing (GGA+U) are clearly seen in DOS plots. Moreover, the minor contribution comes from Si-p state over the entire energy range in ThCo_2Si_2 whereas up to -3.5eV from Fermi level in ThCo_2Ge_2 with a straight line of Th-f state appears over the whole energy range of valence band region through both potentials. For both the compounds the used value in this study is $U=6\text{eV}$ which is reasonably good approximation to deal with Co atom d-states, as reported in past published work [33].

On the other side Th-f state appears sharply toward higher in energy range (2 to 3.5eV through both potentials) for ThCo_2Si_2 and (1.5 to 2.5eV (GGA-PBE) and 0.5 to 2.2eV (GGA+U)) for ThCo_2Ge_2 in the region of conduction band through both channels. Moreover, the minor contribution in various spin state of ThCo_2X_2 comes from Co-d state at the Fermi level toward lower in energy through GGA-PBE while toward higher in energy through GGA+U potential. Lastly the minor appearance of (X= Si, Ge)-p state over the entire energy range in the region of conduction band through both channels are observe while using both GGA-PBE and GGA+U potentials. Interestingly the almost symmetric appearance of ThCo_2X_2 compounds various states (Th-f, Co-d and X-p) spectra through both channels lie in valence and conduction bands indicate its frequent fulfilment of stoner argument [27].

The electronic band structure of ThCo_2X_2 ($\text{X} = \text{Si, Ge}$) plotted (Fig. 4(a, b)) for both channels (spin up and spin down) by two different potentials PBE-GGA and GGA+U, to understand the electronic properties of the structure. In these figures the Fermi energy

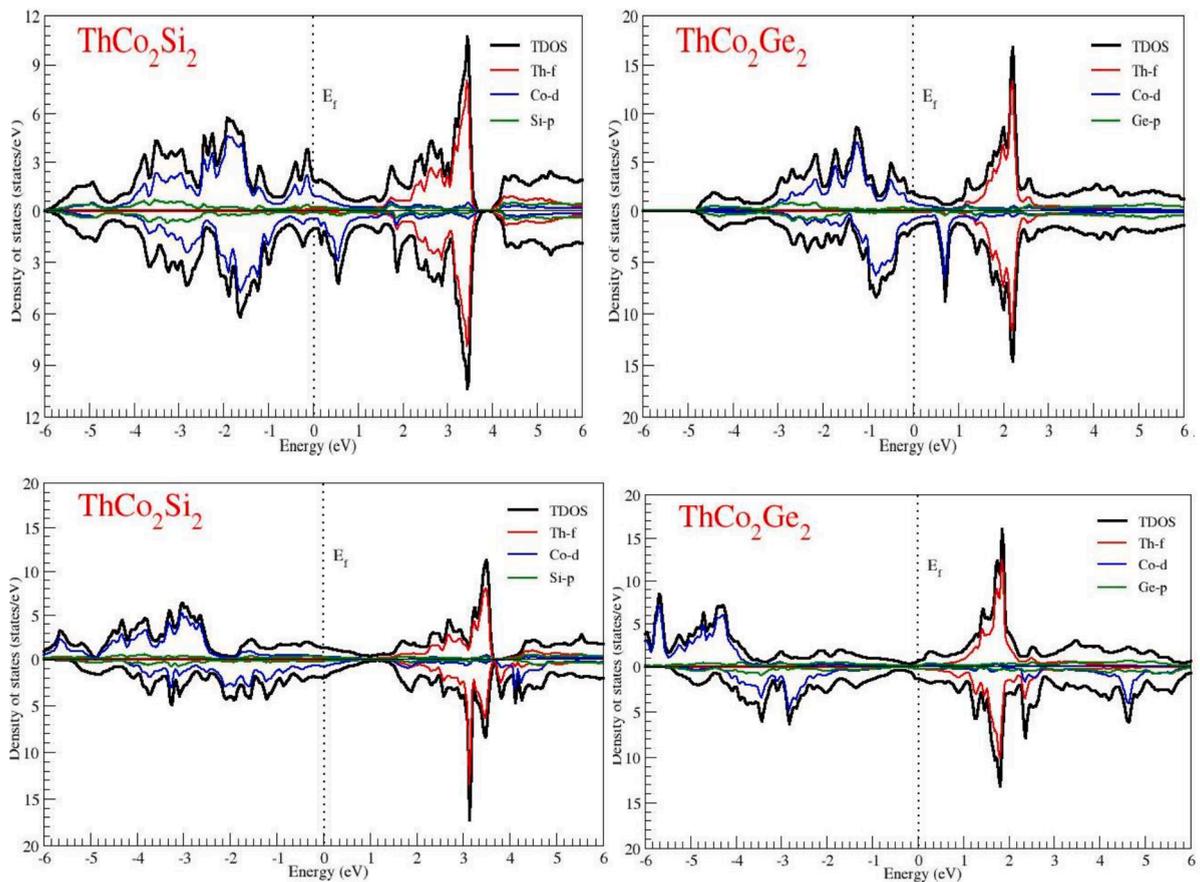


Fig. 3. (a) represents the total and partial density of states of ThCo_2X_2 ($\text{X} = \text{Si}, \text{Ge}$) compounds by computing GGA-PBE potential in both channels. (b) represents the total and partial density of states of ThCo_2X_2 ($\text{X} = \text{Si}, \text{Ge}$) compounds by computing GGA+U potential in both channels

level is set to be at origin for simplicity as a reference point while the examined band structures along the high symmetry Γ , H, N, and (Γ , P) directions in the Brillouin zone (BZ) are also shown.

The prominent dispersion of two valence band maximum at the high symmetry H point is clearly seen. These two bands with shoulders on each side appears dominantly while crossing the Fermi level and remain in the conduction band region in both spin channels of ThCo_2X_2 by using PBE-GGA and GGA+U potentials with minor changes in details. Like the disappearance of second band with shoulder at high symmetry (H point) in ThCo_2Ge_2 compound through (GGA+U) in addition with the minor appearance of narrow band dispersion at (Γ point) through both channels. Apart from this the conduction band minimum follow the same trend for ThCo_2X_2 compounds with dispersion of a single band at high symmetry (N point) from spin-up channel whereas remain in the region of conduction band through (PBE-GGA) from spin-down channel (which means the conduction bands do not hold extra electrons and are completely filled) with absent overlapping mechanism is noticed with available valence bands.

When the GGA+U potential is applied, a clear split in the bands is seen but still both the thorium compounds depict the metallic nature. When d-states are bound by using GGA+U approximation the conduction band moves up and valence band moves down at high symmetry (Γ point). Additionally, the calculation through GGA+U potential gives peculiar behaviour like the compound ThCo_2Si_2 shows the similar trend of single band dispersion in between high symmetry (Γ and H, H and N, Γ and N) basal points through both channels. But for ThCo_2Ge_2 no single dispersion in spin-up state occurs with shifting of the same bands back to the conduction region whereas in spin-down state a clear dispersion in between high symmetry (Γ and H, H and N) basal points while overlapping occurs at (Γ) point.

Moreover, at the Fermi level there is no energy gap which expresses the pure metallic nature while states in spins up channel are much closer toward one another as compare to spin-down channel in the vicinity of Fermi level. Though the closer states enable an easy mobility of electrons which in a long term influence the system in the sense of conductivity. Overall, the thorium compound ThCo_2X_2 band structures depict full-metallic nature because of the crossing and overlapping mechanisms across the Fermi energy level together with absent gap in both-spin channels while computing two different (PBE-GGA and GGA+U) potentials.

The magnetic properties of ThCo_2Si_2 and ThCo_2Ge_2 compounds are investigated by the spin polarized calculations with the PBE-GGA and GGA+U methods. The total each cell m^c magnetic moment, interstitial and local (Th, Co, Si and Ge) individual magnetic moments of the compounds under investigation are summarized in [Table 2](#). From the tabulated data, it is initiated that the Co atom is

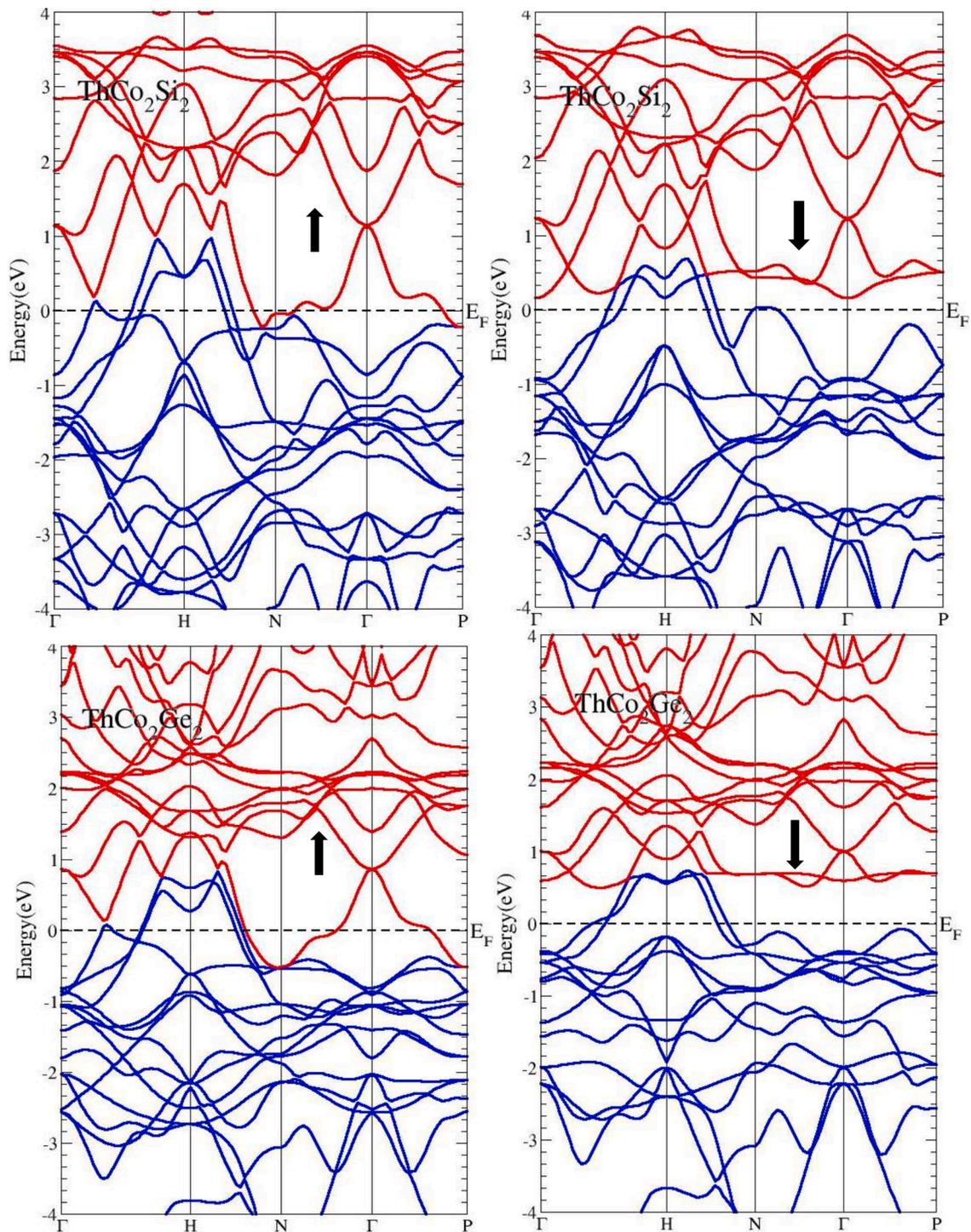


Fig. 4. (a) The calculated band structures of ThCo_2X_2 ($X = \text{Si}, \text{Ge}$) compounds by computing GGA-PBE potential in both channels. The Fermi level (dashed line) is set to 0.0 eV. (b) The calculated band structures of ThCo_2X_2 ($X = \text{Si}, \text{Ge}$) compounds by computing GGA+U potential in both channels. The Fermi level (dashed line) is set to 0.0 eV.

the most active participating atom in the total cell magnetic moment of ThCo_2X_2 ($X = \text{Si}, \text{Ge}$) with high parallel ferromagnetic values in comparison with others like atoms at the interstitial region and individual (Th, Si and Ge) atoms which are contributing with anti-parallel values through both PBE-GGA and GGA+U potentials. The fundamental origin of magnetization in these thorium

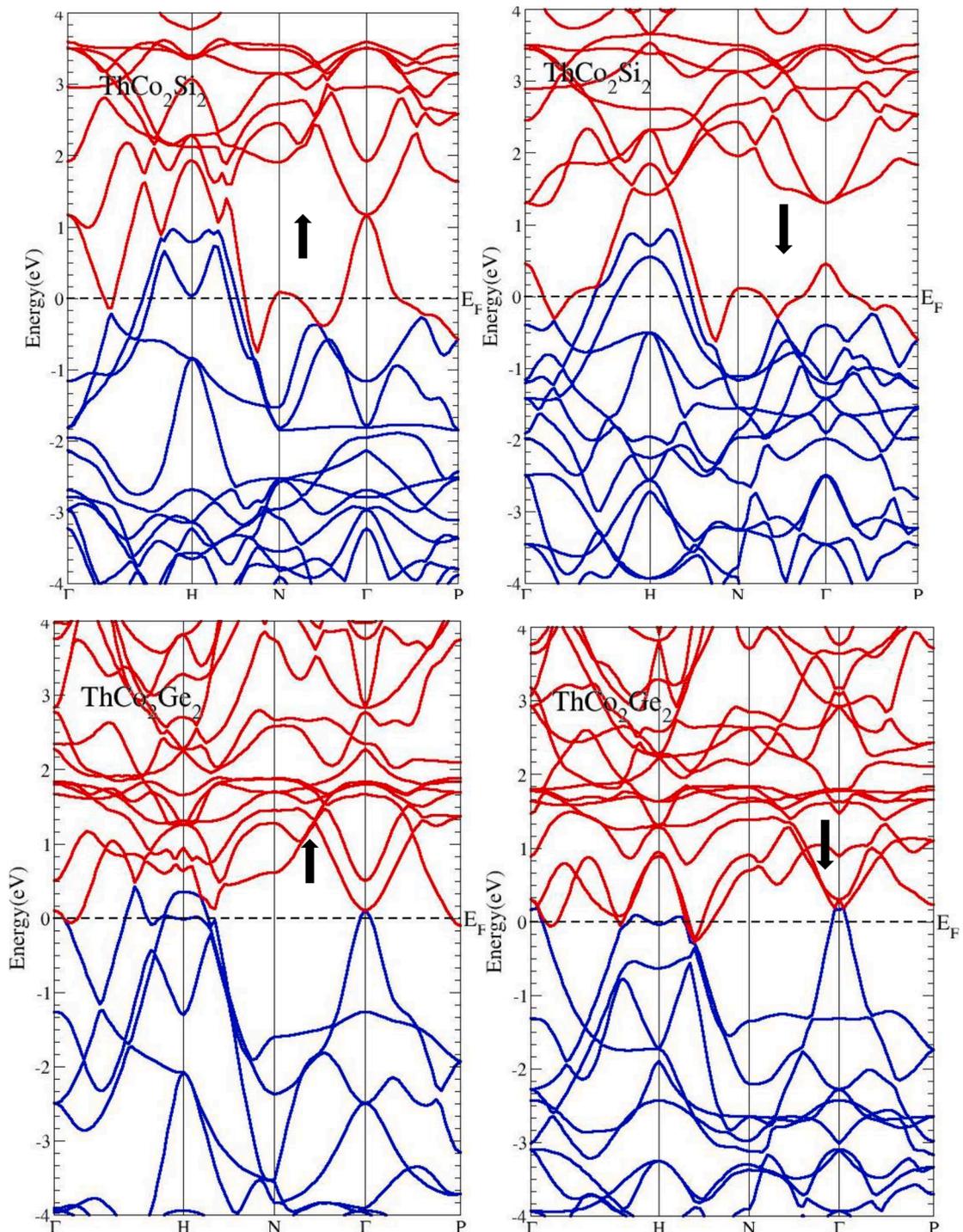


Fig. 4. (continued).

compounds particularly comes from unoccupied Th-f and Co-d orbitals. Hence, except the dominant cobalt site the rest of other sites tend to lower the overall ferromagnetic nature of the said compounds.

In addition to this the non-negative values of the net magnetic moments of ThCo_2Si_2 and ThCo_2Ge_2 compounds through both PBE-GGA and GGA+U potentials indicate that the stable magnetic ground state is ferromagnetic as depicted in the optimization plots in Fig. 2 as well as published in previous experimental studies [15, 26] for both compounds. In this work mostly focused on the parallel magnetic moment is due to the compound's ferromagnetic nature not only in our calculation but in previous studies [15, 26, 28, 30–32] as well. Moreover, the computation due to GGA+U potential gives a value with higher magnitude in comparison with other so far

Table 2Calculated total, interstitial and local magnetic moments of ThCo₂Si₂ and ThCo₂Ge₂ compounds with both PBE-GGA and GGA+U potentials.

Compound	Interstitial	m^{Th}	m^{Co}	m^{Si}	m^{cell}
ThCo ₂ Si ₂	-0.02786	-0.00425	0.47430	-0.00309	0.91032
(PBE-GGA)	-0.19993	-0.07118	1.07536	-0.02928	1.82106
(GGA+U)	—	—	1.42 ^a	—	—
Exp ^a	—	—	—	—	—
ThCo ₂ Ge ₂ (PBE-GGA)	-0.06547	-0.02641	0.83313	-0.00717	1.56004
(GGA+U)	-0.03026	-0.06624	1.97350	-0.01250	3.82550
Exp ^{a,b}	—	—	3.82 ^a	—	1.94 ^b

^a Ref. [15]^b Ref. [26].

known approximation potentials because it mostly deals with localized (d-shell) electrons of the Co atom and increase up to some extent its magnetic moment as compared to PBE-GGA potential.

Furthermore, the investigated values of ThCo₂X₂ compounds magnetic moment through both potentials specifically at interstitial site and individual (Th, Si and Ge) atoms opposes the net magnetic moment, while Co site supports it because of the predominant emergence of Co-d state over the entire energy-range in both channels while calculating through both potentials, as seen in the Fig. 3 (a, b) DOS plots. The appearance of opposite sign among the magnetic moments of Inst, Th, Si/Ge, total cell, and Co element depicts, the interaction between the valence-band electrons in antiferromagnetic (AFM) manner. ThCo₂Ge₂ show stronger ferromagnetism because Co is aligned in the direction of net magnetic moment of the compound. Further by bounding d states of Co atom through GGA+U potential, the value of m^{Co} change from (0.833) to (1.97350) as noted in the Table 2. Finally, the total magnetic moments align parallel through both potentials PBE-GGA and GGA+U confirm that thorium-based ThCo₂Ge₂ metallic compounds show stronger ferromagnetic (FM) behaviour as compared to ThCo₂Si₂ compound because of the electro negativity differences between Ge (2.01) and Si (1.90) atoms in previous published work [34]. So, the higher the electronegativity difference, the greater the magnetic moment shown by ThCo₂Ge₂ compound confirm stronger ferromagnetism.

4. Conclusions

Our investigations of structural, electronic and magnetic properties of tetragonal structure thorium based ThCo₂X₂ (X = Si, Ge) compounds by applying full potential linearized augmented plane wave (FP-LAPW) method through DFT within the generalized gradient approximation (GGA) as implemented in the Wien2k code. The calculations for the structural determination of thorium compounds are obtained with the PBE-GGA potential to achieve theoretical reliability with available experimental results, while for the improvement of electronic and magnetic properties we used GGA+U method. Both the compounds are optimized in a stable ferromagnetic phase which is more suitable for the examination of compounds magnetic properties as compared to paramagnetic and antiferromagnetic phases. The plotted band structures together with the (DOS) plots through both spin channels declare full metallic character in the ThCo₂X₂ compound by strong hybridization appearing among Co-d, X-p and Th-f states. Also, the achieved total magnetic moments align parallel to the overall ferromagnetic direction by both potential reveal's stronger ferromagnetism in the investigated compounds.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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