Materials Today Communications 26 (2021) 102036

Contents lists available at ScienceDirect

Materials Today Communications

journal homepage: www.elsevier.com/locate/mtcomm

Structural, electronic, elastic, magnetic, phonon and thermodynamic properties of inverse-Heusler-Ti_2FeX (X=Si, Ge, and Sn): Insights from DFT-based computer simulation

M. Özduran [a], M.O. Altay [a], A. İyigör [b], M. Çanlı [c,*], N. Arıkan [d]

[a] Department of Physics, Kırşehir Ahi Evran University, Kırşehir, Turkey
[b] Department of Machinery and Metal Technology, Kırşehir Ahi Evran University, Kırşehir, Turkey
[c] Department of Chemistry and Chemical Processing Technologies, Kırşehir Ahi Evran University, 40500, Kırşehir, Turkey
[d] Department of Medical Services and Techniques, Osmaniye Korkut Ata University, 80010, Osmaniye, Turkey

ARTICLE INFO

Keywords:
Band structure
Elastic constants
Inverse-Heusler
Magnetic moment
Phonon

ABSTRACT

The structural, mechanical, electronic and lattice dynamic properties of Ti_2FeX (X = Si, Ge, and Sn) inverse-Heusler alloys have been explored via first-principles calculations based on density functional theory. The equilibrium lattice constant, bulk modulus, electronic band structure and magnetic moment values of these alloys have been computed to be consistent with prior studies. Several mechanical parameters such as elastic constants C_{ij}, bulk modulus B, Young modulus E, shear modulus G and Poisson's ratio υ are calculated, and based on these calculations, mechanical stability is examined. The calculated values of the total magnetic moments are in close agreement with the existing theoretical data and comply with the Slater-Pauling rule. From their calculated electronic band structure, Ti_2FeSi, Ti_2FeGe and Ti_2FeSn are found as half-metallic alloys at the equilibrium lattice constant with a minority-spin energy gap of 0.820, 0.850 and 0.780 eV, respectively. The full phonon spectra, and their total and partial density of states of these alloys have been carried out via the direct method. The calculated phonon spectrum points out dynamic stableness of these alloys. Furthermore, the thermodynamic properties such as the heat capacity, thermal expansion, entropy and Grüneisen parameter have been investigated in the Debye model using the Gibbs2 code with a series of temperature from 0 to 1500 K.

1. Introduction

The first Heusler alloy, Cu_2MnAl, was discovered in 1903 by Fritz Heusler [1]. To obtain this alloy, CuMn alloy was added to Al atoms which is one of the 3rd group elements, and it was observed that the alloy turned into a ferromagnetic half-metal material. These types of Heusler alloys are called full-Heusler alloys. Full-Heusler alloys are found in the Fm-3 m space group with a stoichiometric composition of 2:1:1 and the chemical formula X_2YZ [1]. The family of Heusler alloys is divided into three subfamilies: full-Heusler, half-Heusler, and inverse Heusler. Heusler alloys, the majority of which are spin-polarized, are materials with a spin orientation metallic and the other spin orientation having semiconductor or insulating properties, exhibiting half-metallic magnetic properties.

There are few studies on Ti_2-based half-metallic Heusler alloys. The calculations of Ti_2CoGa full Heusler compound are based on FLAPW method [2]. This material was found to be a half-metallic ferromagnetic material with a magnetic moment of 2μB and an energy band gap of 0.5 eV in the spin-down state at the Fermi level. Feng et al. [3] showed that Ti_2NiAl full-Heusler alloy is a new half-metallic ferromagnet by using the plane wave pseudo-potential method. Subsequently, the electronic and magnetic properties of full-Heusler alloys such as Ti_2CoGa [2], Ti_2CoAl [4], Ti_2FeSi [5] and Ti_2CoB [6] were studied by FLAPW method. In those studies, these alloys were found as fully spin polarized (100 %) around the Fermi level and were half-metallic ferromagnets with a total magnetic moment of 2μB. On the other hand, small number of studies carried out in literature about the new generation of half-metallic Ti_2FeX (X = Si, Ge and Sn) inverse Heusler alloys, which are among the promising candidates for the new generation of recording sensors in ultra-high-density hard disks. The electronic and magnetic properties of the Ti_2FeSi alloy have been studied theoretically by different research groups [5,7–9]. According to these results, Ti_2FeSi

* Corresponding author.
E-mail address: muratbdm@gmail.com (M. Çanlı).

https://doi.org/10.1016/j.mtcomm.2021.102036
Received 7 December 2020; Received in revised form 11 January 2021; Accepted 11 January 2021
Available online 15 January 2021

alloy has a magnetic moment of 2μB and has a half-metallic character. Structural, magnetic, and electronic properties of Ti_2FeGe alloy have been investigated by theoretically, and it has been observed in literature that it is a half-metallic ferromagnetic alloy [9–11]. The electronic, magnetic, structural, and half-metallic properties of Ti_2FeSn alloy were investigated by Ahmadian [12], Birsan and Palade [13] using the FPLAPW method. However, no further studies have been carried out on this alloy combination. To the best of our knowledge, there is a need for gathering information about phonon properties.

The goal of this study is to find out the structural, electronic, elastic, mechanical, thermodynamic, and phonon properties of inverse Heusler Ti_2FeX (X = Si, Ge and Sn) using the first principle pseudopotential method based on a generalized approximation of the density functional theory (DFT). Full phonon spectra, total density of states (DOS) and projected density of states (PDOS) of Ti_2FeX (X = Si, Ge, and Sn) alloys have also been investigated by direct method.

This manuscript has been organized as follows. A brief explanation of the computational methods is presented in Section 2. The results and discussions are exhibited and analyzed, including structural, electronic, mechanical, thermodynamic and phonon properties are given in Section 3. In Section 4, a summary of our work is given in detail.

2. Materials and methods

DFT calculations were performed using the MedeA-VASP package program [14,15] with the projected augmented-wave (PAW) potentials. For the exchange–correlation energy functional, the generalized gradient approximation (GGA) of Perdew–Burke–Ernzerhof (PBE) [16] was chosen. An energy cut-off of 500 eV was used for the spin-polarized calculation of structural, electronic, elastic, thermodynamic and phonon properties. The energy convergence criteria were arranged to value 10^{-10} eV using the Normal (blocked Davidson) algorithm and reciprocal space projection operators. The k-point sampling was performed on an 8 × 8×8 Gamma-point grid for the integration in the irreducible Brillouin zone. The Fermi distribution function with a smearing parameter of 0.2 eV was smeared to integrate the bands at Fermi level. Elastic constant was calculated via stress-strain technique [17–19]. The phonon dispersion curves were determined using the MedeA-Phonon module with the forces found from the VASP by the direct method. A 2 × 2×2 supercells containing 128 atoms for XA phase were used. Thermodynamic properties such as the heat capacity, thermal expansion, entropy and Grüneisen parameter were assigned in the Debye model using the Gibbs2 code [20].

3. Results

3.1. Structural properties, magnetic and electronic properties

In this study, the crystal structures of Ti_2FeX (X = Si, Ge, and Sn) alloys with F-43 m space group in the XA phase are presented as in Fig. 1. In the XA phase, the Ti atoms are placed in the Wyckoff positions 4a (0,0,0) and 4c (0.25, 0.25, 0.25) while Fe and X in 4b (0.5, 0.5, 0.5) and 4d (0.75, 0.75, 0.75) positions, respectively. The geometric optimization has been performed with a convergence error less than 10−10 eV in interatomic force without changing the crystal structure of inverse-Heusler alloys with F-43 m space group in XA phase. The minimum energy lattice constant values have been obtained for Ti_2FeX (X = Si, Ge, and Sn) alloys. The values of the calculated lattice constants and bulk modules of inverse-Heusler alloys Ti_2FeX (X = Si, Ge, and Sn) are given in Table 1 by comparing with other theoretical studies in previous efforts. Also, the formation energies of Ti2FeX (X = Si, Ge, and Sn) XA phase were calculated as −0.500, −0.398 and −0.268 eV / atom, respectively. These calculated formation energy values show that these alloys can be synthesized structurally stable and experimentally. According to the comparison, the obtained lattice constant value for Ti_2FeSi alloy was calculated by FPLAPW method in a study [5] with a

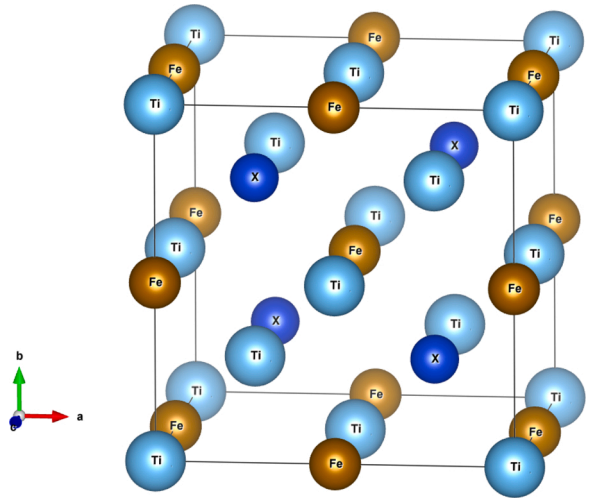

Fig. 1. The crystal structure of Ti_2FeX (X = Si, Ge, and Sn) inverse-Heusler alloys in the Hg_2CuTi-type structure.

Table 1
The lattice constants a_0, (Å) and bulk modulus B (GPa) of Ti_2FeX (X = Si, Ge, and Sn) inverse-Heusler alloys.

Materials	Ref.	a_0	B
Ti_2FeSi	This work	5.993	161.91
	Ref. 7	6.057	168.75
	Ref. 5	5.997	161.82
	Ref. 8	5.999	–
Ti_2FeGe	This work	6.076	152.40
	Ref. 9	6.090	144.88
	Ref. 10	6.075	–
	Ref. 11	6.074	165.48
Ti_2FeSn	This work	6.334	130.88
	Ref. 12	6.350	125.84
	Ref. 13	6.342	–

difference of 0.07 % and in another study [7] with a difference of 1% by using the GGA + U. The computed lattice constant value of Ti_2FeGe alloy is 0.02 % higher than the value obtained by VASP codes [10] and was obtained with a difference of 0.23 % lower than the value obtained using FPLAPW method [9]. The lattice constant value of Ti_2FeSn alloy has been found to be lower with a difference of 0.25 % than the study by FPLAPW method [12], and higher with a difference of 0.13 % than another study using FPLAPW method by Birsan and Palade [13]. When Ti_2FeSi, Ti_2FeGe and Ti_2FeSn inverse-Heusler alloys are compared with the bulk modulus values with the literature in Table 1, it is seen that there is a difference between 0.06 % and 7.9 %. Despite this difference, it is possible to say that this difference between the bulk moduli is within acceptable limits. By examining bulk modules, which is also an expression of compressibility, it is seen that they are in order of $B_{Si} > B_{Ge} > B_{Sn}$ with respect to X atoms. Accordingly, we can say that the alloy with the lowest compressibility is Ti_2FeSi and the alloy with the highest compressibility is Ti_2FeSn. In addition, when the lattice constants and bulk modules of these alloys are examined according to the atomic and covalent radius of the X atoms in the alloys; As the covalent radius of the X atoms increase, the lattice constant values increase ($a_{Sn} > a_{Ge} > a_{Si}$), and as the atomic radius of the X atoms increase, the bulk modulus values decrease. Therefore, there is a direct proportion between atomic radius and lattice constant values of X atoms, and inverse proportion between bulk moduli and covalent radius of X atoms.

The spin contribution for Ti_2FeX (X = Si, Ge, and Sn) inverse-Heusler alloys in the XA phase (F-43 m space group) has been calculated considering spin polarization. The total magnetic moments of Ti_2FeX (X = Si, Ge, and Sn) inverse-Heusler alloys exhibit Slater-Pauling

behavior (SP). The total magnetic moment of the inverse-Heusler alloys, whose nine minority bands are completely filled, is determined by the rule $M_t = (Z_t - 18)\mu_B$ [21,22]. Here Z_t is expressed as the total number of the valence electrons per unit cell or the sum of the number of electrons in the spin orbits ($Z_t = N\uparrow + N\downarrow$). When Ti_2FeX (X = Si, Ge, and Sn) inverse Heusler alloys are calculated according to SP, the total magnetic moments of Ti_2FeSi, Ti_2FeGe and Ti_2FeSn alloys are found 2 μ_B. The calculated magnetic moment values of the alloys are presented in Table 2 and compared with the available theoretical data. According to Table 2, it seems that the total magnetic moments of Ti_2FeSi, Ti_2FeGe and Ti_2FeSn alloys fit to both theoretical data and SP values. Compared to the results obtained with SP, the obtained results for three alloys can be said to be a reasonable value. The major contribution to the total magnetic moment of these magnetic inverse-Heusler alloys showing magnetic properties comes from the Ti atoms. In Fig. 2, the spin-dependent electronic band spectra of Ti_2FeX (X = Si, Ge, and Sn) inverse Heusler alloys are clearly noticed. While the black energy bands are for up spin, the red solid lines represent down spin electrons [23]. When the spin-dependent energy band curves of Ti_2FeX (X = Si, Ge, and Sn) inverse-Heusler alloys are studied in terms of conductivity, majority-spin (up) electrons of all alloys show metallic property. For the minority-spin (down) electrons, Ti_2FeSi, Ti_2FeGe, and Ti_2FeSn alloys have an energy gap around Fermi level, and it is understood that these alloys are half metals (HM). These calculated energy gap values are presented in Table 2 with a comparison of the available data. It is clearly seen from Fig. 2 that there is indirect band transition through the gaps formed between the minimum of the conductivity band calculated for the spin-down orientation of these alloys and the maximum of the valence band. The fact that the half-metallic gap values of Ti_2FeSi and Ti_2FeGe alloys are different from zero indicates that these two alloys are true half-metallic ferromagnet. Also, these alloys have 100 % spin polarization around the fermi energy level. PDOS is calculated to investigate the electronic band structures of the alloys in more detail and to enlighten the contributions of different atoms and chemical bonding connection among the alloys in Fig. 3. While a sharp peak of the DOS at the E_F means the structural instability, a deep and wide valley of DOS point out the structural stability. All three alloys have similar band profiles as it can be seen from Figs. 2 and 3. The main contribution in the majority-spin states at the Fermi level comes from thed-electrons of Ti (a), Ti(b) and Fe. The reason for majority-spin and minority-spin bands of all three alloys around −1 eV is d electrons of Fe atoms. DOS curves over Fermi level are due to d electrons of both Fe and Ti (b) for majority-spin and d electrons of Ti(a) for minority-spin. These compounds have the conductive nature proved by non-zero DOS at Fermi level.

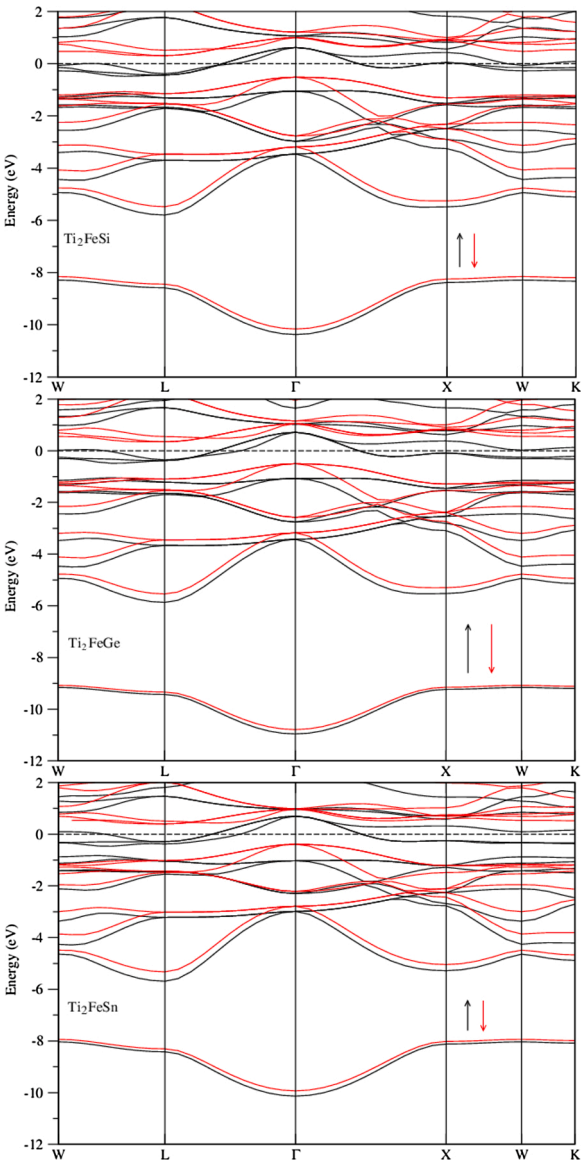

Fig. 2. The calculated electronic band structure for Ti_2FeSi, Ti_2FeGe and Ti_2FeSn alloys in the Hg_2CuTi structure.

3.2. Elastic and mechanical properties

Elastic constants are vital parameters give insights about structural and mechanical stability for a solid material. In addition, elastic properties are related to physical properties of solid materials, Debye temperature, melting point, specific heat, and coefficient of thermal expansion. Since these alloys are in the cubic XA phase (gap group F-43 m), they have three independent elastic constants such as C_{11}, C_{12} and C_{44}. The calculated three elastic constants for these alloys are presented in Table 3. For these alloys, bulk modulus (B), shear modulus (G), Young modulus (E), B/G and Poisson's ratio (σ) obtained from these

Table 2
Calculated magnetic moment (μ_B), spin-minority gap (E_g) and half-metallic gap (E_{HM}) of Ti_2FeX (X = Si, Ge, and Sn) inverse-Heusler alloys.

Materials	Ref.	$M_{Ti(A)}(\mu_B)$	$M_{Ti(B)}(\mu_B)$	$M_{Fe}(\mu_B)$	$M_X(\mu_B)$	$M_{tot}(\mu_B)$	$E_g(eV)$	E_{HM} (eV)
Ti_2FeSi	This work	1.262	0.62	−0.100	0.005	2.020	0.820	0.03
	Ref. 7	1.275	0.796	–	–	2.000	0.612	–
	Ref. 5	1.050	0.489	−0.090	−0.005	2.000	0.450	–
	Ref. 8	1.105	0.524	−0.096	−0.005	2.000	0.454	–
Ti_2FeGe	This work	1.289	0.687	−0.198	−0.006	2.019	0.850	0.02
	Ref. 9	1.080	0.550	−0.190	−0.004	2.000	0.840	–
	Ref. 10	1.619	1.063	−0.651	0.002	–	–	–
	Ref. 11	1.367	0.772	−0.313	0.004	1.965	0.628	–
Ti_2FeSn	This work	1.348	0.786	−0.471	−0.001	2.015	0.780	0.00
	Ref. 12	1.140	0.650	−0.500	−0.001	2.000	0.790	–
	Ref. 13	1.258	0.718	−0.486	−0.0014	0.509	0.489	–

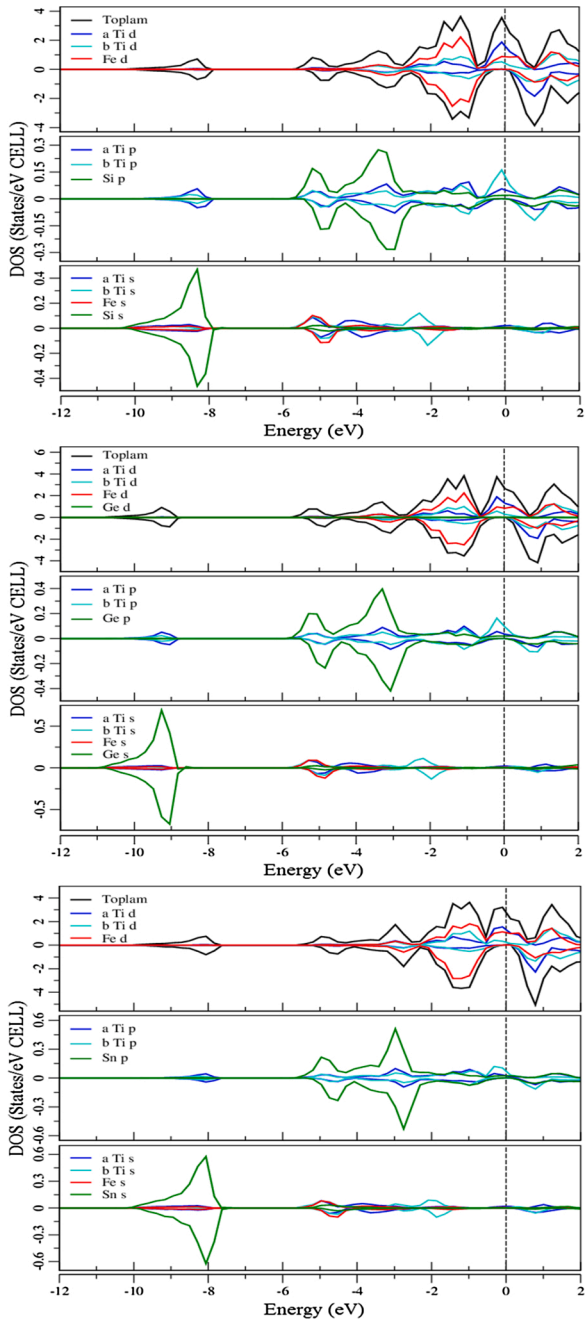

Fig. 3. The calculated projected partial density of states forTi_2FeSi, Ti_2FeGe and Ti_2FeSn alloys in the Hg_2CuTi structure.

Table 3
Calculated elastic constants (C_{11}, C_{12} and C_{44}; GPa) for Ti_2FeX (X = Si, Ge, and Sn) inverse-Heusler alloys.

Materials	C_{11}	C_{12}	C_{44}
Ti_2FeSi	213.12	136.31	69.35
Ti_2FeGe	194.23	131.49	74.37
Ti_2FeSn	173.89	109.38	68.47

elastic constants are presented in Table 4.

Mechanical stability conditions for cubic crystals, known as Born stability criteria for elastic constants, are as follows:

$$C_{11} > 0,\ (C_{11}/C_{12} > 1\ ),\ \left(C_{11}^2 - C_{12}^2\right) > 0,\ (C_{11} + 2C_{12}) > 0 \quad (1)$$

Table 4
Calculated bulk modulus B (GPa), shear modulus G (GPa), Pugh's ratio B/G, Young modulus E (GPa) and Poisson's ratio (σ) for Ti_2FeX (X = Si, Ge, and Sn) inverse-Heusler alloys.

Materials	*B*	*G*	*G/B*	*E*	σ
Ti_2FeSi	161.91	54.71	0.34	147.51	0.35
Ti_2FeGe	152.40	52.60	0.35	141.52	0.35
Ti_2FeSn	130.88	50.62	0.39	134.51	0.33

Considering Born stability conditions of these inverse Heusler alloys whose elastic constants are calculated, it is clearly seen from Table 3 that all these alloys meet the stability conditions. Therefore, it can be said that these alloys meeting Born stability conditions are mechanically stable with F-43 m space group in XA phase. There is no available experimental or theoretical data to compare the elastic constants of these materials.

A material can be classified as either ductile or brittle as a matter of its elastic constant. Whenever the value of Pugh's ratio is below 0.57, that material is called ductile, the ratio is over 0.57, the material is accepted as brittle. The G/B ratio is one of the commonly used criteria to obtain information on the brittleness (ductility) of materials by Pugh's index [24]. According to the calculated G/B ratio of Ti_2FeX (X = Si, Ge and Sn) alloys, all of them are lower than the limit of 0.57. Therefore, all the alloys have a ductile nature. Poisson's ratio value is between ($0.25< \sigma <0.35$) for most metals having ductile and brittle behavior. As seen from Table 4, the calculated values of Poisson's ratio (σ) are between 0.33 and 0.35, indicating ductile nature of the alloys. Besides, the Ti_2FeX material in this study has a positive Cauchy pressure (C_{12}–C_{44}) showing the material as a ductile one. All four indicators approve the material as ductile.

The resistance of a material against longitudinal stress which is called stiffness is determined by comparing the Young's moduli (E). From the calculated Young's moduli (E) listed in Table 4, it is seen that Ti_2FeSn has the lowest stiffness and Ti_2FeSi has the highest stiffness. It is understood from our calculations that Ti_2FeSi alloy has the highest ductility and the least stiffness alloy compared to other alloys.

The calculated value of Poisson's ratio (σ) can generally be considered as a measure of the covalent bond characteristic. This value is close to 0.1 for covalent materials, while it is close to 0.25 for ionic materials [23–26]. As represented in Table 4, the Poisson's ratio values of these alloys are between 0.33 and 0.35, and this shows that they are in ionic character. In addition, the Cauchy pressure (CP = C_{12}-C_{44}) can be consulted for information on the covalent or ionic character of solids [27]. If the Cauchy pressure is positive, the material is ionic, and when it is negative, the material shows covalent properties. Accordingly, all these alloys have ionic nature according to both Cauchy pressure and Poisson's ratio.

3.3. Phonon and thermodynamic properties

Full phonon spectra, total DOS and PDOS of Ti_2FeX (X = Si, Ge, and Sn) inverse-Heusler alloys in the XA phase are presented in Fig. 4. In respect of the XA phase containing four atoms in the primitive cell, Ti_2FeX (X = Si, Ge, and Sn) inverse-Heusler alloys have a total of 12 phonon modes of which are 3 acoustics and 9 optics. However, it is seen that phonon modes decreased to eight because of the double degeneration of Ti_2FeX (X = Si, Ge, and Sn) inverse-Heusler alloys along the directions of L-Γ-X high symmetry. All phonon modes of these alloys in phase XA are positive and do not contain any negative vibration frequency. Therefore, we can see that Ti_2FeX (X = Si, Ge, and Sn) inverse-Heusler alloys in the XA phase are dynamically stable. It is also seen that there is a band gap between the upper optical phonon modes and the other optical phonon modes for the alloys other than Ti_2FeSi alloy. These band gap values have been calculated as 1.18 THz for Ti_2FeGe and 0.85 THz for Ti_2FeSn. It can be said that the band gap occurs due to the

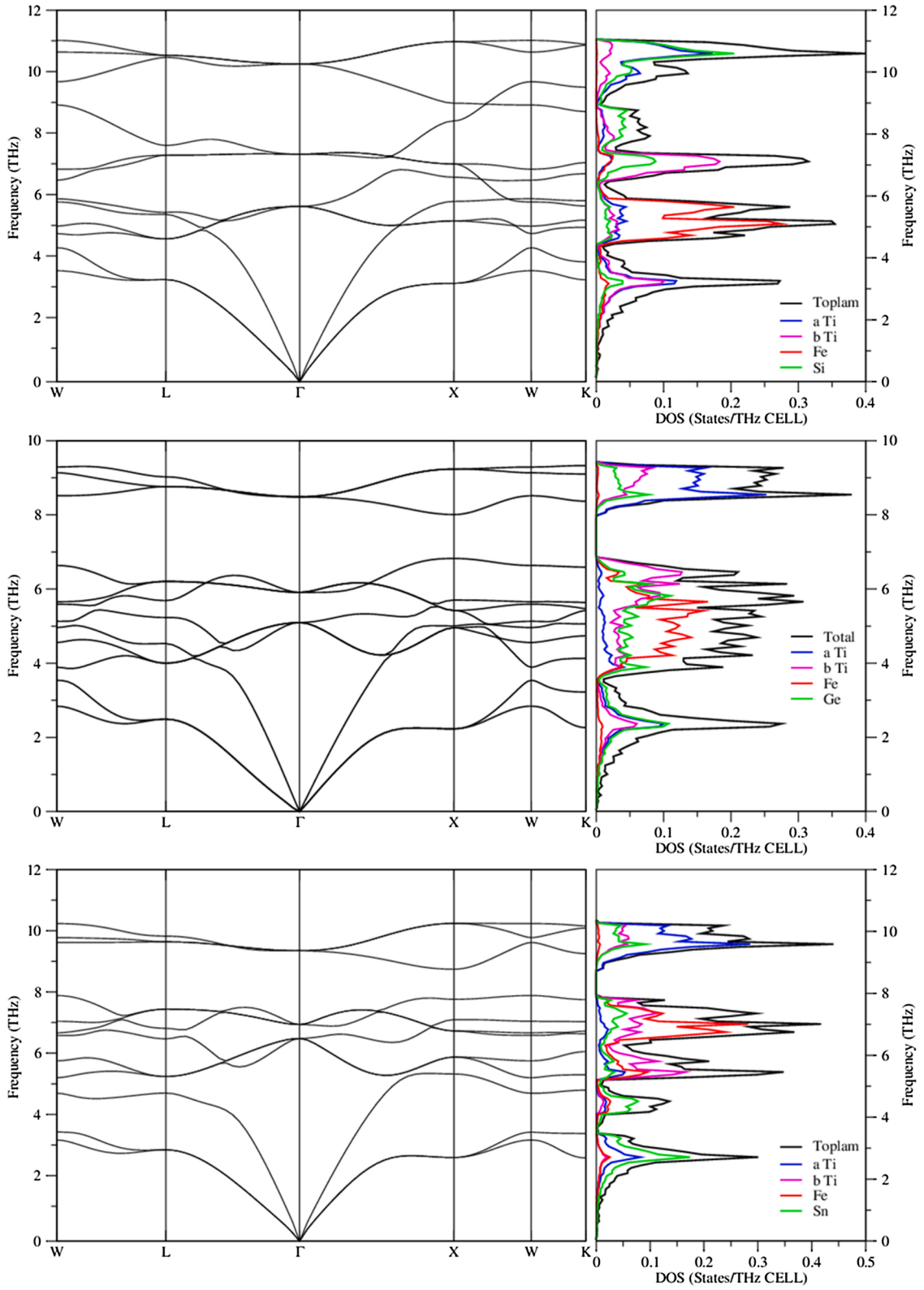

Fig. 4. The phonon dispersion curves and partial density of states for Ti_2FeSi, Ti_2FeGe and Ti_2FeSn alloys in the Hg_2CuTi structure.

mass difference among atoms and the weak interactions of the atoms forming the crystal. Zone center (Γ) optical phonon frequencies have been calculated and given in Table 5. It was understood that these alloys are Raman and IR active at zone center optical phonon frequencies. To enlighten the characteristics of atomic vibration properties of Ti_2FeX (X = Si, Ge and Sn) inverse-Heusler alloys, PDOS of these alloys have been found and shown in right panel in Fig. 4. The upper optical phonon modes of Ti2FeSi alloy are because of vibrations of Si atoms. However, highest phonon modes of Ti_2FeGe and Ti_2FeSn are coming from vibrations of Ti(a) atoms. The major contributions to acoustic phonon modes of Ti_2FeGe and Ti_2FeSn alloys are provided by heavier Ge and Sn atoms vibrations, respectively. On the other hand, for Ti_2FeSi, Ti atoms have

Table 5
Calculated zone center (Γ) optical phonon frequencies (THz) for Ti_2FeX (X = Si, Ge, and Sn) inverse-Heusler alloys.

Materials	Optical Phonon Frequencies
Ti_2FeSi	5.615; 7.316; 10.251
Ti_2FeGe	5.096; 5.911; 8.486
Ti_2FeSn	6.483; 6.933; 9.346

higher vibration frequency than Si atoms because the lowest frequencies of Fe vibration confirm rather weak bonding forces between Ti and Fe atoms. The vibration frequencies between 4 and 7 Thz for Ti_2FeGe and between 5 and 8 THz for Ti_2FeSn are caused by Fe and Ti (b) atoms. No comparison has been made between the experimental and theoretical studies on the phonon properties of these alloys because of lacking enough available data.

Heat capacity, thermal expansion, entropy and Grüneisen parameter play an important role in determining thermal properties of the materials and understanding their behavior under high temperatures. These parameters give an idea about atomic interactions, anharmonicity of lattice vibrations and thermodynamic stability of the materials. Thermodynamic properties have been obtained for different temperatures using the energy-volume relationship. Debye model with gibbs2 codes have been applied for the calculations [28]. We obtained the macroscopic properties as a function of temperature from total energy and standard thermodynamic relations calculated as a function of primitive cell volume (E–V) data in the static approach. The thermal properties of Ti_2FeX (X = Si, Ge, and Sn) compounds were investigated in the temperature range from 0 to 1500 K. The heat capacity, entropy, Grüneisen parameter and thermal expansion coefficient of Ti_2FeX (X = Si, Ge and Sn) inverse-Heusler alloys were calculated according to the temperature and were plotted in Figs. 5a–d, respectively. As it can be seen from Fig. 5a, the heat capacity increases rapidly at approximately $T \leq 250$ K, while it increases slowly at approximately $T > 250$ K. In addition, the heat capacity for inverse-Heusler alloys with four atoms in the unit cell exhibits $\approx T^3$ behavior at low temperatures, approaching the Dulong-Petit limit [29], known as ≈3NR, as it ascends towards high temperatures. Thus, a saturation level is reached by approaching the Dulong-Petit limit. The calculated heat capacity C_v approaches the Dulong - Petit limit (99.77 J / mol K) at high temperatures, indicating that our thermodynamic calculations and phonon calculations for Ti_2FeX (X = Si, Ge, and Sn) inverse-Heusler alloys are reliable. In Fig. 5b, when the change of entropy is examined in the temperature values changing from 0 to 1500 K, the entropy value increases as the temperature increases. While the increase of entropy from low temperature values to high temperatures is fast, it is seen that the entropy increases gradually toward the high temperature values. For Ti_2FeX alloys, the variation of the thermal expansion coefficient with temperature is illustrated in Fig. 5c. There is a rapid increase in the thermal expansion coefficients of these alloys up to 300 K. Over this point, a gradual increase with temperature is observed for all the alloys. To estimate the anharmonic properties of an alloy and describe anharmonic effects in the vibrating mesh, the Grüneisen parameter is calculated by administering the Debye model with the data. The Grüneisen parameters of all alloys are presented in Fig. 5d. Grüneisen parameters show little sensitivity and increase slowly with increasing temperature. The Grüneisen parameter is different from zero at 0 K, indicating that the thermal expansion coefficient and heat capacity approach the same asymptotically zero. Therefore, the Grüneisen parameter at 0 K is proportional to the logarithmic derivative of the T^3 coefficient in the heat capacity [30].

4. Conclusions

In this study, the structural, electronic, mechanical, vibration and thermodynamic properties of Ti_2FeX (X = Si, Ge, and Sn) inverse-Heusler alloys in the XA phase are calculated using the DFT within the generalized gradient approximation. The lattice constants and bulk

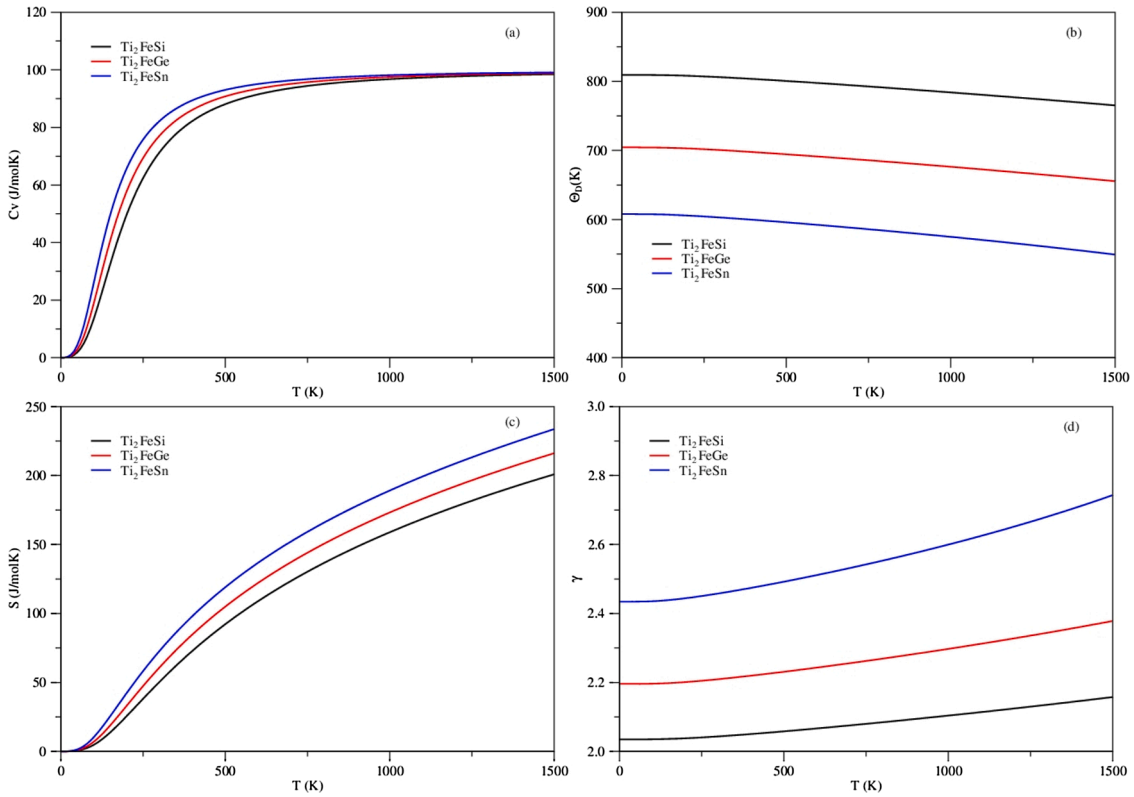

Fig. 5. a) Specific heat capacity at constant volume, b) Debye temperature, c) entropy change and d) Grüneisen parameter with temperature for Ti_2FeSi, Ti_2FeGe and Ti_2FeSn alloys in the Hg_2CuTi structure.

modulus of all the alloys are calculated and are consistent with the available experimental and theoretical data. In the calculations of the magnetic properties of the examined inverse-Heusler alloys, it was seen that all the alloys exhibited magnetic properties. The computed magnetic moment values of these alloys are compatible with the values calculated according to SP. It is seen that the total magnetic moments of Ti_2FeSi, Ti_2FeGe and Ti_2FeSn alloys are in good agreement with both theoretical data and SP values. Also, the electronic band spectra, total DOS and PDOS of these alloys are obtained. All these alloys have metallic properties in spin-up states overlapping of valence and conduction bands near the Fermi level (E_F), while these alloys have a gap and have a semiconductor property in spin-down states. Thus, it is understood that these alloys have half-metallic character. The calculated elastic constants of Ti_2FeX (X = Si, Ge, and Sn) inverse-Heusler alloys show that the alloys in the XA phase are mechanically stable. The calculated B/G ratio shows that all three alloys have a ductile nature. Both Poisson's ratio and Cauchy pressure calculated for these alloys verify their ionic character and ductile nature. The full phonon spectra, total DOS and PDOS of Ti_2FeX (X = Si, Ge, and Sn) alloys in the XA phase are calculated using the direct method. From the calculated phonon properties, it was concluded that all these alloys are dynamically stable because all phonon modes are positive.In addition to phonon properties, the thermodynamic properties of both compounds were investigated and analyzed. A rapid increase was observed up to about 250 K, and then reached a saturation level approaching the Dulong-Petit limit. Unfortunately, there were no data available in the literature for further comparison of our results. Eventually, since Ti_2FeX (X = Si, Ge, and Sn) inverse-Heusler alloys are not sufficiently examined in theoretical and experimental arguments, the results of this study will bring broader perspective for designing future theoretical and experimental studies.

Declaration of Competing Interest

The authors report no declarations of interest.

References

[1] F. Heusler, Über magnetische manganlegierungen, Verhandlungen der Deutschen Physikalischen Gesellschaft 5 (1903) 219.
[2] N. Kervan, S. Kervan, A first-principle study of half-metallic ferrimagnetism in the Ti_2CoGa Heusler compound, J. Magn. Magn. Mater. 324 (2012) 645–648.
[3] F. Lei, C. Tang, S. Wang, W. He, Half-metallic full-Heusler compound Ti_2NiAl: a first-principles study, J. Alloys Compd. 509 (2011) 5187–5189.
[4] E. Bayar, N. Kervan, S. Kervan, Half-metallic ferrimagnetism in the Ti_2CoAl Heusler compound, J. Magn. Magn. Mater. 323 (2011) 2945–2948.
[5] N. Kervan, S. Kervan, Half-metallic properties of Ti_2FeSi full-Heusler compound, J. Phys. Chem. Solids 72 (2011) 1358–1361.
[6] S. Kervan, N. Kervan, Spintronic properties of the Ti_2CoB Heusler compound by density functional theory, Solid State Commun. 151 (2011) 1162–1164.
[7] Q.L. Fang, J.M. Zhang, K.W. Xu, V. Ji, Electronic structure and magnetism of Ti_2FeSi: a first-principles study, J. Magn. Magn. Mater. 345 (2013) 171–175.
[8] X. Fan, J. Li, Y. Jin, Effects of strain on the half-metallicity and spin gapless feature of Ti_2YSi (Y= Fe, Co) alloys, Mod. Phys. Lett. B 32 (2018), 1850153.
[9] F. Ahmadian, Half-metallic ferromagnetism in the Ti_2FeGe Heusler compound: a first-principles study, J. Supercond. Nov. Magn. 26 (2013) 381–388.
[10] Y. Hu, J.M. Zhang, First-principles study on the thermodynamic stability, magnetism, and half-metallicity of full-Heusler alloy Ti_2FeGe (001) surface, Phys. Lett. A 38 (2017) 1592–1597.
[11] M. Liping, S. Yongfan, Ti_2FeZ (Z= Al, Ga, Ge) alloys: structural, electronic, and magnetic properties, J. Magn. Magn. Mater. 369 (2014) 205–210.
[12] F. Ahmadian, Half-metallicity in a new Heusler alloy Ti_2FeSn: a density functional study, J. Korean Phys. Soc. 64 (2014) 277–282.
[13] A. Birsan, P. Palade, Band structure calculations of Ti_2FeSn: a new half-metallic compound, Intermetallics 36 (2013) 86–89.
[14] G. Kresse, J. Hafner, Ab initio molecular dynamics for liquid metals, Phys. Rev. B 47 (1993) 558.
[15] G. Kresse, J. Furthmüller, Efficient iterative schemes for ab initio total-energy calculations using a plane-wave basis set, Phys. Rev. B 54 (1996) 11169.
[16] J.P. Perdew, K. Burke, M. Ernzerhof, Generalized gradient approximation made simple, Phys. Rev. Lett. 77 (1996) 3865.
[17] P.A.M. Dirac, Note on exchange phenomena in the Thomas atom, Math. Proc. Cambridge Philos. Soc. 26 (3) (1930) 376–385.
[18] E. Teller, On the stability of molecules in the Thomas-Fermi theory, Rev. Mod. Phys. 34 (4) (1962) 627.
[19] Z. Yin, Microscopic Mechanisms of Magnetism and Superconductivity Studied From First Principle Calculations, University of California, Davis, 2009.
[20] P. Neveux, A. Chambarel, Debye modelisation for the soil moisture measurement in TDR, in: IEEE Instrumentation and Measurement Technology Conference Proceedings, Sorrento, Italy, 2006, pp. 187–190, 24-27 April 2006.
[21] L.H. Thomas, The calculation of atomic fields, Math. Proc. Cambridge Philos. Soc. 23 (5) (1927) 542–548, 1927 January Cambridge University Press.
[22] E. Fermi, Statistical method to determine some properties of atoms, Rend. Accad. Naz. Lincei. 6 (602-607) (1927) 5.
[23] M.M. Rahaman, M.H. Rubel, M.A. Rashid, M.A. Alam, K.M. Hossain, M.I. Hossain, N. Kumada, Mechanical, electronic, optical, and thermodynamic properties of orthorhombic $LiCuBiO_4$ crystal: a first–principles study, J. Mater. Res. Technol. 8 (2019) 3783–3794.
[24] J.C. Slater, A simplification of the Hartree-Fock method, Phys. Rev. 81 (1951) 385–390.
[25] Y. Cao, J. Zhu, Y. Liu, Z. Lai, Z. Nong, First-principles studies of the structural, elastic, electronic and thermal properties of γ'-Ni_3Ti, Physica B 412 (2013) 45–49.
[26] J. Hafner, Theoretical Solid State Physics, Lecture Notes, University of Vienna, 2005.
[27] A.L. Fetter, J.D. Walecka, Quantum Theory of Many- Particle Systems, McGraw-Hill, New York, 1971.
[28] A. Otero-de-la-Roza, D. Abbasi-Pérez, V. Luaña, Gibbs2: a new version of the quasiharmonic model code. II. Models for solid-state thermodynamics, features and implementation, Comput. Phys. Commun. 182 (2011) 2232–2248.
[29] D. Pines, Electron interaction in metals, Solid State Phys. 1 (1955) 367–450.
[30] A. İyigör, M. Özduran, M. Ünsal, O. Örnek, N. Arıkan, Ab-initio study of the structural, electronic, elastic and vibrational properties of HfX (X= Rh, Ru and Tc), Phil. Mag. Lett. 97 (2017) 110–117.