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Investigations of structural, electronic, mechanical and lattice dynamic properties of $TiRu_3$ and $TiOs_3$ compounds

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ABSTRACT

Ab initio calculations of structural, electronic, elastic, and phonon properties of $TiRu_3$ and $TiOs_3$ compounds have been studied using the density functional theory (DFT) within the generalized gradient approximation (GGA). The basic structural properties such as lattice constants, bulk modulus and pressure derivative of bulk modulus of these compounds were studied and compared with the previous theoretical data. Electronic band structures and partial densities of states for $TiRu_3$ and $TiOs_3$ compounds were computed and analyzed. The electronic band calculations showed that the $TiRu_3$ and $TiOs_3$ compounds have metallic nature. Phonon spectra, their total and projected densities of states for these compounds were computed by using a linear-response method in the framework of the density functional perturbation theory. The specific heat capacities at a constant volume C_V and Debye temperature of $TiCr_3$ and $TiOs_3$ compounds were also calculated and discussed.

1. Introduction

Intermetallic XY_3 compounds have been received intensive scientific interest for researchers due to their high temperature, mechanical and structural applications [1–3]. The XY_3 compounds can be crystallized in the L_{12} and DO_{24} phases. The L_{12} phases of these compounds are more ductile than their D_{24} phases. Titanium-based TiX_3 (X = Ru and Os) compounds are binary intermetallic compounds with the cubic $L1_2$ phase (the Cu_3Au) and crystallize in the Pm-3 m space group. The crystal structure for $TiRu_3$ and TiO_3 in $L1_2$ phase is presented in Fig. 1. There are few studies on $TiRu_3$ and TiO_3 compounds in the literature available [4,5]. Therefore, these studies have been conducted to study the structural, structural stability, enthalpy formation and elastic properties of the $TiRu_3$ and $TiOs_3$ compounds in the $L1_2$ phase [4,5]. Xing et al. [4] computed the structural phase stability and enthalpies of formation of the binary intermetallic $TiRu_3$ and $TiOs_3$ compounds. From their calculated results, it was observed that the stable structures of $TiRu_3$ and $TiOs_3$ compounds were in the $L1_2$ or DO_{24} phases. In addition, they noted that the energy differences between the two structures $L1_2$ and DO_{24} are usually very small. The elastic constants of the $TiOs_3$ compound were calculated and their mechanical stability was evaluated [5].

The phonon properties of these compounds are necessary for understanding the microscopic dimensions of their lattice dynamics. It is important to determine the dynamic properties of the solids in the determination of various basic solid state properties such as specific heat, thermal expansion, heat conduction, phase transitions, and electron-phonon interaction. In order to complete the few previously performed studies, this work aims to examine the electronic, elastic, thermal, structural and vibration properties of TiX_3 (X = Ru and Os) compounds in $L1_2$ phase using *ab initio* calculations. The electronic band structures of these compounds are

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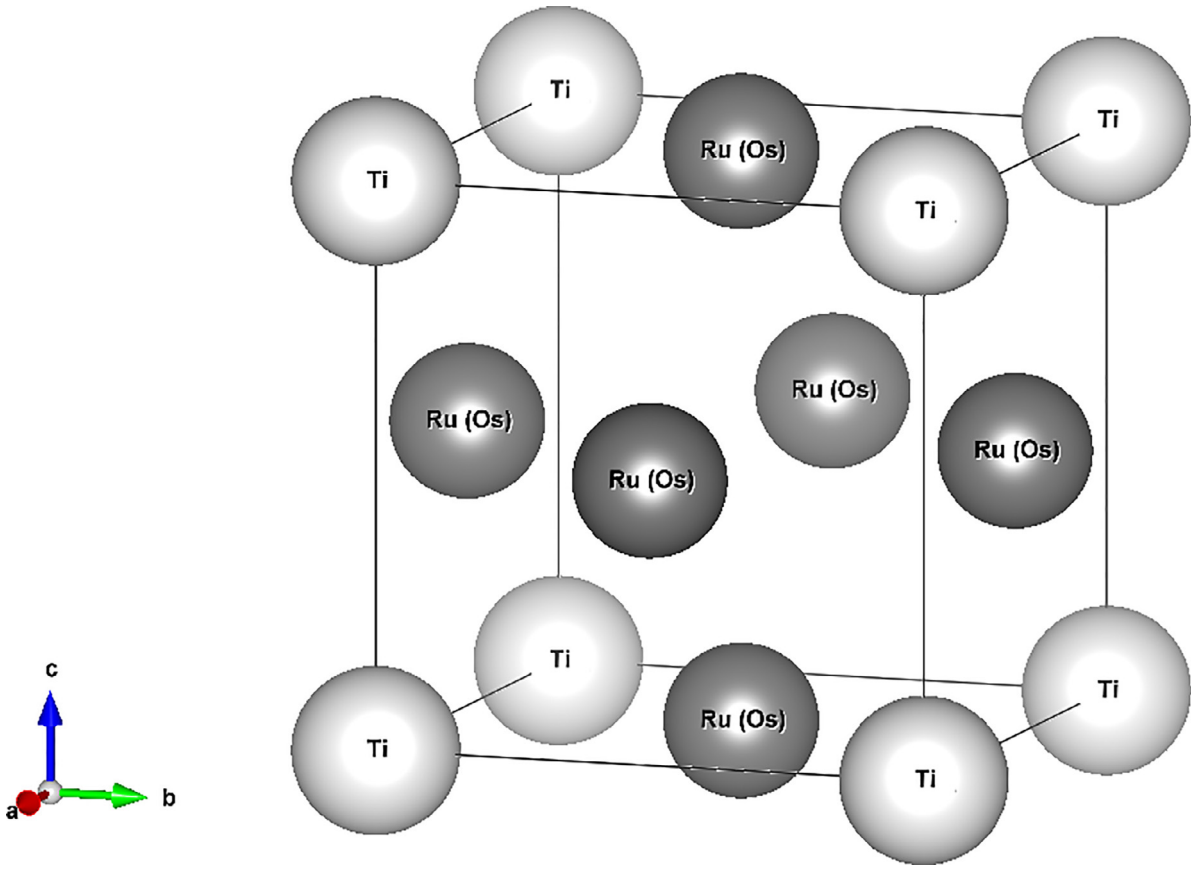

Fig. 1. The crystal structure of $TiRu_3$ and $TiOs_3$ compounds in the $L2_1$ phase.

examined by applying the plane-wave pseudopotential method in the generalized gradient approximation (GGA). These compounds are used for Density Functional Perturbation Theory (DFPT), which determine the full phonon spectra and the their density of states (DOS). The following parts of this paper are; definition of the calculation methods, electronic, mechanical and vibrational properties and a summary for the TiX_3 compounds are presented and evaluated.

2. Computational method

The TiX_3 (X = Ru and Os) compounds crystallized in the cubic Cu_3Au crystal phase containing four atoms in the unit cell. The first principle studies of the TiX_3 (X = Ru and Os) compounds were performed using a self-consistent ultrasoft pseudopotential method [6] based on density functional theory in the generalized gradient approach (GGA) included in the Quantum-Espresso code [7]. The Perdew-Burke-Ernzerhof (PBE) [8] for the change-correlation potential was used. The wave functions were expanded on the basis of a plane wave set with 40 Ry kinetic energy cut off for the $L1_2$ structure. The electronic charge density, kinetic energy cut off was evaluated up to 400 Ry. Brillouin zone integrations were performed using 10 × 10 × 10 k-point mesh. The integration up to the fermi surface was performed using the smearing technique and smearing parameter 0.02 Ry [9]. After obtaining the self-consistent solutions of Kohn Sham equations, the dynamic properties of the mesh were calculated within the framework of self-consistent density functional perturbation theory [10,11]. To obtain full phonon spectra and state of density, eight dynamic matrices were calculated on a 4 × 4 × 4 q point mesh. These dynamic matrices can be evaluated by a Fourier deconvolution on this cluster. The elastic constants were calculated as a function of volume-energy dependence.

The bulk module, B, C_{44} and shear modulus $C' = (C_{11} - C_{12})/2$ have been computed from hydrostatic pressure ($e = \delta, \delta, \delta$, 0,0,0), three-axial shear force from, respectively (e = 0,0,0, δ,δ,δ) and the volume-conserving orthorhombic strain $e = (\delta, \delta, (1 + \delta)^{-2}$–1,0,0,0), respectively [12].

Here, B is derived from the following equation;

$$\frac{\Delta E}{V} = \frac{9}{2} B\delta^2 \tag{1}$$

where V is the volume of unstrained lattice cell, and ΔE is the change in energy due to applied strain with vector. C' can be obtained as follow;

$$\frac{\Delta E}{V} = 6C'\delta^2 + O\delta^3 \tag{2}$$

from the above two values (B and C'), $C_{11} = \frac{3B+4C'}{2}$ *and* $C_{12} = (3B - 2C')/3$ are obtained and $C_{44}$is obtained using the following equation;

$$\frac{\Delta E}{V} = \frac{3}{2}C_{44}\delta^2 \tag{3}$$

The shear modulus G value for cubic structure is defined from Voigt (G_v) and Reuss (G_R) modules as follows;

$$G = \frac{G_V + G_R}{2}, \quad G_V = \frac{C_{11} - C_{12} + 3C_{44}}{5} \; and \; G_R = \frac{5C_{44}}{[4C_{44} + 3(C_{11} - C_{12})]} \tag{4}$$

Anisotropy factor (A) is obtained from the following equation;

$$A = \frac{2C_{44}}{(C_{11} - C_{12})} \tag{5}$$

The Young module is calculated as follows;

$$E = \frac{9BG}{3B + G} \tag{6}$$

Poisson's ratio is given by the following equation;

$$\sigma = \frac{3B - 2G}{2(3B + G)} \tag{7}$$

Debye temperatures and specific heat capacities were computed at different temperatures from vibrational frequencies obtained from the quasi harmonic approximation (QHA) [13]. Helmholtz free energy is given by the following equation;

$$U = nk_bT\left[\frac{9}{8}\frac{\theta_D}{T} + 3ln\left(1 - e^{-\frac{\theta_D}{T}}\right) - D\left(\frac{\theta_D}{T}\right)\right] \tag{8}$$

$D(\frac{\theta_D}{T})$ is the Debye function and is given by the following equation;

$$\left(\frac{\theta_D}{T}\right) = 3\left(\frac{T}{\theta_D}\right)\int_0^{\theta_D/T}\frac{z^2dz}{e^z - 1} \tag{9}$$

3. Results

Both studied $TiRu_3$ and $TiOs_3$ compounds have a cubic crystal phase of Au_3Cu type belonging to the space group Pm-3 m. The crystal structures of $TiRu_3$ and $TiOs_3$ compounds, shown in Fig. 1, are positioned in a molecule of four atoms in the unit cell, Ti atoma are located at 1*a* (0, 0, 0) and X atoms are positioned at 3c (0, 1/2, 1/2). Thus, the structural information of these compounds are defined completely without the need for any experimental data by determining the equilibrium lattice constants *a*. The computed values for the equilibrium lattice constants (a), bulk modulus (B) and the it's pressure derivative (B') are presented in Table 1, together with the earlier available results. The lattice constants for $TiRu_3$ and $TiOs_3$ compounds are in good agreement with the previous data. The bulk modulus for both compounds is in line with the existing theoretical values [5]. However, no experimental results exist for both lattice constant and bulk modulus values. The computed elastic constants help us to investigate the mechanical stability status of the crystal systems. A cubic system must be adhered to the principle of Born stability [14] so as to be mechanically stable: $C_{11} > C_{12}$, $C_{44} > 0$, and $C_{11} + 2C_{12} > 0$. For the two studied compounds in Table 1, the obtained values of these elastic constants confirm the Born stability criteria. As it is clear from Table 1 that $TiRu_3$ and $TiOs_3$ compounds have stable nature in $L1_2$ phase. Other various elastic parameters obtained from second order elastic constants, such as Young's modulus E, shear modulus G, anisotropic factor A, Poisson's ratio σ, B/G and Cauchy's pressure ($C_P = C_{12} - C_{44}$), are shown in Table 2 along with existing values. For $TiOs_3$, the computed values of these elastic parameters are quite consistent with the values in the previous VASP calculations [5].

Table 1
The calculated lattice constants (a, in Å), bulk modulus (B, in GPa), its pressure derivative of bulk modulus (B'), Cauchy pressures C_P and elastic constants (C_{ij}, in GPa) for $TiRu_3$ and $TiOs_3$ compounds in the $L2_1$ phase.

Materials	Ref.	a	B	B'	C_{11}	C_{12}	C_{44}	$C_P = (C_{12} - C_{44})$
$TiRu_3$	This study	3.870	326.005	4.25	536.83	220.59	175.93	44.66
	VASP [5]	3.852	231.33					
	VASP [4]	3.852						
$TiOs_3$	This study	3.915	309.989	4.21	421.96	254	162.246	91.754
	VASP [5]	3.888	308		442	241	158	83
	VASP [4]	3.879						

Table 2
Computed bulk modulus (B, in GPa), shear modulus (G, in GPa), B/G, Young's modulus (E, in GPa), Poisson's ratio σ, anisotropy factor A for $TiRu_3$ and $TiOs_3$ compounds in the $L2_1$ phase.

Materials	*Ref.*	*B*	*G*	G_V	G_R	*B/G*	*E*	*σ*	*A*
$TiRu_3$	This study	326	168.58	168.81	168.34	1.93	431.37	0.28	1.11
$TiOs_3$	This study	309.96	124.55	130.94	118.19	2.49	329.56	0.32	1.93

On the other hand, there are no experimental or theoretical values for the elastic constants of $TiRu_3$.

As it is known, there are three main ways to determine the ductility and brittleness of the materials [15,16]; the shear modulus ratio (B/G) of the bulk modulus, the Poisson's ratio σ and the Cauchy's pressure Cp. If the values of $B/G > 1.75$, $\sigma > 0.26$, and the positive C_P value, the materials behave in a ductile manner. As can be seen in Table 2, B/G values and Poisson's σ are greater than 1.75 and 0.26 respectively, while the value of Cp is positive. therefore, both studied compounds exhibit ductile behavior. As can be seen from these results, the results of B/G, Poisson's ratio σ and Cauchy's pressure Cp support each other. The Poisson's ratio σ and Cauchy pressure Cp can be used to determine the atomic band characters in the alloy and compounds. In the literature, Poisson's ratio σ is 0.25 for ionic materials and 0.1 for covalent materials. On the other hand, if the Cauchy pressure Cp value is positive, the type of bonding is metallic ionic character. Poisson ratios σ for $TiRu_3$ and TiO_3 are found to be 0.28 and 0.32, respectively, indicating that both compounds have ionic-metal interactions. These computed results are well consistent with the Cauchy pressures of the above compounds.

Young modulus (E) of the materials defines the ratio of tensile stress to tensile strain in determining the hardness of a material [17]. The Young modulus (E) values obtained from the calculations for $TiRu_3$ and TiO_3 are calculated as 431.37 and 329.55 GPa, respectively. As the Young modulus (E) decreases, the material becomes less stiff. As can be seen from Table 2, $TiRu_3$ has higher Young modulus between the two compounds, so $TiRu_3$ is stiffer than $TiOs_3$ compound. Anisotropy factor A is an indication of elasticity of the crystals. The material with Anisotropy factor value 1 is completely isotropic. As can be clearly seen from Table 2, the calculated anisotropy factors of both compounds are close to 1.

The electronic band structures of $TiRu_3$ and TiO_3 in the $L2_1$ structure are calculated and presented in Fig. 2. In the electronic band

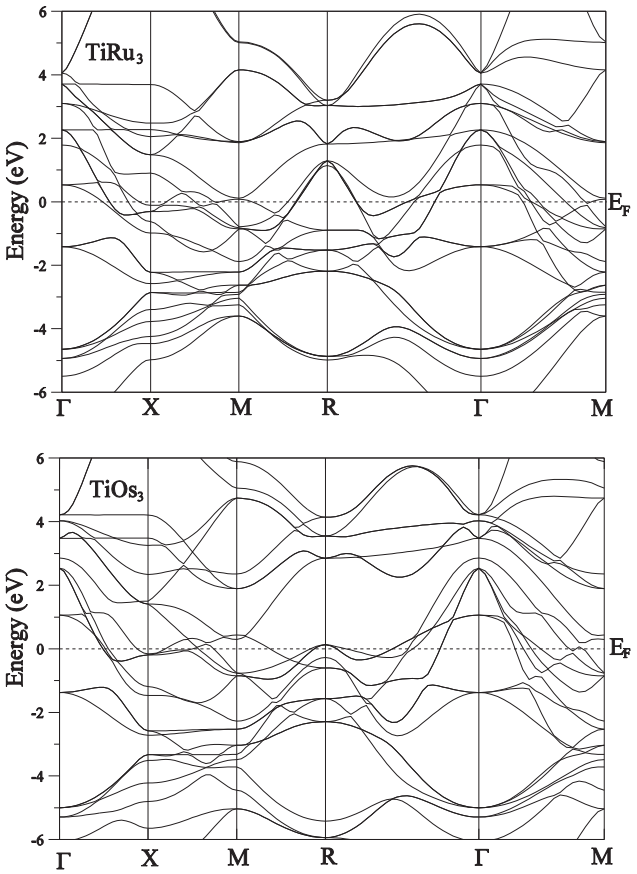

Fig. 2. The electronic band structure of along several selected high-symmetry directions for $TiRu_3$ and $TiOs_3$ in the $L2_1$ phase.

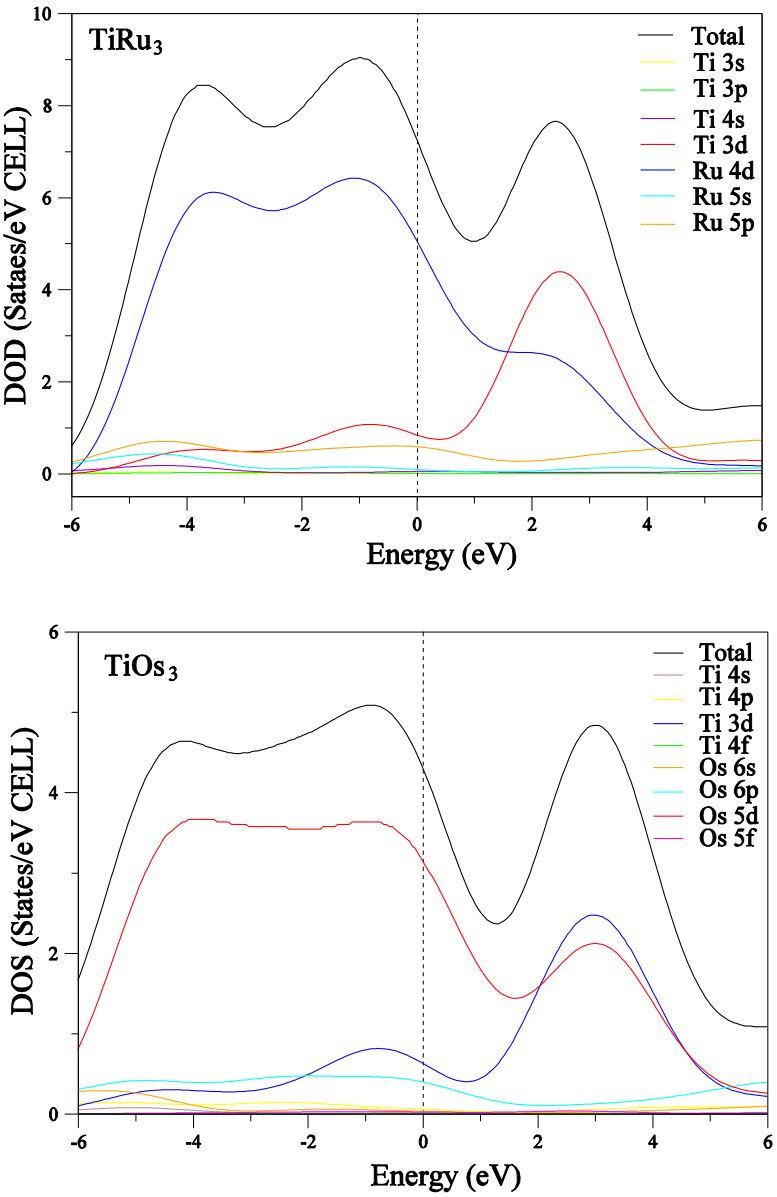

Fig. 3. The calculated total and partial density of states for $TiRu_3$ and $TiOs_3$ compounds in the $L2_1$ phase.

structure of a material, the overlapping of the Fermi level of any band reveals the metallic character [18]. Thus, both compounds appear to exhibit a metallic behavior due to the overlap of the bands at the Fermi level. So as to examine the nature of the electronic bands of TiX_3 compounds, their total and partial state density (DOS) is shown in Fig. 3. A critical evaluation of partial DOS showed that both compounds present a peak of around 3 eV, are from the d bands of Ti and Ru for $TiRu_3$ and the d bands of Ti and Os for TiO_3. For the $TiRu_3$ and TiO_3 compounds, the Fermi level $N(E_F)$ values are 7.15 and 4.22 states/eV, respectively. The contributions of Ru-4d states and Os-5d states to N (E_F) for compounds $TiRu_3$ and TiO_3 are about 70%. The dispersive bands below the Fermi level of $TiRu_3$ and TiO_3 compounds are mainly contributed to the Ru-d state and Os-d status, respectively.

The computed phonon spectra, total and projected density of the Cubic $TiRu_3$ and $TiOs_3$ compounds along with the high symmetry directions in the Brillouin zone are illustrated in Fig. 4. The phonon spectrum can be evaluated via the phonon density of states. Total and projected densities of states for these compounds are given in the right panel of Fig. 4. There is no gap between the phonon spectra of $TiRu_3$ and the density of states. Thus, the heavier Ru atoms vibrate at low frequency regions below 5.56 THz, while the vibrations of the lighter Ti atoms are above this frequency. In contrast to $TiRu_3$, the full phonon spectrum of TiO_3 can be divided into two distinct regions: a wide region up to 5.74 THz and a narrow zone between 7.12 and 8.53 THz. The 2.1 THz gap between the two regions is formed by the large mass difference between the Ti and Os atoms. While the projected density of states of $TiOs_3$ shows the dominance of heavier Os atoms in the large region below 5 THz, the narrower upper frequency region is greatly contributed to the

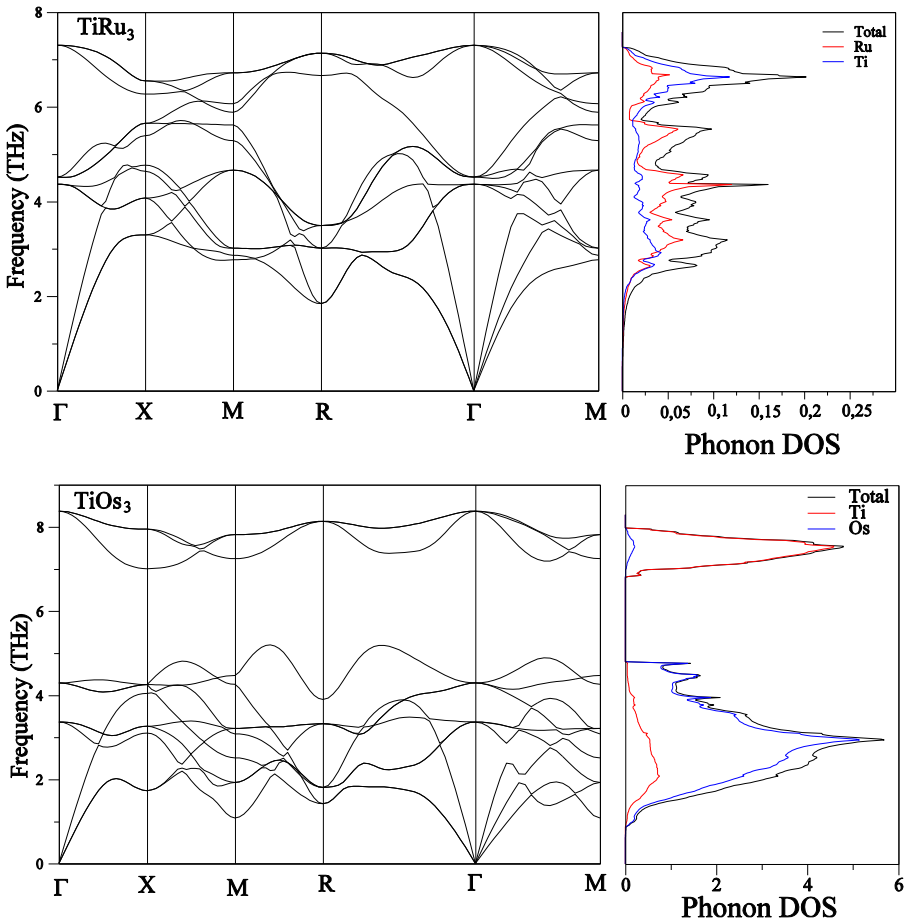

Fig. 4. The full phonon dispersion curves, total and projected density of states for $TiRu_3$ and $TiOs_3$ compounds in the $L2_1$ phase.

vibrations of lighter Ti atoms. The zone centre optical phonon branches of $TiRu_3$ (TiO_3) have been computed as 4.31 THz (3.42), 4.52 THz (4.31) and 7.3 THz (8.4), respectively. The $TiRu_3$ and TiO_3 compounds are dynamically stable because the phonon dispersion curves for both compounds do not have any imaginary phonon modes. There is no experimental and theoretical study in the available literature concerning the phonon properties of TRu_3 and TiO_3 compounds.

The change in specific heat capacity at constant volume (C_v) with temperature of $TiRu_3$ and $TiOs_3$ compounds are identified within the quasi harmonic approximation (QHA) based on the computed phonon spectra. The computed specific heat capacities of $TiRu_3$ and $TiOs_3$ compounds are presented in the Fig. 5. It is obvious from Fig. 5 that C_V increases rapidly in the range 0–150 K before starting saturation. The computed specific heat capacity C_V is very close to the classical asymptotic Dulong-Petit limit [19] in the region of high temperatures, that is in line with all compounds at high temperatures. The optical and acoustic modes on the heat capacity have a great contribution.

The Debye temperature θ_D as a function of time is presented in Fig. 6. The vibration frequency is proportional to the square root of the hardness in the harmonic approach; the hardness of the solids can also be estimated from the Debye temperature and called Debye stiffness. The maximum phonon frequency of the frequency spectrum is proportional to square root of the stiffness within the harmonic approximation. Both θ_D and the maximum phonon frequency can be used as estimated of the Debye stiffness of solids. Thus, it can be seen from Fig. 6 that the Debye stiffness of $TiRu_3$ is greater than the $TiOs_3$.

4. Conclusions

In this study, first principle computation was performed to examine the structural, elastic, electronic and lattice-dynamic features of the intermetallic $TiRu_3$ and TiO_3 compounds in the $L1_2$ phase. The values obtained for the lattice constants and bulk modulus is in line with the existing theoretical data. Mechanical properties of these compounds were also investigated. As a result of the evaluations of the calculated elastic constants, these compounds found to be mechanically stable. The obtained bulk modulus, Young's modulus and the Anisotropy parameters indicate that the $TiRu_3$ compound is stiffer than the $TiOs_3$ compound. The considered compounds show ductile nature based on Pugh's rule [20]. These compounds have a metallic-ionic bonding character according to Poisson's ratio and Cauchy's pressure values. According to the analysis of elastic anisotropy indexes, these compounds have an elastic

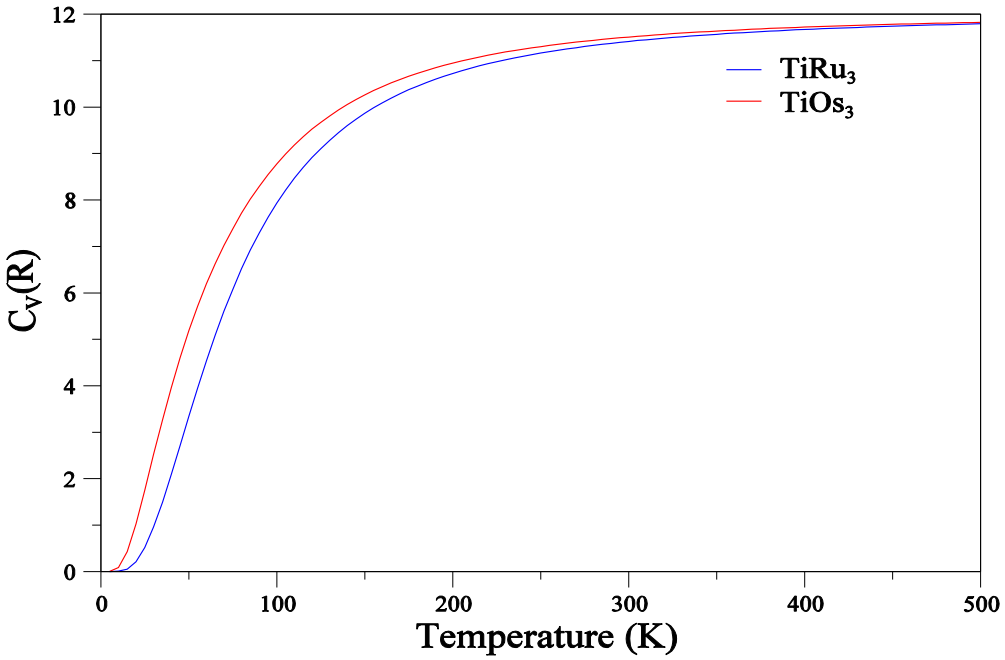

Fig. 5. The variation of specific heat at constant volume at various absolute temperatures for $TiRu_3$ and $TiOs_3$ compounds in the $L2_1$ phase.

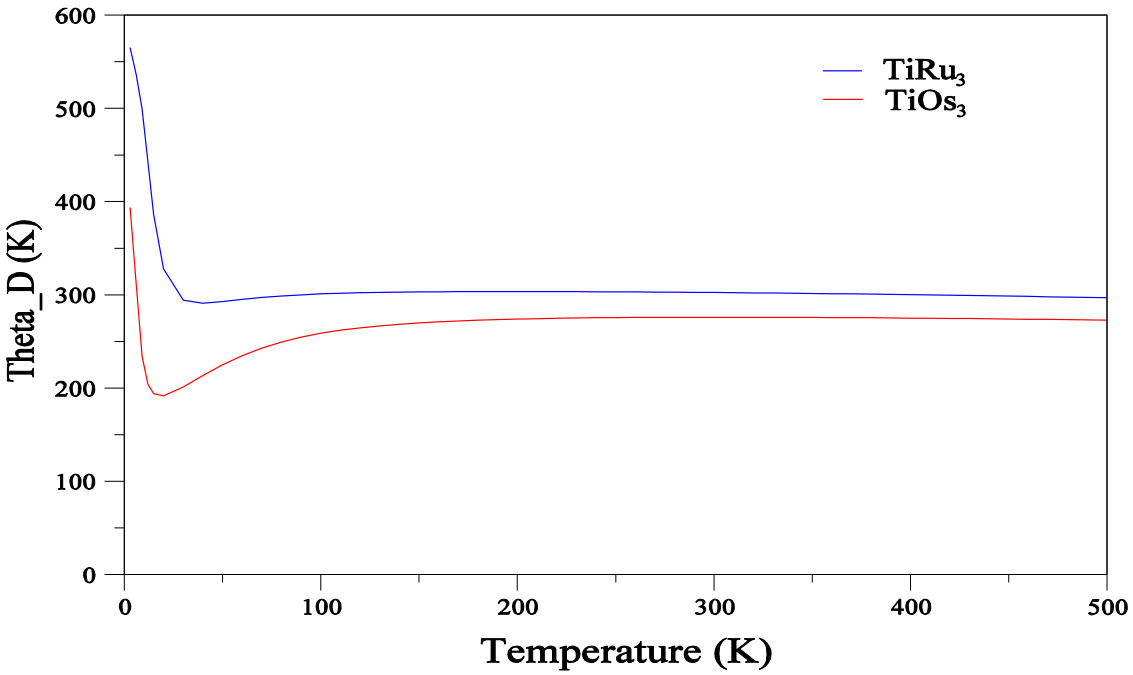

Fig. 6. Debye temperature variation with temperature of $TiRu_3$ and $TiOs_3$ compounds in the $L2_1$ phase.

anisotropy. The electronic structure and their corresponding total and projected density of states DOS of these compounds are calculated and evaluated. They verify the metallic character of the $TiRu_3$ and $TiOs_3$ compounds in the $L1_2$ phase. The phonon frequencies and their density of states for $TiRu_3$ and $TiOs_3$ compounds in the $L1_2$ phase have been calculated by means of the functional perturbation theory. Various thermodynamic properties, such as specific heat capacities and Debye temperatures for these compounds, have been calculated within the quasi harmonic approach.

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