Computational investigations of mechanical and dynamical properties of gold-based compounds (X_3Au, X = Ti, Zr and V)

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A B S T R A C T

The structural, elastic, electronic and phonon properties of X_3Au (X = Ti, Zr and V) compounds in the A15 structure were obtained in the framework of the density functional theory (DFT) within the generalized gradient approximation (GGA). The equilibrium lattice constants, bulk modulus and elastic constants were calculated. The calculation of elastic constants revealed that V_3Au has the highest hardness nature and incompressibility along the x-axis among them. The computed elastic constants also provided information about the ductility of X_3Au compounds which were predicted using Pugh's criteria. The results indicated that all three compounds have ductile nature. The density of states calculations revealed that electrons of Ti, Zr and V provide most contribution to the conductivity of the compounds and thus cause a metallic bonding. The investigation of stability via phonon spectra of compounds showed that these compounds are dynamically stable in the A15 structure.

1. Introduction

Intermetallic compounds with the A15 type structure (space group Pm − 3n) and A_3B (A is a transition metal and B can be any element) composition mostly exhibit excellent properties such as high superconducting transition temperatures, melting points and critical field [1,2]. Therefore, there are ongoing investigations and renewed interest on those materials, especially with those having high superconducting transition temperatures. A number of experimental and theoretical studies have been carried out in order to understand structural, elastic, electronic, phase stability and thermodynamic properties for X_3Au (X = Ti, Zr and V) in the A15 structure [1,3–27]. The structural, elastic and electronic properties of Ti_3Au have been investigated theoretically using density functional theory [1,5]. Shinohara et al. [3] have measured the effect of heat treatment temperature on the precipitation behaviour of A15 Ti_3Au using by tensile tests, X-ray diffraction measurement (XRD) and scanning electron microscopy (SEM) observation. The diffusion parameters and activation energies were obtained for Ti_3B (B = Au, Pt, Ir) [6]. Zr_3Au has been studied very earliest in terms of its structural, thermodynamic and formation enthalpy using XRD [12–16]. Unfortunately, the physical properties of this compound studied less in literature. Recently, the electronic, structural and thermodynamic properties of vanadium intermetallic compounds V_3B (B = Au, Pt, Ir) have been explored using first principle calculations by Wang et al. [21]. The effect of crystallographic structure on superconducting transition temperature was investigated by Blaugher et al. [22] for a number of intermetallic compounds. The tracer diffusion coefficients of vanadium, gallium and silicon for V_3Ga [23] and V_3Si [24] were determined using the tracer and diffusion coupling methods. V_3Au demonstrated increasing transition temperature (from 0.980 K to 1.7850 K) after annealing at high
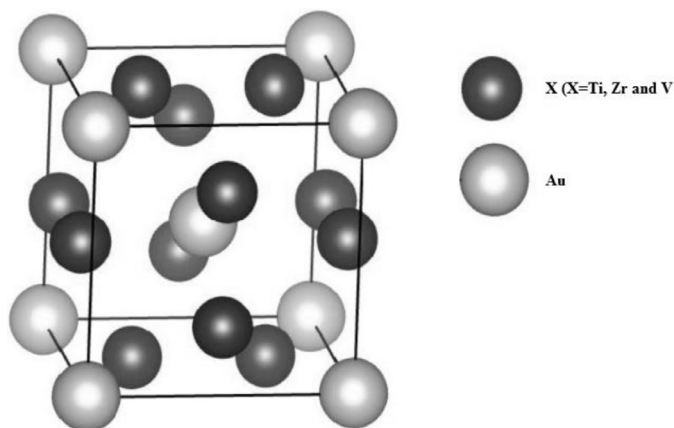
Fig. 1. Crystal structure of X_3Au compounds in the A15 struture.

Table 1
Calculated lattice constant a, bulk modulus B (GPa), elastic constants C_{ij} (GPa) and shear modulus G (GPa), B/G for X_3Au (X = Ti, Zr and V) compounds, compared with the available experimental and theoretical data.

Materials		a	B	C_{11}	C_{12}	C_{44}	G	B/G
Ti_3Au	This work	5.104	135.086	245.086	80.086	58.984	67.483	2.002
	TB-LMTO [1]	5.0875	137					
	FP-LAPW [5]	5.112	140.162	287.776	71.461	70.311	83.502	1.678
	Exp. [10]	5.098						
	Exp. [20]	5.0960						
	Theory [11]	5.1						
	Theory [17]	5.098						
	Exp. [18]	5.0974						
	Exp. [19]	5.0974						
Zr_3Au	This work	5.518	116.758	213.591	68.342	37.417	48.959	2.385
	Exp. [14]	5.483						
	Theory [17]	5.486						
V_3Au	This work	4.867	193.113	359.695	53.473	111.022	75.541	2.567
	Exp. [9]	4.874						
	Exp. [14]	4.883						
	Theory [17]	4.884						
	Exp. [18]	4.8813						
	Exp. [19]	4.881						
	Exp. [25]	4.882						
	Exp. [20]	4.87						
	CASTEP-GGA[21]	4.887	189.7	339.6	45.0	114.8	65.6	2.894
	CASTEP-LDA [21]	4.784	225.6	387.6	48.0	144.6	70.3	3.208

temperature in their results. The transition temperature of V_3Au from electronic structure results was obtained by Jarlborg et al. [26]. The impact of high pressure on transition temperature for V_3Au was explored by Smith [27]. Even tough, several structural and thermodynamic data exist in literature for V_3Au and Ti_3Au compounds, there is less study about elastic properties and electronic band structure of Zr_3Au and all compounds` phonon properties which are crucial in order to understand lattice dynamics in microscopic scale. This kind of knowledge can provide information about phase transition, thermodynamic stability, defect transport and thermal properties. Thus, this study considers whole investigations about the following three A15 type compounds, namely; Ti_3Au, Zr_3Au and V_3Au in terms of structural, elastic properties, electronic and phonon using first principles calculations. Our first principles calculations also provide information about chemical bonding, ductile and electronic density of states of the compounds that allow us to compare the data with the existing as well as adding new data to the literature.

2. Method of computation

The calculations were carried out by using MedeA-VASP package [28,29] using projected augmented wave method [30]. This is placed on first principles calculations within the plane-wave pseudopotential density functional theory (DFT) method. The exchange-correlation energy was calculated by using the generalized gradient approximation of Perdew–Burke–Ernzerhof (PBE) [31]. A cut off energy of 500 eV was used in all calculations of structural, elastic and phonon properties. A 10^{-9} eV energy convergence criteria was used within Normal (blocked Davidson) and reciprocal space projection operators. An $8 \times 8 \times 8$k-point mesh for all X_3Au (A = V, Ti and Zr) compounds following the convention of Monkhorst and Pack [32] was conducted for the best convergence and relaxation
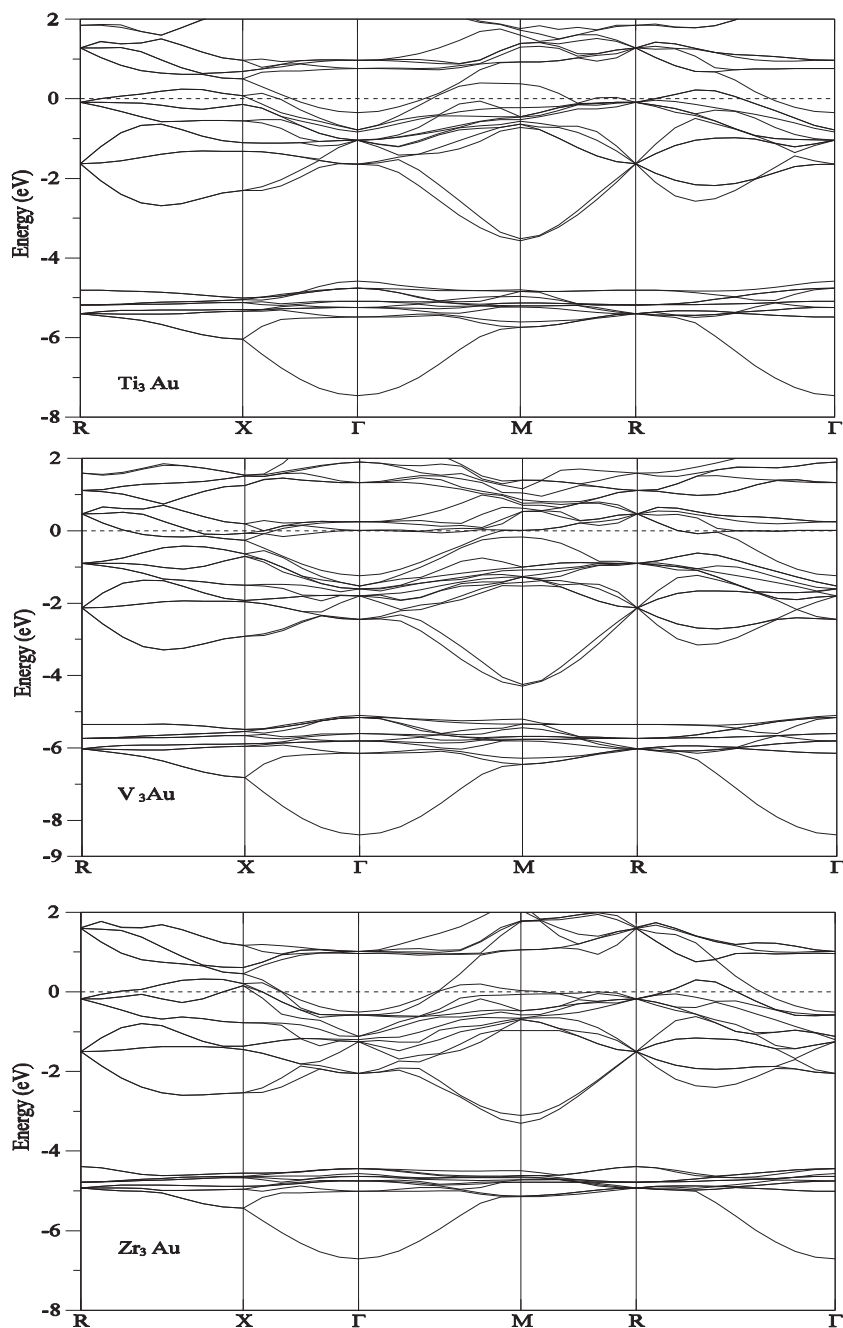
Fig. 2. The electronic band structure of X_3Au (X = Ti, Zr and V) in the A15 structure.

zero strain. The Methfessel-Paxton type was used to smear Fermi level [33] with a width of 0.225 eV. The elastic constants were calculated using stress-strain approach [34], whereas the stress due to an applied strain was directly computed. The phonon spectra were obtained using the MedeA-Phonon together with MedeA-Vasp by the direct method. The simulation cell consisted of 54 atoms with periodic boundary conditions $3 \times 3 \times 3$ supercells.

3. Result

The study of gold-based compounds X_3Au (X = Ti, Zr and V) is an important step to understand the physical properties of intermetallic compounds containing rare earth elements. It was said that X_3Au (X = Ti, Zr and V) compounds are stable in A15 structure [14]. Those are in the space group Pm-3n, with Au and X atoms located at Wyckoff position 2a (0, 0, 0) and 6c (1/4, 0, 1/2), respectively (see Fig. 1). For all the investigated compounds in this study, the calculated equilibrium lattice constants and the bulk
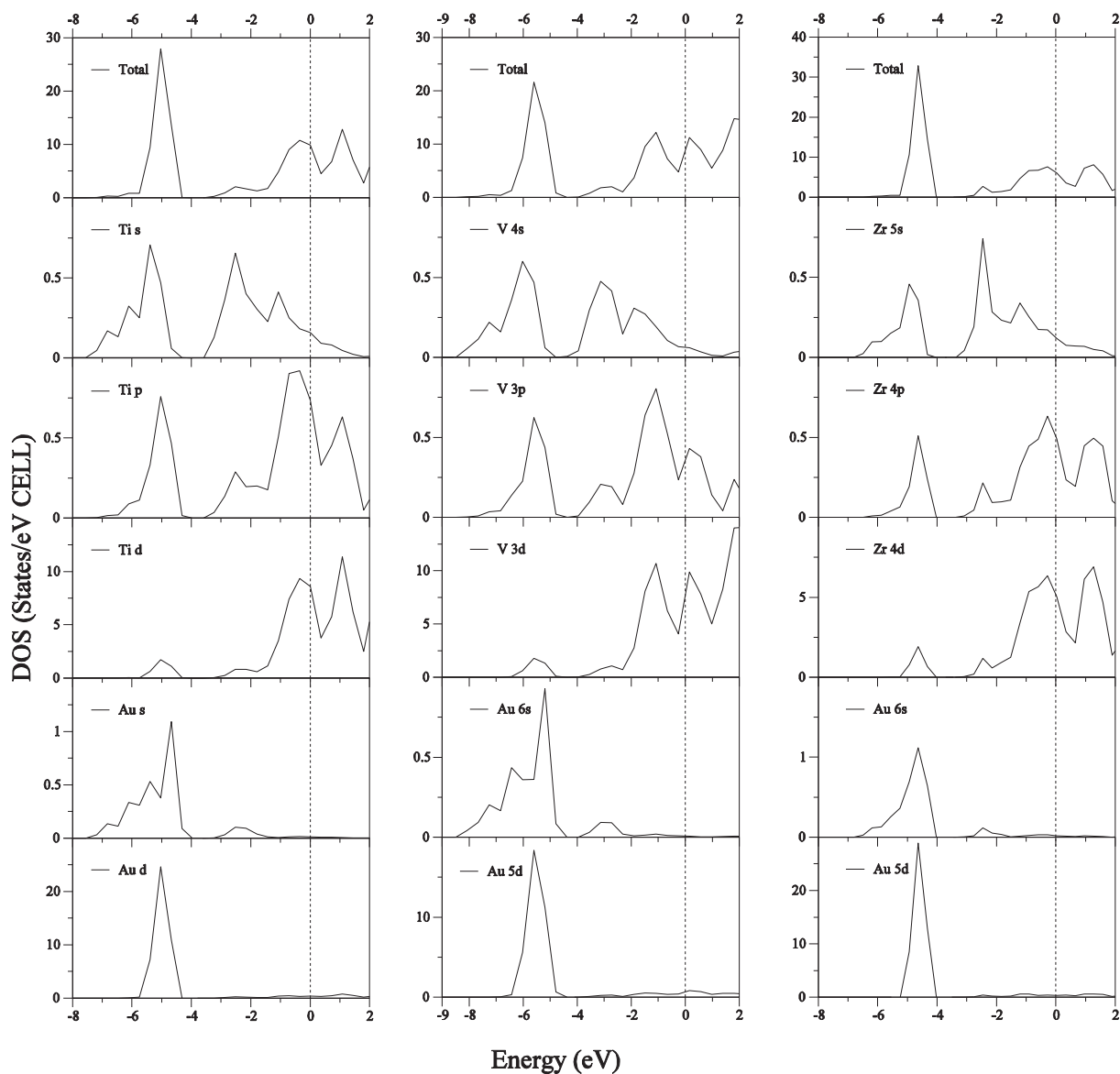
Fig. 3. The total and partial density of states for X₃Au (X = Ti, Zr and V) in the A15 structure.

modulus are presented in Table 1 together with the available experimental and theoretical data. The computed values of the lattice constants for Ti₃Au, Zr₃Au and V₃Au are fairly in a good agreement with the given data in Table 1, the deviations are only about 0.1%, 0.6% and 0.3%, respectively. Our computed values of bulk modules for Ti₃Au and V₃Au are 135.13 GPa and 193.113 GPa, respectively. The obtained bulk module for Ti₃Au is less than the values that were calculated by Sathyakumari et al. [1] and Rajagopalan et al. [5]. The reason for this might be the difference in lattice constants. If the lattice constant is higher as in ours, the bulk module tends to be smaller. On the other hand, our computed bulk module of V₃Au is higher than the one that was obtained by Wang et al. [21]. This is also due to the difference in lattice constants. Unfortunately, there is no reported data for bulk module of Zr₃Au in literature for comparison. This is reported in this work for the first time to best of our knowledge. The overall bulk modules of Ti₃Au and V₃Au are in a good agreement with the previous values [1,5,21].

Elastic constants describe the mechanical resistance of crystal materials against external applied stress. It is enough to define elastic properties for a cubic crystal with three independent elastic constants; namely C_{11}, C_{12} and C_{44}. The computed values of three elastic constants for these materials are presented in Table 1, along with the theoretical results for comparison. Our computed values of the elastic constants of all compounds satisfy Born's [35] stability conditions for cubic crystals.

$$C_{11} + 2C_{12} > 0: C_{11} - C_{12} > 0; C_{44} > 0 \tag{1}$$

The calculated elastic constants for Ti₃Au and V₃Au are in a good accordance with the theoretical results [5,21]. As it is clear from
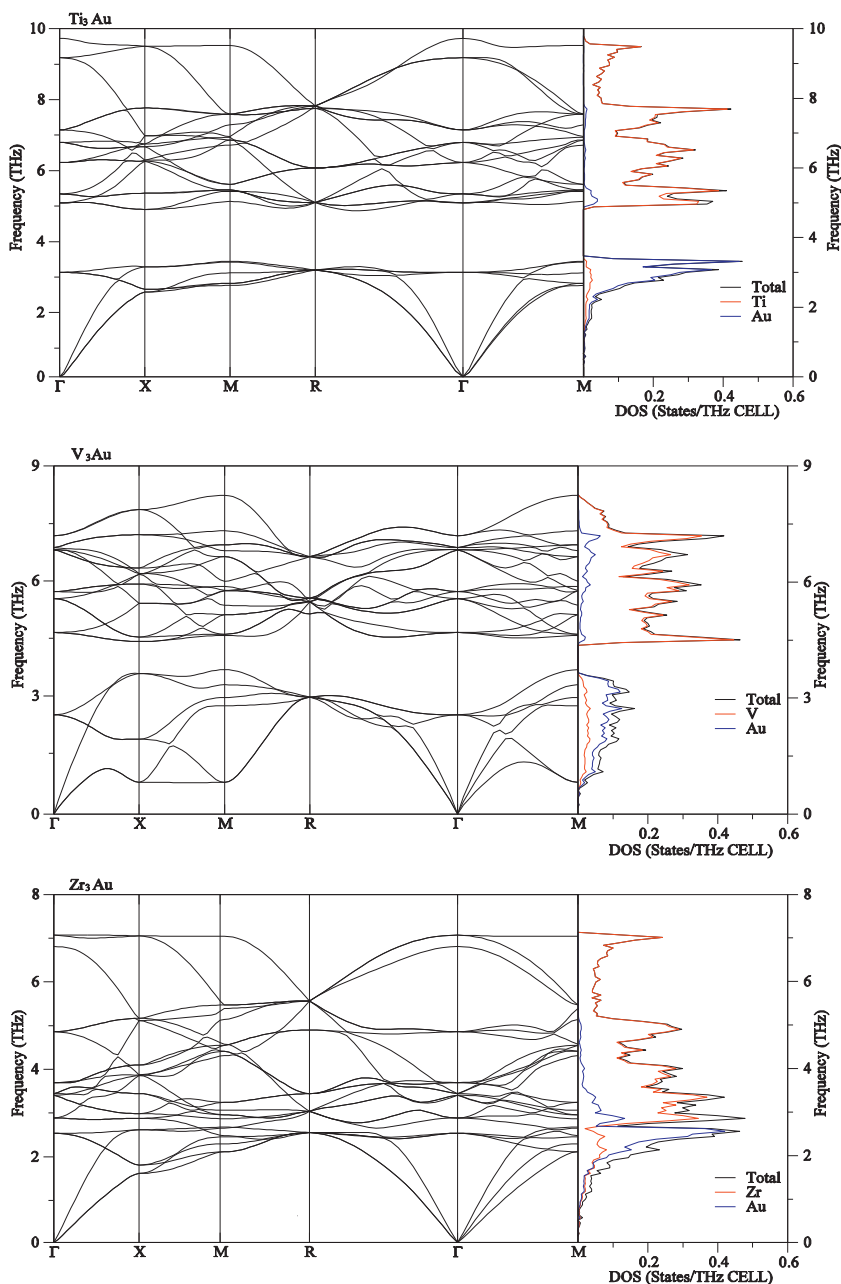
Fig. 4. The phonon dispersion curves, total and projected density of states for X$_3$Au (X = Ti, Zr and V) in the A15 structure.

Table 1 that the value of C_{11} is higher among the calculated elastic constants for all three compounds. The importance of the value of C_{11} is that it provides an insight about compressibility along the x-axis. Higher value of C_{11} indicates that X$_3$Au compounds are incompressible under applied stress along the x-axis. V$_3$Au seems to be least compressive material due to having the highest C_{11} value among the three compounds. In addition, the hardness of the material can be determined by evaluating C_{44} value. The higher value of C_{44} shows the ability to resist monoclinic shear in the (001) plane and so thus the highest hardness. Hence, V$_3$Au exhibits the highest hardness among these compounds. The hardness of a material can also be determined by evaluating bulk modules indirectly. From Table 1, it is clearly seen that the bulk modulus of V$_3$Au is the highest among them. This suggests the highest hardness of this material.

On the other hand, the B/G ratio provides quantitative information about the brittle or ductile nature of the compounds, as proposed by Pugh [36]. If the B/G ratio is greater than 1.75, the compound has a ductile nature. At the opposite case, the compound is brittle. Our calculated B/G values for Ti$_3$Au, Zr$_3$Au and V$_3$Au are 2.002, 2.385 and 2.567, respectively. It is clear that all three compounds exhibit a ductile property which contradicts the result reported by Rajagopalan et al. [5].

The density of states and electronic band structures give information about bonding characteristics of compounds and their mechanical stability. Electrons with energies at the Fermi level play an important role in chemical bonding. The electronic band structures for X_3Au (X = Ti, Zr and V) are presented in Fig. 2, in which $E_F = 0$. These materials show metallic behaviour since there is no energy gap at the Fermi level in Fig. 2. The calculated band structures of Ti_3Au and V_3Au are in well accordance with previously reported data [1,5,26]. Again, there is no existing data for Zr_3Au for comparison. The electronic structure of Zr_3Au is firstly reported in this study. It is seen that the electronic band structures of all three compounds are similar to each other. The total and projected density of states (DOS) to understand the band characteristics of all three compounds are presented in Fig. 3. The main contributions to the density of states at the Fermi level for Ti_3Au, Zr_3Au and V_3Au are Ti d state, Z d states and V d sates, respectively. These results indicate that electrons of Ti, Zr and V provide most contribution to the conductivity of the compounds and thus cause a metallic bonding. The partial density of states for Ti and Au exhibited in Fig. 3 that s- and p- electrons of Ti are dominant in the region of $E < E_F$ which suggests that the bonding of Ti_3Au is determined by s- and p- electrons of Ti. Similar effects are seen in partial density of states for Zr_3Au and V_3Au with participation of d- electrons. The results also display a sharp peak below $-4\,eV$ for all three compounds which are caused by Au d states.

The stabilities of compounds are associated with low value of density of state (DOS) at the Fermi energy E_F [37]. A lower value of $N(E_F)$ is an indication of a higher stable phase. For all three compounds in A15 structure, the total state density at the Fermi level $N(E_F)$ was calculated. This calculated values of this parameter are 9.8, 9.1 and 7.2 states/cell.eV for Ti_3Au, Zr_3Au and V_3Au, respectively. According to these $N(E_F)$ values, Zr_3Au has better structural stability than the other two compounds. As can be seen from Fig. 3 that Ti d, Zr d and V d states in X_3Au (X = Ti, Zr and V) shift to higher energies in the following sequence from Zr_3Au, to V_3Au and to Ti_3Au.

The per primitive cubic unit cell of a A15 structure contains eight atoms, corresponding to twenty four phonon modes in the dispersion relations, with three of them being the acoustic mode. The calculated full phonon spectra and their projected density of states for X_3Au compounds are displayed in Fig. 4. These compounds are dynamically stable since the phonon frequencies ω in all directions of the X_3Au compounds are not imagers. For Ti_3Au and V_3Au, the acoustic and the lower optical modes overlap and the other upper optical modes are separated from the rest of the phonon modes. These gaps of Ti_3Au and V_3Au compounds are calculated as 1.5 THz and 2.1 THz, respectively. For Ti_3Au and V_3Au, the phonon frequencies above the band gap are completely composed of the vibrations of the Ti and V atoms, as the atomic mass of Au is heavier than the atomic mass of them. For Zr_3Au, the upper optical region entirely consists of the vibrations of Zr atoms, while and the acoustic and the lower optical region is due to the vibrations of Au atoms. Unfortunately, theoretical or experimental phonon spectrums of X_3Au (X = Ti, Zr and V) compounds are not available in literature for further comparison. Our phonon calculations of these compounds are in a good agreement with our earlier work [38,39] which belongs to the some space groups.

4. Conclusions

In this study, the structural, elastic, electronic and phonon properties of X_3Au (X = Ti, Zr and V) compounds in the A15 structure were investigated in the framework of the density functional theory (DFT) within the generalized gradient approximation (GGA). The structural properties such as the lattice constants and bulk modules were computed and are well in compliance with available experimental and theoretical values. The analysis of the computed elastic constants demonstrated that all three compounds are mechanically stable. According to Pugh's criteria of ductile or brittle, the studied materials have a ductile nature. The computed electronic band structure and their total and partial density of states are in a good agreement with existing data. Band structures and state densities confirmed the metallic character of X_3Au compounds in A15 structure. Phonon-dispersion curves and their corresponding projected density of states of X_3Au (X = Ti, Zr and V) compounds in structure A15 were obtained using MedeA-Phonon in conjunction with MedeA-Vasp by the direct method.

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