



STUDY OF STRUCTURAL, ELASTIC, MECHANICAL AND THERMAL BEHAVIOR OF LuPt_3 COMPOUND: A FP-LAPW STUDY

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ABSTRACT

The structural, electronic, elastic, mechanical and thermal properties of isostructural and isoelectronic nonmagnetic LuPt_3 compound, which crystallize in AuCu_3 -type structure, are studied using first principles density functional theory based on full potential linearized augmented plane wave (FP-LAPW) method. The calculations are carried out within PBE-GGA, WC-GGA and PBE-sol GGA for the exchange correlation potential. Our calculated ground state properties such as lattice constant (a_0), bulk modulus (B) and its pressure derivative (B') are in good agreement with the available experimental and other theoretical results. We first time predict the elastic constants for this compound using GGA approximations. This compound is found to be ductile in nature in accordance with Pugh's criteria. The computed electronic band structures show metallic character of LuPt_3 compound. The charge density plot and density of states (DOS) reveals that the chemical bond between Lu and Pt is mainly ionic. The elastic properties including Poisson's ratio (σ), Young's modulus (E), shear modulus (G_H) and anisotropy factor (A) are also determined using the Voigt-Reuss-Hill (VRH) averaging scheme. The average sound velocities (v_m), density (ρ) and Debye temperature (θ_D) of LuPt_3 compound are also estimated from the elastic constants for the first time.

Keywords: Density functional theory, Density of states, Charge density plot, Elastic constants, Electronic band structure

I. INTRODUCTION

In recent decades the intermetallic compounds with the formula AB_3 are currently under intense investigations due to their structural and physical properties. These compounds have interesting mechanical properties. They are used for ultra high temperature applications and generally they have high melting points and good corrosion resistance. Platinum and its alloys readily form intermetallics, therefore the platinum group metal based intermetallics are of particular interest due to high temperature stability, better oxidation or corrosive resistance than refractory metals.

Arikan *et.al.* [1] have reported the structural, electronic and elastic properties of scandium based compound ScX_3 (X= Ir, Pd, Pt and Rh) using ab-initio calculations. Meddar *et.al.* [2] have studied the structure and morphology of Pt_3Sc alloy thin film using pulsed laser deposition (PLD). Xing *et.al.* [3] have studied the



structural stability and enthalpies of formation of refractory intermetallics TM and TM_3 ($T = Ti, Zr, Hf; M = Ru, Rh, Pd, Os, Ir, Pt$). Kumar et al. [4] studied the electronic structure and magneto-optical properties of XPt_3 ($X = V, Cr, Mn, Fe, Co, Ni$) compounds. Archarya *et. al* [5] have reported the structure and electronic properties of $ScPt_3$ and YPt_3 compounds. $LuPt_3$ compound is binary intermetallics compounds with $AuCu_3$ structure, which belongs to $Pm-3m$ space group. It is known that the elastic properties of a solid are closely associated with various fundamental solid-state properties, such as interatomic potentials, equation of state and phonon spectra. These parameters provide a link between the mechanical and dynamic behavior of a crystal. To understand the physical properties of this compound and provide significant information on the application and design of platinum based compounds, it is necessary to study further the electronic structure and elastic constants of $LuPt_3$ compounds. Hence in the present paper, we have made efforts to shed more light on structural, electronic, elastic, mechanical and thermal behavior of $LuPt_3$ compound using three different approaches under generalized gradient approximation (GGA) at ambient pressure. The paper is organized as follows: "Computational method" section is devoted to the description of our methods of calculation. In "Result and discussion" section, the results are presented including comparison with experimental and theoretical data, followed by discussion. Conclusions are given in "conclusion section".

II. COMPUTATIONAL METHOD

The structural, electronic, elastic, mechanical and thermal properties of $LuPt_3$ compound is investigated using first principle full potential-linearized augmented plane wave method within the density functional theory. We used Perdew and Wang-generalized gradient approximation, which is based on exchange correlation energy [6]. The wave vector cut-off for the plane wave expansion of the wave function in the interstitial region was chosen, $R_{MT} * K_{max} = 7$ where R_{MT} is the smallest muffin-tin radius in the unit cell and K_{max} is the maximum of reciprocal lattice vector. A dense mesh of $10 \times 10 \times 10$ k points is used and tetrahedral method [7] has been used for the Brillouin Zone integration. The calculations are iterated until the total energies are converged below 10^{-4} Ry. The total energies are calculated as a function of volume and fitted to Birch-Murnaghan equation of state [8] to obtain the ground state properties like zero-pressure equilibrium volume. Information on the influences of pressure and temperature on the elastic moduli and related aggregate properties of single crystals plays an essential role in predicting and understanding the interatomic interactions, strength, mechanical stability, phase transition mechanisms and dynamical response of materials. For a cubic crystal, the three elastic moduli C_{11} , C_{12} and C_{44} fully describe its elastic behavior. The elastic moduli required knowledge of the derivative of the energy as a function of the lattice strain. The symmetry of the cubic lattice reduced 21 elastic constants to three independent elastic constants, namely C_{11} , C_{12} and C_{44} . The elastic stability criteria for a cubic crystal at ambient conditions are $C_{11} + 2C_{12} > 0$, $C_{44} > 0$, $C_{11} - C_{12} > 0$ and $C_{12} < B < C_{11}$. In the present work, the elastic constants were calculated using the tetrahedral and rhombohedral distortions on the cubic structure using the method developed by Charpin and integrated it in the WIEN2k package [9]. The systems were fully relaxed after each distortion in order to reach the equilibrium state. C_{44} is proportional to the shear modulus and could be used as a measure of shear resistance. The longitudinal and transverse sound velocities (v_l and v_t) were obtained by using these elastic constants as follows:

$$v_l = \sqrt{\frac{C_{11} + \frac{2}{5}(2C_{44} + C_{12} - C_{11})}{\rho}} \tag{1}$$

$$v_t = \sqrt{\frac{C_{44} - \frac{1}{5}(2C_{44} + C_{12} - C_{11})}{\rho}} \tag{2}$$

Where C_{11} , C_{12} and C_{44} are second-order elastic constants and ρ is mass density per unit volume, and the average sound velocity v_m was approximately calculated from [10, 11]:

$$v_m = \left[\frac{1}{3} \left(\frac{2}{v_l^3} + \frac{1}{v_t^3} \right) \right]^{-1} \tag{3}$$

One of the standard methods to calculate the Debye temperature was from elastic constants, since θ_D may be estimated from v_m by the following equation [10, 12]:

$$\theta_D = \frac{h}{k_B} \left[\frac{3n}{4\pi V_a} \right]^{\frac{1}{3}} v_m \tag{4}$$

where h is Planck’s constant, k_B is Boltzmann’s constant and V_a is the average atomic volume.

III. RESULT AND DISCUSSION

3.1 Ground state properties

In order to calculate the ground state properties, the total energies are calculated in $AuCu_3$ type structure for different volumes around the equilibrium cell volume V_0 . The variation of total energy as a function of volume for this compound is shown in Fig.1 The calculated total energies are fitted to the Birch- Murnaghan equation of state [8] to determine the ground state properties like lattice constant (a_0), bulk modulus (B) and its pressure

Table 1: Calculated lattice constant (a_0), bulk modulus (B), its pressure derivative (B’) of $LuPt_3$ compound at ambient pressure

Solid	Work	Approximation	a_0 (Å)	B(GPa)	B'	N(E_F)
$LuPt_3$	Pre.	PBE-GGA	4.080	209.85	4.01	3.53
		WC-GGA	4.038	224.04	4.61	3.46
		PBEsol-GGA	4.029	223.07	4.71	3.46
	Expt.		4.029 ^a	-	-	-

^aRef. [13]

derivative (B') at minimum equilibrium volume V_0 using exchange correlation as PBE-GGA, Wu–Cohen (WC) GGA and PBE-sol GGA. It is seen from Table 1 that our calculated values of lattice parameter a_0 is found to be

in close agreement with the available experimental data. We could not compare the calculated value of bulk modulus of LuPt₃ due to the lack of availability of experimental as well as theoretical data. The further calculations have been carried out using only PBE-GGA.

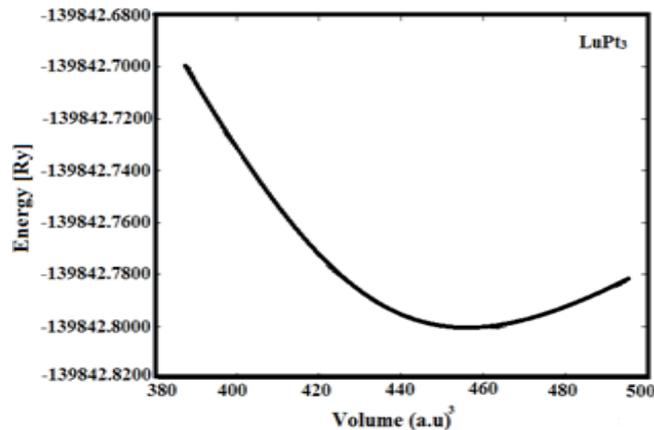


Fig. 1 Variation of total energy with volume of LuPt₃ compound in AuCu₃ structure

3.2 Electronic properties

The calculated electronic band structure of LuPt₃ compound, along with the higher symmetry directions in the Brillouin zone using (GGA) approach is shown in Fig. 2. It is seen that there is no band gap at the Fermi level which shows that LuPt₃ compound exhibit a metallic behavior. The Fermi level is considered at zero. In the band structure of LuPt₃ compound, the main contribution to the total DOS comes from the 'd' like states of Lu respectively with significant contribution of 's' and 'p' like states of Pt. The lowest lying bands originate from -

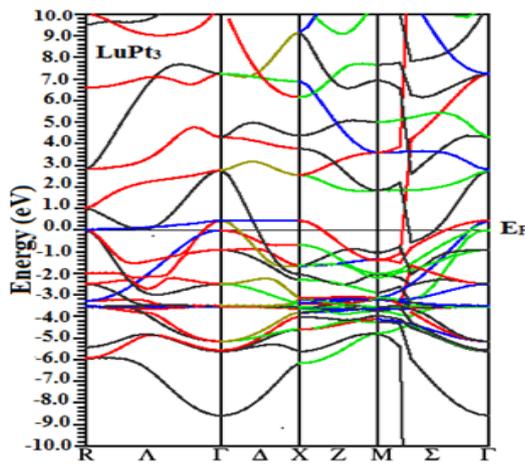


Fig. 2 Band structure for LuPt₃ compound in AuCu₃ phase at ambient pressure

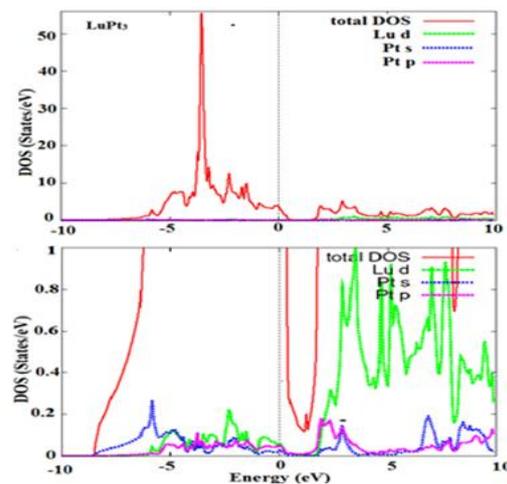


Fig. 3 Density of states (total and partial) for LuPt₃ compound at ambient pressure

's' like states of Pt. The flat bands are obtained in LuPt₃ around -3.6eV which is mainly due to 'f' like states of Lu. The bands spread above the Fermi level is due to 'd' like states of Lu respectively. The valence band and conduction bands overlap considerably, and there is no band gap at the Fermi level which confirms the metallic nature of this compound. The density of states (DOS) plot provides an even more comprehensive picture of the elemental contribution to the electronic structure of LuPt₃ compounds. The total and partial DOS for LuPt₃

compound at ambient pressure is presented in Fig. 3. The metallic character is clearly seen from the finite DOS at the Fermi level. Traditionally the stability in compounds is associated with low density of states (DOS) at the Fermi level E_F [14]. We have calculated the density of states at the Fermi level $N(E_F)$. The value of this parameter is 3.53states/eV for LuPt_3 respectively, seen in Table 1.

3.3 Electronic charge density

The charge density distribution is an important property of solid materials and provides good information about the chemical bonding. Fig. 4 shows the contour plots of the distribution of the electron charge densities in the (100) plane for LuPt_3 compounds. The corner atoms are Lu, and the central atom is Pt respectively. The obtained charge density plots reveal the spherically symmetric concentration [15] centered on Lu and Pt atoms with some distortions near the region of contact with neighbouring atoms which indicates the possibility of the presence of ionic bonding along with weak covalent bonding in this compound. Large difference in electronegativity is responsible for charge

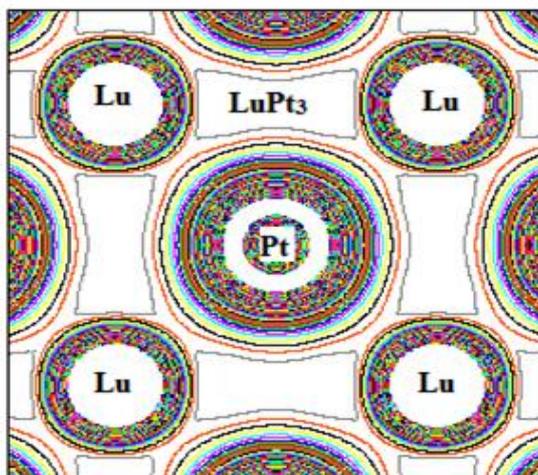


Fig. 4 Electronic charge density plots of LuPt_3 at ambient conditions

transfer among different atoms resulting in ionic bonding nature whereas small electronegativity difference results in charge sharing and responsible for covalent bonding nature. Electronegative values for Lu and Pt are 1.27 and 2.28 respectively. We found the electronegativity differences are large, indicating the presence of ionic bonding. For covalent and ionic materials, the typical relations between bulk and shear moduli are $G_H = 1.1B$ and $G_H = 0.6B$ [16] respectively. In our case, the ratio for LuPt_3 is 0.32 respectively, which confirm the ionic nature of bonding. All the evidence for the bonding charge densities indicates the ionic characteristics of LuPt_3 compound.

3.4 Elastic properties

The elastic properties play an important role in providing valuable information about the binding characteristic between adjacent atomic planes and provide the important information on the mechanical and dynamical properties, such as interatomic potentials, equation of state and phonon spectra. The second order elastic constants (SOECs) fo

Solids	Approx.	C_{11}	C_{12}	C_{44}	E	G_H	A	B/ G_H	σ 597	$C_{12}-C_{44}$ e
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LuPt ₃	GGA	265.44	159.01	71.75	172.18	63.65	1.34	3.05	0.35	87.25
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Table 2: Calculated elastic constants and mechanical properties of LuPt₃

LuPt₃ compound have been calculated with PBE-GGA as exchange correlation functional in their AuCu₃ structure at ambient pressure. The calculated values of elastic constants are given in Table 2. It can be noted that our calculated elastic constants satisfy the elastic stability criteria for a cubic crystal at ambient conditions. To the best of our knowledge, no experimental as well as theoretical values for the elastic constants of LuPt₃ compound have been appeared in the literature, so our results can serve as a prediction for future investigations

3.5 Mechanical Properties

Mechanical stability has been analyzed in terms of their elastic constants. In order to investigate the mechanical properties of LuPt₃ compound, we determine the Young’s modulus (*E*), shear modulus (*G_H*), Poisson’s ratio (*σ*) and anisotropic ratio (*A*) for useful applications. These are fundamental parameters which are closely related to many physical properties like internal strain, thermo elastic stress, sound velocity, fracture, toughness. We have calculated these properties of LuPt₃ compound and presented them in Table 2. The shear modulus *G_H* describes the material’s response to shearing strain using the Voigt-Reuss-Hill (VRH) method [17-19]; the effective modulus for the polycrystals could be approximated by the arithmetic mean of the two well known bounds for monocrystals.

The bulk and shear modulus, defined as-

$$B = \frac{1}{3}(C_{11} + 2C_{12}) \tag{5}$$

$$G_H = \frac{G_V + G_R}{2}$$

where

$$G_V = \frac{C_{11} - C_{12} + 3C_{44}}{5} \text{ is the Voigt shear modulus} \tag{6}$$

And

$$G_R = \frac{5C_{44}(C_{11} - C_{12})}{4C_{44} + 3(C_{11} - C_{12})} \text{ is the Reuss shear modulus} \tag{7}$$

Anisotropy factor of a material is another important parameter, which gives a measure of the anisotropy of the elastic wave velocity in a crystal and it is given as:

$$A = \frac{2C_{44}}{C_{11} - C_{12}} \tag{8}$$



and used to determine whether the structural properties remain the same in all directions or not. For $A=1$, the material is isotropic otherwise it shows different properties along the different directions.

The calculated elastic anisotropic factor for LuPt_3 compound is found to be far from 1, so we conclude that the compound under consideration in this work is strongly anisotropic elastically. The bulk modulus is usually assumed to be a measure of resistance to volume change by applied pressure [20]. The ratio of the bulk modulus to shear modulus of crystalline phases can predict the brittle and ductile behavior of materials.

As suggested by Pugh [21], if $B/G_H > 1.75$; a material behaves in a ductile manner otherwise, the material behaves in a brittle manner. In the present work, the value of B/G_H ratio indicates that the studied compound is ductile in nature. Ganeshan *et.al.* [22] have established a correlation between the bonding properties and ductility. Pettifor [23] has suggested that the angular character of atomic bonding in metals and compounds, which also relates to the brittle or ductile characteristics, can be described by the Cauchy's pressure ($C_{12} - C_{44}$). Compounds having more positive Cauchy's pressure tend to form bonds which are primarily metallic in nature where as for directional bonding with angular character, the Cauchy pressure is negative, with larger negative pressure representing a more directional character. Based on the calculated equilibrium Cauchy pressure (see Table 2), we may conclude that this compound belongs to class of ductile materials. The Young's modulus (E) is important for technological and engineering application. Young's modulus is defined as the ratio of stress and strain, and is used to provide a measure of the stiffness of the solid, *i.e.*, the larger value of E , the stiffer is the material. And the stiffer solids have covalent bonds [24].

Young's Modulus (E) is given by

$$E = \frac{9BG_H}{3B + G_H} \tag{9}$$

Bulk modulus is still used as a preliminary measure of the hardness of material but in order to confirm it, other properties must also be taken into account. A high bulk modulus does not mean that a material is hard. Elastic characteristics must be considered as well, and shear modulus might even provide a better correlation with hardness than bulk modulus. Covalent materials generally have a high shear modulus. The nature of bond can be predicted using Poisson's ratio and reflect the stability of a crystal against shear [25].

The Poisson's ratio (σ) is given by-

$$\sigma = \frac{3B - 2G_H}{2(3B + G_H)} \tag{10}$$

The value of Poisson's ratio is found to be ≈ 0.1 for covalent materials and ≈ 0.33 for metallic materials [26, 27]. It is observed from Table 2 that the value of Poisson's ratio is 0.35 for this intermetallic compound, signifying metallic bonding of LuPt_3 compounds. Frantsevich *et al.* [28] devised a rule on the base of Poisson's ratio ' σ ' to make a distinction between ductile and brittle materials. With respect to his criterion, the critical value of ' σ ' is 0.26. For brittle materials the value of ' σ ' should be less than 0.26. The value of Poisson's ratio ' σ ' in our calculation as reported in Table 2 is 0.35 for LuPt_3 respectively, endorsing their ductile nature.

3.6 Thermal properties

As an important thermodynamic index, the Debye temperature is closely related to many fundamental solid-state properties, such as elastic modulus, expansion thermal coefficient and melting point. At low temperature, the vibrational excitation arises solely from acoustic mode. Hence, at low temperature Debye temperature calculated from elastic constants. There are various methods to obtain the values of Debye temperature. A usual method for Table-3 Calculated density (ρ), Longitudinal (v_l), transverse (v_t), average elastic wave velocities (v_m) and Debye temperature (θ_D) of RPt_3 compounds at ambient pressure estimating the θ_D value can be obtained from the values of the elastic constants and the wave velocities such as average wave velocity, transverse and longitudinal elastic wave velocities. We first time predicted sound velocities, Debye temperature and density are given in Table 3. Because of the lack of availability of experimental as well as theoretical data of this compound, we could not compare them. Hence, our results can be considered as a prediction for these properties and it will testify future experimental work.

Solids	$\rho \times 10^3$ (kg/m ³)	v_l (m/s)	v_t (m/s)	v_m (m/s)	θ_D (K)
LuPt ₃	18.543	3887	1862	2094	192

IV. CONCLUSION

The structural, electronic, elastic, mechanical and thermal properties of states of LuPt₃ compound have been studied by using FP-LAPW method based on density functional theory as the exchange correlation energy. The calculated value of lattice constants is in good agreement with the available experimental data. We have also studied the mechanical properties of this compound. The elastic constants have been calculated using the approach, the energy-strain method. The calculated elastic constants satisfy the mechanical stability criterion and the ductility of LuPt₃ is predicted by Pugh's criterion. The band structure and densities of states DOS for this compound are analyzed and compared. They showed that the studied materials exhibit metallic character. We have also calculated thermal properties for this compound. For the lack of experimental as well as other theoretical results, we could not compare them. Hence our results can be considered as a prediction for these properties, which would be tested in the future both by experimentally and theoretically.

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