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DFT study on the Rh_3Zr and Rh_3Nb compounds

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Dedicated to Prof J R Durig

Due to the attractive high-temperature physical properties, platinum metal-base alloys such as Rh-base alloys make them important materials for various technological applications. To understand deeply the structural, and lattice dynamical properties of the L12-type (space number 221) of intermetallic compounds Rh_3Zr and Rh_3Nb , we have performed *ab-initio* density-functional theory within the local density approximation (LDA). Specifically, the phonon dispersion curves and corresponding one-phonon density of states (DOS) for both compounds are computed. Some basic physical parameters such as lattice constant, bulk modulus, elastic constants, shear modulus, Young's modulus, and Poisson's ratio are also calculated. Our structural results are consistent with the available experimental and other theoretical data. © Anita Publications. All rights reserved.

Keywords: Lattice Dynamic; Elastic properties; Thermal properties; *Ab-initio* calculations.

1 Introduction

Ni-based super alloys are important materials for various technological applications, especially for gas turbine engines and aircraft engines [1] due to their high-temperature physical properties. Recently, some studies [2-15] on this subject have directed to shed light on the mechanical properties of platinum metal-base alloys, such as Ir- and Rh-base alloys, because it is thought that they are more promising materials than Ni-base superalloys owing to their high-melting temperatures, good high-temperature strengths and good oxidation resistances [12,13]. The mechanical findings of Rh-base alloys are more convenient for high temperature structural applications as compared to Ir-base alloys, hence present study is focused on these compounds.

Crystallographically, the rhodium based $L1_2$ intermetallic compounds Rh_3Zr and Rh_3Nb crystallize in Cu_3Au type structure with the space group symmetry $Pm\bar{3}m$ (space number 221) [16]. The constituent atom Zr or Nb is positioned at (0,0,0) position, and the Rh atom is positioned at (0,1/2,1/2) position.

A few theoretical [4,5] and experimental [3,6,13] studies exist in the literature dealing with the structural, elastic, and electronic properties of Rh_3Zr and Rh_3Nb . Theoretically, Chen *et al* [4] investigated the elastic and mechanical properties of these compounds based on the *ab initio* density functional theory. Rajagopalan and Sundareswari [5] reported the structural and electronic properties using the self-consistent tight binding linear muffin tin orbital (TB-LMTO) method for Rh_3Zr and Rh_3Nb . On the other hand, Terada *et al* [3] measured the thermal conductivity and thermal expansion for the same compounds in the temperature range between 300 and 1100 K. Miura *et al* [6] studied experimentally the mechanical properties at various temperatures for Rh_3Ti . Yamabe-Mitarai *et al* [13] investigated the microstructure evolution and high-temperature strengths of Rh-base alloys.

Up to now, to the best of our knowledge, no systematic study on the vibrational, and thermodynamical properties of Rh_3Zr and Rh_3Nb have been reported. Therefore, we have aimed to provide some additional information to the existing data on the physical properties of Rh_3Zr and Rh_3Nb by using the *ab-initio* total energy calculations. Especially, we focus our attention on the mechanical, and the lattice dynamical

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behaviors, which are the important bulk properties of solids. The calculated properties are compared with the previous works.

2 Method of Calculation

Although the superiority of general gradient approximation (GGA) to local density approximation (LDA) is generally accepted for most of physical properties and materials, but the accurate results of Grobowski *et al* [17] for phonon dispersion curves of elemental Rh have shown that using LDA in this work instead of GGA could be a good choice for obtaining the physical properties of Rh₃Nb and Rh₃Zr. Also, recently Barrera *et al* [18] have observed the superiority of LDA on GGA for anharmonic properties of alkali metal hydrides compounds at high-temperatures. These results have encouraged us to use LDA instead of GGA for Rh₃X compounds. All calculations have been carried out using the Vienna *ab initio* simulation package (VASP) [18-22] based on the density functional theory (DFT). The electron-ion interaction was considered in the form of the projector-augmented-wave (PAW) method with plane wave up to energy of 400 eV [21,23]. This cut-off was found to be adequate for studying the structural and lattice dynamical properties. We have not observed statistically significant changes in the key parameters when the energy cut-off is increased from 300 to 500 eV. For the exchange and correlation terms in the electron-electron interaction, Perdew and Zunger-type functional [24] was used within the local density approximation (LDA) [25]. For k-space summation the 12×12×12 Monkhorst and Pack grid of k-points have been used.

3 Results and Discussion

3.1 Structural and Elastic Properties

Firstly, the equilibrium lattice parameters have been computed by minimizing the crystal total energy calculated for different values of lattice constant by means of Murnaghan's equation of state (Eos) [26]. The bulk modulus, and its pressure derivative have also been calculated based on the same Murnaghan's Eos and the results are listed in Table 1 along with the experimental [3,6,13] and other theoretical [4,5] values. The present values of lattice parameters are found to be 3.875 and 3.826 Å in L1₂ phase for Rh₃Zr and Rh₃Nb, respectively. It is seen that the present lattice constants are in agreement with the theoretical and experimental ones. The bulk modulus is a fundamental physical property of solids and can also be used as a measure of the average bond strengths of atoms of the given crystals [14]. Our results for bulk moduli are about 15% higher than the theoretical values in Ref [4], about 11% lower than the other theoretical value given in Ref [5] for these compounds. As can be seen from Table 1 that the lattice constants slightly increase as one goes from Rh₃V to Rh₃Ti in accordance with the mass of the anions, and opposite situation occurs for the bulk moduli. The similar trend has also been observed [2-4] for Ir₃X and Rh₃X (X = Zr, Hf, Nb, and Ta) compounds.

Table 1. Calculated equilibrium lattice constants (a_0), bulk modulus (B), and pressure derivative of bulk modulus (B') for Rh₃X (X = Zr and Nb).

Materials		a_0 (Å)	B (GPa)	B'
Rh ₃ Zr	Present-LDA	3.875		
	Theory-LDA ^a	3.893	244	4.58
	Theory-GGA ^b	3.966	277	-
	Experimental ^c	3.927	200	-
	Experimental ^d	3.929	-	-
Rh ₃ Nb	Present-LDA	3.826	289	4.75
	Theory-LDA ^a	3.832	35	-
	Theory-GGA ^b	3.896	246	-
	Experimental ^{c,d}	3.857	-	-

^a Reference [5], ^b Reference [4], ^c Reference [7, 8], ^d Reference [9].

The elastic constants of solids provide a link between the mechanical and dynamical behavior of crystals, and give important information concerning the nature of the forces operating in solids. In particular, they provide information on the stability and stiffness of materials, and their *ab initio* calculation requires precise methods. Since the forces and the elastic constants are functions of the first-order and second-order derivatives of the potentials, their calculation will provide a further check on the accuracy of the calculation of forces in solids.

Here, the elastic constants are computed by using the both “volume-conserving” technique [27] and “stress-strain” relations [28], and are listed in Table 2 along with the other theoretical values of Ref [4]. The present values of elastic constants in both methods are consistent with each other, but significantly higher (about 25%) than the GGA results of Ref [4]. It has already been expected that the elastic constants are overestimated in the LDA calculations due to the theoretical lattice constant from LDA being smaller than the GGA one, see Table 1.

Table 2. The calculated elastic constants (in GPa unit), Poisson’s ratio (ν), Young’s modulus (E), and Shear modulus (G) for Rh₃X (X = Zr and Nb).

Materials		C_{11}	C_{12}	C_{44}	C'	G	G_v	G_r	ν	A	E
	volume-conserving (Present-LDA)	378	202	159	290	125	130	120	0.35	1.81	320
Rh ₃ Zr	stress-strain (Present-LDA)	371	191	161	281	127	132	122	0.34	1.79	324
	Theory-GGA ^a	300	150	133	-	-	110	101	0.27	-	269
	volume conserving (Present-LDA)	461	214	206	337	168	173	163	0.31	1.67	422
Rh ₃ Nb	stress-strain (Present-LDA)	456	210	202	333	165	170	161	0.31	1.64	415
	Theory-GGA ^a	395	172	175	-	-	150	143	0.25	-	366

^a Reference [4].

The traditional mechanical stability conditions in cubic crystals on the elastic constants are known as $C_{11} - C_{12} > 0$, $C_{11} > 0$, $C_{44} > 0$, $C_{11} + 2C_{12} > 0$, and $C_{12} < B < C_{11}$. Our results for elastic constants in Table 2 satisfy these stability conditions, and they are about 15-20% higher than the GGA results of Ref [4].

The Zener anisotropy factor (A) is an indicator of the degree of anisotropy in the solid structures. For a completely isotropic material, the A factor takes the value of 1, when the value of A is smaller or greater than unity it is a measure of the degree of elastic anisotropy. Poisson’s ratio (ν), shear modulus (G), and Young’s modulus (E), which are the most interesting elastic properties for applications, are often measured for polycrystalline materials when their hardness has been investigated. These quantities are calculated in terms of the computed data using the following relations [29]:

$$A = \frac{2C_{44}}{C_{44} - C_{44}}, \quad (2)$$

$$\nu = \frac{1}{2} \left(\frac{(B - \frac{2}{3}G)}{(B + \frac{1}{3}G)} \right), \quad (3)$$

and

$$E = \frac{9GB}{G + 3B}, \quad (4)$$

where $G = (G_V + G_R)/2$ is the isotropic shear modulus, G_V is Voigt's shear modulus corresponding to the upper bound of G values, and G_R is Reuss's shear modulus corresponding to the lower bound of G values, and can be written as $G_V = (C_{11} - C_{12} + 3C_{44})/5$, and $5/G_R = 4/(C_{11} - C_{12}) + 3/C_{44}$. The calculated Zener anisotropy factor (A), Poisson's ratio (ν), Young's modulus (E), and Shear modulus [$C' = (C_{11} - C_{12} + 2C_{44})/4$] are given in Table 2 with the theoretical ones [4]. The present values of A show that our compounds (Rh₃X) have elastically anisotropic character as NiAl alloy with higher $A = 2.01$ value of [30].

It is known that the isotropic shear modulus and bulk modulus can measure the hardness of a compound. The bulk modulus is a measure of resistance to volume change by applied pressure, whereas the shear modulus is a measure of resistance to reversible deformations upon shear stress [31]. Therefore, isotropic shear modulus is a better predictor of hardness than the bulk modulus. The other commonly used empirical relations between bulk and shear modulus for covalent and ionic materials on their brittle/ductile behavior are $G \sim 1.1 B$ and $G \sim 0.6 B$, respectively [32, 33]. The present values of G/B are 0.58 (Rh₃Nb) and 0.51 (Rh₃Zr) and they are higher than the critical value of 0.5. These results also support their ionic and brittle character. According to this G/B criterion, Rh₃Nb is more brittle than Rh₃Zr compound.

The Poisson's ratio is small ($\nu = 0.1$) for covalent materials, and it has a typical value of $\nu = 0.25$ for ionic materials [33]. In the present case the ν values are 0.35, 0.31 for Rh₃Zr and Rh₃Nb, respectively. Our ν values are consistent (about 4% higher) with the experimental values of Miura *et al* [6] found for Ir₃X (X = Ti, Ta, Nb, V, Zr, Hf) compounds. Therefore, the ionic contributions to the atomic bonding are dominant for these compounds.

The Young's modulus is defined as the ratio of the tensile stress to the corresponding tensile strain, and is an important quantity for technological and engineering applications. It provides a measure of the stiffness of a solid, and the material is stiffer for the larger value of Young's modulus. The Young's modulus of Rh₃Nb is higher than that of Rh₃Zr, and these are seriously lower than the theoretical values of Chen *et al* [11] for Ir₃X (X = Ti, Ta, Nb, V, Zr, Hf). The above mentioned elastic data for the present compounds are summarized in Table 2 with available theoretical ones.

3.2 Phonon Dispersion Curves

The present LDA phonon frequencies of Rh₃X (X = Zr, Nb) compounds in L1₂ phase are calculated by the PHON program [34] using the Hellmann-Feynman forces obtained from the VASP. The PHON code calculates force constant matrices and phonon frequencies using the "Small Displacement Method" as described in References [35,36]. The present phonon dispersion curves and one-phonon density of state have been calculated in high symmetry directions using a $2 \times 2 \times 2$ cubic supercell of 32 atoms. The obtained results along the high symmetry directions are illustrated in Fig 1 and Fig 2 for Rh₃Zr and Rh₃Nb, respectively. Unfortunately, there is no experimental or other theoretical data available on the lattice dynamics of these compounds for comparison.

It is seen from Fig 1 and Fig 2 that Rh₃Zr and Rh₃Nb have very similar dispersion curves and corresponding density of states. It is well known that the mass difference between anions and cations strongly affects the maximum and minimum values of the acoustic and optic branches. Here, the maximum values of the phonon frequencies for optical branches decrease on going from V to Ti atom, and a clear gap between the acoustic and optic branches is not observed for these compounds. The general trend of these curves is similar to those obtained for Ni₃Al alloy [1] in the same structure. The curve on the right-side of the phonon dispersion curves shows the corresponding total phonon density of states for each compound. Analysis of eigenvectors reveals that while the main contribution to acoustic phonons results from the Rh atoms, the high frequency phonons stem from the Zr or Nb atoms. This is expected because the mass of Zr and Nb atoms are less than Rh atom.

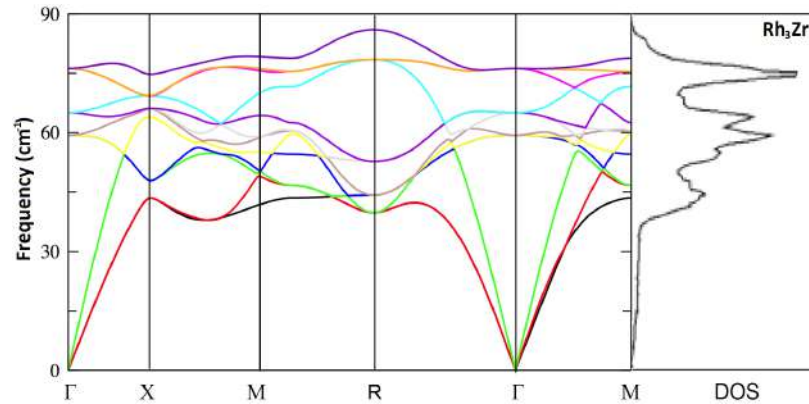


Fig 1. The phonon dispersions and corresponding density of states for Rh_3Zr .

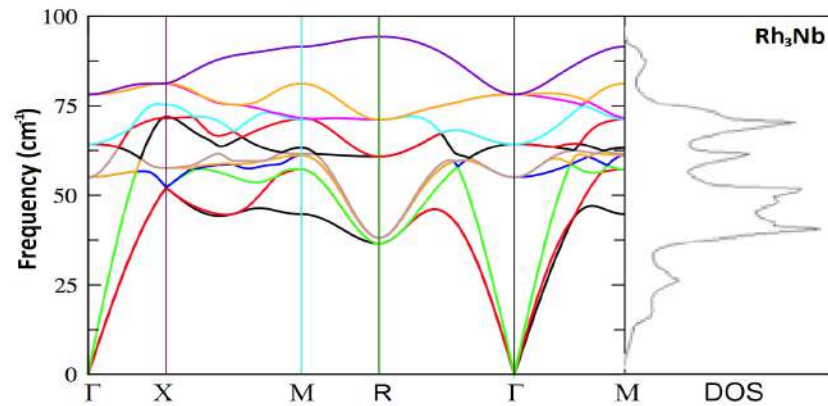


Fig 2. The phonon dispersions and corresponding density of states for Rh_3Nb .

4 Summary and Conclusion

In summary, we have performed the first principles total energy calculations for Rh_3Zr and Rh_3Nb using the plane-wave pseudopotential approach to the density functional theory within the local density approximation. The calculated lattice parameters and bulk modulus are, reasonably, consistent with the literature values. The present values of elastic constants satisfy the traditional mechanical stability conditions and their values from both “volume-conserving” and “stress-strain” methods are consistent with each other, but they differ from the other theoretical GGA results. Beside the other contributions, the original aspects of the present paper concern the phonon dispersion curves results, which have not been considered so far.

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