International Journal of Theoretical & Applied Sciences, Special Issue-NCRTAST 8(1): 52-56(2016)

ISSN No. (Print): 0975-1718
ISSN No. (Online): 2249-3247

A DFT Study on Phase Stability, Electronic, Optical, Elastic and Mechanical Properties of RhZr

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(Received 11 April, 2016 Accepted 20 May, 2016)
(Published by Research Trend, Website: www.researchtrend.net)

ABSTRACT: We present structural stability, electronic, optical, elastic, mechanical and thermal properties of RhZr intermetallic compound. The computational method is based on full-potential linearized augmented plane wave (FP-LAPW) method. The exchange-correlation energy is described in generalized gradient approximation of i.e. PBE-GGA and WC-GGA. Total energy of RhZr as a function of the unit cell volume has been calculated in B_1, B_2 and B_3 crystal structure to obtain the ground state properties. The study of different structures regarding their enthalpy vs. pressure variation is also presented. The calculated lattice parameter for RhZr is in good agreement with the available experimental and other theoretical data for B_2 crystal structure. The linear optical properties are also studied under zero pressure for the first time. The results obtained from density of states (DOS) and optical spectra shows that the present compound is metallic. The second order elastic constants are also presented. Ductile nature of RhZr compound is predicted in accordance with Pugh's criteria. The sound velocities for longitudinal and shear waves, Debye average velocity and Debye temperature have been successfully calculated.

Keywords: Equation of states; Optical properties; Elastic constants; Debye temperature.

I. INTRODUCTION

Over the past decade, compounds of 'd' block transition metal family have captured the curiosity of many scientist and researchers, only due to their appealing physical and mechanical properties such as low density, high melting point, good thermal conductivity, and excellent environmental resistance [1-3]. Almost of all these intermetallics exists in B_2-type (CsCl) crystal structure. The specified space group for B_2 crystal structures is 221/Pm-3m. The alloys prepared with the combination of zirconium atom are employed as cladding materials and structural component in light and heavy water nuclear reactors. This application has become possible because zirconium has very low absorption cross-section of thermal neutrons. In context of the technological importance of zirconium, there have been a number of theoretical and experimental [4-8] studies carried out to determine different properties of Zr based intermetallic compounds. Baranov [4] predicted structural stability of pure elements and binary intermetallic compounds assuming the density of atoms as stationary and un-deformable in internal and external spherical symmetrical shell. To investigate the structural, mechanical, thermodynamic and electronic properties of eight binary Cu-Zr intermetallic compounds, first-principles calculations within density functional theory (DFT) using Vienna *ab-initio* simulation package (VASP) has been reported by Du *et. al.* [5]. They found that CuZr possesses the most ductile phase amongst all the studied Cu-Zr binary compounds namely $CuZr_2$, CuZr, $Cu_{10}Zr_7$, Cu_8Zr_3, $Cu_{51}Zr_{14}$, Cu_5Zr, Cu_2Zr and Cu_5Zr_8. Ali *et. al.* [6] have performed the density functional based (DFT) first-principles investigation to study the cohesive, elastic and electronic properties of binary Fe-Zr intermetallics. Density functional study has been performed by Fatima *et. al.* [7] to study the structural, electronic, elastic, bonding and mechanical properties of ScRh, YRh (group III) and TiRh, ZrRh (group IV). By employing the self consistent ultra soft pseudopotential method Ugur *et al.* [8] reported the structural, electronic and vibrational properties of ordered intermetallic alloys CoZ (Z = Al, Be, Sc and Zr).

Despite above extensive efforts in computational materials science, a systematic first-principles study on optical properties of RhZr is still not available. For better understanding the physics of this compound, we have initiated a step to highlight optical properties in the present study. Secondly, the phase stability of RhZr in three different structures (B_1, B_2 and B_3) is presented from their energy against volume and enthalpy vs. pressure curves for the first time. The paper is organized as follows. The method of Calculation is briefly described in Section 2. Section 3 deals with the results with discussion of the present work.

II. METHOD OF CALCULATION

For the calculation of total energy full potential linearized augmented plane wave (FP-LAPW) method based on density functional theory is used. It is implemented in the WIEN2k code [9].

PBE-GGA [10] and WC-GGA [11] versions of GGA was used as a exchange correlation energy calculations. Generally the convergence is achieved by expanding the basis function up to $R_{MT}*K_{max} = 7$, where R_{MT} is the smallest atomic radius in the unit cell and K_{max} gives the magnitude of the largest k vector in the plane wave expansion. The maximum value for partial waves inside the atomic sphere is $l_{max} = 10$ while the charge density is Fourier expanded up to $G_{max} = 12$ $(Ryd)^{1/2}$. The self-consistent calculations are converged when the total energy of the system is stable within 10^{-4} Ry. A dense mesh of 1000 k points and the tetrahedral method have been employed for the Brillouin zone integration. The total energies are fitted to Birch's Murnaghan's equation of state [12] to obtain the ground state properties.

$$P = \frac{3B_0}{2}\left[\left(\frac{V_0}{V}\right)^{\frac{7}{3}} - \left(\frac{V_0}{V}\right)^{\frac{5}{3}}\right]\left[1 + \frac{3}{4}\left(B_0^{'} - 4\right)\left\{\left(\frac{V_0}{V}\right)^{\frac{2}{3}} - 1\right\}\right] \quad (1)$$

where P is the pressure, V is the volume at pressure P, V_0 is the volume at ambient pressure, B_0 is the bulk modulus at ambient pressure and $B_0^{'}$ is the pressure derivative of bulk modulus B_0.

III. RESULT AND DISCUSSION

A. Structural Properties

In order to determine the ground state properties, total energy is calculated with different volumes for B_1 (NaCl), B_2 (CsCl) and B_3 (ZnS) crystal structures (space group symmetry 221_pm-3m, 225_fm-3m and 216_F-43m respectively) in their non-magnetic phase for RhZr. The total energies vs. volume curves have been shown in Fig. 1(a) for RhZr. Calculation of enthalpy has strongest influence on phase stability for the present compound. The Gibbs free energy (*G*) [13] must be calculated by $G = E_o + PV - TS$, where E_0 is the total energy, P is the pressure, V is the volume, T is the temperature and S is the entropy. For the theoretical calculations T = 0 K, Gibbs free energy becomes the enthalpy $H = E_0 + PV$. It is concluded that RhZr possesses minimum value of energy and enthalpy in its B_2-phase. Hence the B_2-phase is the most stable phase and it is taken into consideration for the further calculations. The pressure vs. enthalpy plots of RhZr are also presented in Fig. 1(b) for all the three phases. The lattice constant (a_0), bulk modulus (B) and its pressure derivative (B') are presented in Table 1 with the experimental and other theoretical data available for comparison. Our calculated result of lattice constant and bulk modulus for B_2-phase are in good agreement with the experimental [14] and other theoretical results [4, 7]. But due to the unavailability of any data regarding B_1 and B_3 crystal structure, the values could not be compared. One of the most interesting results obtained from present calculation is that the values of bulk modulus are decreasing according to their stability in different crystal structures.

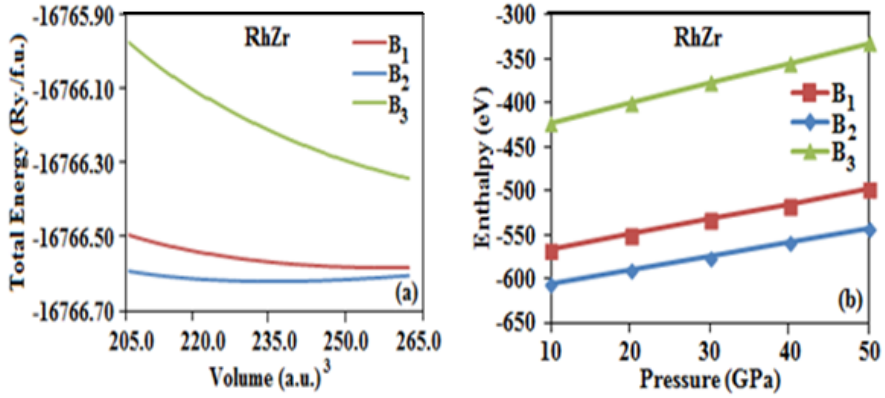

Fig. 1(a). E-V and **1(b)** H-P Curves for RhZr

B. Electronic Properties

In order to gain understanding on the principal features of electronic properties of RhZr the density of states are presented in Fig. 2. It is clearly seen that there is zero band gap between valence band and conduction band. The largest occupied peak for RhZr is located nearly -3.5 eV below the Fermi level, which is dominated by Rh '*d*' state. The metallicity of RhZr is observed due to major contribution of '*d*' like state of Rh along with little participation of '*d*' like state of Zr. The states above the Fermi level are mainly due to '*d*' like states of Zr for the present compound.

Table 1: Calculated ground state and elastic properties of RhZr.

Approximation	**a_o (Å)**	**B (GPa)**	**B'**	**N(E_F) (States/eV)**	**C_{11} (GPa)**	**C_{12} (GPa)**	**C_{44} (GPa)**
PBE-GGA B_2	3.299	162	4.68	2.23	253	126	59
WC-GGA B_2	3.264	180	4.73	-	248	148	98
Experimental	3.260[a]	-	-	-	-	-	-
Other Theory	3.239[b]	113[b]	-	-	-	-	-
	3.30[c]	170[c]	3.51[c]	2.31[c]	-	-	-
PBE-GGA B_1	5.344	168	4.03	-	-	-	-
PBE-GGA B_3	5.934	76	5.03	-	-	-	-

[a]Ref [14], [b]Ref [4] and [c]Ref [7]

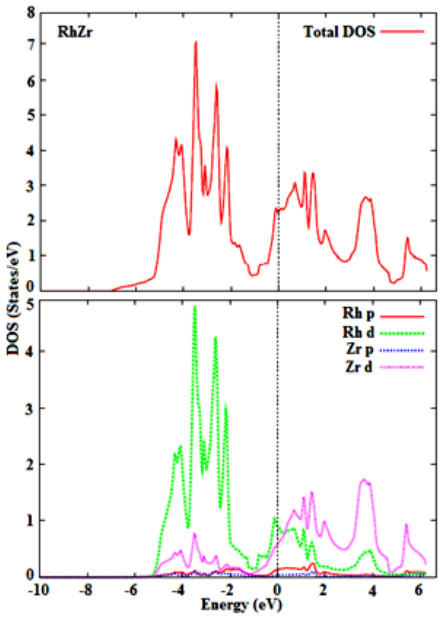

Fig. 2. Density of states for RhZr Intermetallic Compound.

For CuZr the DOS value at Fermi level is found to be 2.23 states/eV/F.U. (see Table 1) which verifies the metallic nature of the present compound.

C. Optical Properties

The analysis of optical spectra helps to give a better understanding of electronic structure of solids. The energy band structures are directly related to the complex dielectric function, which depends on frequency: $\varepsilon(\omega)=\varepsilon_1(\omega)+i\varepsilon_2(\omega)$. The imaginary part $\varepsilon_2(\omega)$ is obtained from the momentum matrix elements between the occupied and the unoccupied electronic states and calculated directly using [15]:

$$\varepsilon_2(\omega)=\frac{4\pi^2e^2}{3m^2\omega^2}\sum_{l,n}\int_{BZ}\frac{2}{(2\pi)^3}d^3k\left|P_{nl'}\right|^2\times\delta[E_1(k)-E_n(k)-\hbar\omega] \quad (2)$$

By using the Kramers-Kronig relation, the real part $\varepsilon_1(\omega)$ of the frequency-dependent dielectric function can be derived from the imaginary part [16]:

$$\varepsilon_1(\omega)=1+\frac{2}{\pi}P\int_0^\infty\frac{\omega'\varepsilon_2(\omega')}{\omega'^2-\omega^2}d\omega' \quad \ldots(3)$$

where P implies the principal value of the integral.

Since RhZr have cubic symmetry, it requires only one non zero second order dielectric tensor component to visualize the linear optical spectra. Therefore, a precise full potential linear augmented plane wave (FP-LAPW) method is suitable to study their optical behavior. The variation of real $\varepsilon_1(\omega)$ and imaginary $\varepsilon_2(\omega)$ part of the dielectric function corresponding to their incident photon energy up to 15 eV under zero pressure are depicted in Fig 3. The broadening was taken to 0.1 eV. [17]. The main peaks of the $\varepsilon_1(\omega)$ are obtained accurately at 0.12 eV for RhZr (Fig. 3).

(3)

These peaks are generated from the electronic transition from top of the valence band to the bottom of the conduction band. An important quantity of $\varepsilon_1(\omega)$ is the zero frequency limit $\varepsilon_1(0)$, which is the electronic part of the static dielectric constant. Dielectric constant $\varepsilon_1(0)$ RhZr is found to be 3.43. Furthermore, it is noticed from Fig. 3 that each $\varepsilon_2(\omega)$ has a prominent peak nearly at 0 eV for which is due the Drude term [16].The effect of the Drude term is significant for energies less than 1.0 eV. Due to the lack of both experimental and theoretical results we could not compare our calculated values.

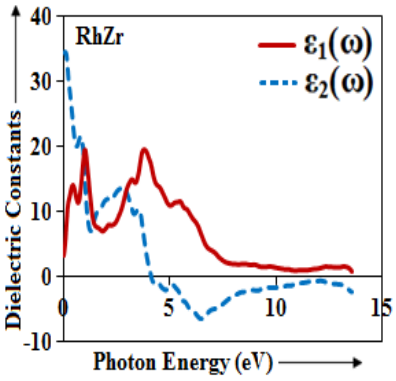

Fig. 3. Real and imaginary part of dielectric function versus photon energy for RhZr.

D. Elastic Properties

Elastic constants often provide the valuable information of interatomic bonding strength, anisotropy factor and structural stability. There are three independent elastic constants for a cubic crystal i.e. C_{11}, C_{12} and C_{44}, involves calculation of bulk modulus (B), which is related to the elastic constants as:

$$B = \frac{1}{3}(C_{11} + 2C_{12}) \quad \ldots(4)$$

The second order elastic constants are calculated using PBE-GGA and WC-GGA listed and compared in Table 1. The calculated elastic constants follow the stability criteria which is $C_{11} - C_{12} > 0$, $C_{11} > 0$, $C_{44} > 0$, $C_{11} + 2C_{12} > 0$ and $C_{12} < B < C_{11}$ [18] for B_2-phase.

E. Mechanical Properties

The elastic constant can be used to investigate the mechanical properties mainly shear modulus (G_H), Young's modulus (E), Poisson's ratio (σ) etc. It is known that the shear modulus plays a dominant role in predicting the hardness rather than the bulk modulus.

It can be calculated using the Voigt-Reuss-Hill (VRH) method [19]. The effective modulus for the polycrystals could be approximated by the arithmetic mean of the two well known bounds for mono crystals.

Table 2: Calculated mechanical and thermal properties of RhZr using PBE-GGA in B_2 phase.

Approximation	**B/G_H**	**G_H**	***E***	**σ**	**v_l (m/s)**	**v_t (m/s)**	**v_{avg} (m/s)**	**θ_D (K)**
PBE-GGA B_2	2.76	61	163	0.33	5272	2604	2923	332

The Hill shear modulus G_H is given as:

$$G_H = \frac{\frac{C_{11} - C_{12} + 3C_{44}}{5} + \frac{5C_{44}(C_{11} - C_{12})}{4C_{44} + 3(C_{11} - C_{12})}}{2} \quad \ldots(5)$$

The value of G_H is found to be 61 GPa for RhZr (see Table 2). The Young's modulus provides a measure of stiffness of the solids. Larger value of E indicates that the material is stiffer and stiffer solids have covalent bonds [20]. It can be seen from Table 2 that this value for RhZr is 163 GPa.. It can be E is given by:

$$E = \frac{9BG_H}{3B + G_H} \quad \ldots(6)$$

We have analyzed the ductility using (B/G_H) ratio. As suggested by Pugh [21], if B/G_H > 1.75, the material behaves in ductile manner otherwise brittle. The (B/G_H) ratio for RhZr compounds is found to be 2.76 (see Table 2). In accordance to above criteria RhZr is found to be excellent ductile. For good evidence we may also refer Frantsevich [22] who distinguished the ductility and brittleness of materials in terms of Poisson's ratio (σ). The critical value of Poisson ratio of a material is 1/3. The value of Poisson's ratio σ > 1/3 (< 1/3) reveals ductile (brittle) character. According to the above criteria RhZr possess ductile nature.

F. Thermal Properties

The Debye temperature (θ_D) can be used in characterizing the excitation of phonons and to describe various lattice thermal phenomena. At low temperature the vibrational excitations arise solely from acoustic vibrations. Hence, at low temperature the Debye temperature calculated from elastic constants. The equation for calculating θ_D is given below [23, 24].

$$\theta_D = \frac{h}{k_B}\left[\frac{3n}{4\pi V_a}\right]^{\frac{1}{3}} v_m \quad \ldots(7)$$

where h is a Planck's constant, k_B is Boltzmann's constant, V_a is the atomic volume, n is the number of atoms per formula unit and v_m is average sound velocity, which is approximately calculated from [23, 25]:

$$v_m = \left[\frac{1}{3}\left(\frac{2}{v_t^3}+\frac{1}{v_l^3}\right)\right]^{\frac{-1}{3}} \quad \ldots (8)$$

where v_t and v_l are the transverse and longitudinal sound velocities respectively obtained by using the elastic constants as follows:

$$v_l = \sqrt{\frac{\left[C_{11}+\frac{2}{5}\left(2C_{44}+C_{12}-C_{11}\right)\right]}{\rho}} \quad \ldots (9)$$

$$v_t = \sqrt{\frac{\left[C_{44}-\frac{1}{5}\left(2C_{44}+C_{12}-C_{11}\right)\right]}{\rho}} \ldots (10)$$

The longitudinal (v_l), transverse (v_t) and average elastic wave velocities (v_m) including Debye temperature of RhZr were obtained in B_2-phase from calculated elastic constants. The results are listed in Table 2.

IV. CONCLUSION

By using FP-LAPW method within PBE generalized gradient approximation of DFT, we have performed a study on phase stability of RhZr in B_1, B_2 and B_3 phases. The calculated total energy is fitted to the Birch Murnaghan's equation of state. The ground state properties such as lattice constants, bulk modulus and its pressure derivative are calculated using PBE and WC GGAs in all the three phases. From energy-volume and enthalpy-pressure curves, the B_2-type (CsCl) crystal structure is found be the most stable. The obtained lattice constant and bulk modulus for B_2-phase is in good agreement with the experimental and available theoretical data. Calculated density of state shows the metallic nature RhZr compound which is mainly due to '*d*' Rh. The optical spectra is plotted and analyzed using the calculated values of real and imaginary parts of dielectric function versus incident photon energy for the first time. Calculated elastic constants satisfy the mechanical stability criterion for RhZr in B_2-phase. The ductility for RhZr is analyzed by $B/G_H > 1.75$ ratio. Thermal properties of present compound are also reported in the present work.

ACKNOWLEDGEMENTS

The authors are thankful to University Grants Commission (UGC) and Madhya Pradesh council of Science and Technology (MPCST) for their financial support.

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