

DFT Investigation of Electronic, Phonon and Thermodynamic Behavior: RuZr

Ekta Jain^{1*, a)}, Gitanjali Pagare¹⁾ and Shubha Dubey¹⁾

¹⁾*Department of Physics, Sarojini Naidu Government Girls P. G. Autonomous College, Bhopal-462016, India*

^{a*)}Corresponding Author E-mail: jainekta05@gmail.com

Abstract. Theoretical investigations on electronic structure, phonon and thermodynamic properties of RuZr intermetallic compound has been performed using first-principles density functional theory in B₂-type (CsCl) crystal structure. The ground state properties have been obtained within generalized gradient approximation of Perdew, Burke and Ernzerhof (PBE) as an exchange correlation potential. The Electronic band structure and density of states reveals the metallic character of this compound. Phonon dispersion curve and phonon density of states (PhDOS) are studied to confirm the stability of RuZr intermetallic compound in B₂ phase. It is seen that PhDOS at high frequencies mainly composed of Zr atom. We have predicted the variation of volume, bulk modulus, heat capacity at constant volume and pressure, entropy, Debye temperature, Gruneisen parameter and thermal expansion with temperature range (0-2000 K) at different values of pressure (0-100 GPa) for the first time.

INTRODUCTION

The platinum group-metals (PGM) alloys, here Ru-base alloys make them important material due to their attractive high temperature physical properties such as high melting temperatures, lower specific gravity, larger temperature strength, good oxidation resistance, greater ductility and high thermal conductivity [1-4]. The ruthenium alloys show excellent chemical and electrical stabilities at high temperatures. As the literature is reviewed, we found a variety of work presented on ruthenium based intermetallic compounds. Jain et. al. [5] have comprehensively focused on phase stability, electronic structure, elastic, mechanical and thermal properties of RuX (X = Sc, Ti and V and Zr) intermetallic compounds using full potential linearized augmented plane wave (FP-LAPW) method within DFT. Mehl et. al. [6] have reported first-principles calculations within the framework of local density approximation (LDA) for elastic properties of many binary compounds including RuAl and RuZr using density functional theory. Ab-initio FP-LAPW calculation has been performed by Novakovic et. al. [7] to investigate structural stability of some CsCl structured HfTM (TM = Co, Rh, Ru, Fe) compounds. In spite of above routine calculations of transition metal (TM) intermetallic compounds, the application of first-principles calculations in condensed matter physics and material science has greatly expanded when phonon and phonon exerted thermodynamic properties are taken into an account. The previous literature [8-10] available regarding the phonon properties of TM intermetallics which exists in B₂ phase. The structural, thermo-elastic, and lattice dynamical properties of the platinum metal-base alloy such as Rh-base alloys have been reported by Surucu et. al. [8] by using the Vienna ab-initio simulation package (VASP) based on the density functional theory. In Ref. [9-10], the lattice dynamical properties for many binary compounds like ZrRu, ZrZn and Sc-TM (TM = Ag, Cu, Pd, Rh, Ru) have been investigated.

In this study, we presented structural, electronic, vibrational and thermodynamical properties of RuZr compound obviously not only due the lack of data available but also to focus their high temperature structure use as expected like other PGM alloys presented earlier [4]. Except high cost, the favorable properties (might be use in aircraft engine) of PGM alloy motivated us for the further investigations for RuZr intermetallic compounds. This study will serve as a reference for other PGM (Rh, Os, Ir and Pd) and their intermetallics may display similar properties lower cost and may fulfill the commercial requirements. We have first time presented a wide variety of structural parameter like volume, bulk modulus, heat capacity at constant volume and pressure, entropy, Debye temperature,

Gruneisen parameter, thermal expansion and also examined their behavior on different temperature (0-2000 K) and pressure (0-100 GPa) range.

METHOD OF CALCULATION

We have calculated the phonon spectra and thermodynamical properties of RuZr intermetallic compound using first-principles calculations based on full potential linearized augmented plane wave (FP-LAPW) method within DFT. For lattice dynamical properties, we have used PHONON software [11] within the approach of the supercell by using an external *ab-initio* program i.e. WIEN2k code [12]. The generalized gradient approximations (GGA) with the exchange correlation function of Perdew et. al. [13] is used. The convergence is achieved by expanding the basis function up to $R_{MT} * K_{max} = 7.0$, 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. A dense mesh of $10 \times 10 \times 10$ k points in tetrahedral method has been employed for the Brillouin zone integration. For phonon dispersion curve the finite force displacement is fixed at 0.01 Å. Thermodynamic calculations are carried out with quasi-harmonic Debye model [14].

RESULT AND DISCUSSION

Initially to get an insight on physical properties, we have performed the structural optimization for RuZr in B_2 -type (CsCl) crystal structure under the minimum condition of the total energy using equation of states (EOS) by Birch-Murnaghan [15]. We have obtained the lattice constant (a), bulk modulus (B) and first-order pressure derivative of the bulk modulus (B'), tabulated and compared in Table 1. On inspection of this Table, we found a satisfactory agreement of lattice constant between our calculated value and available experimental [16] and theoretical results [6].

The non spin polarized self consistent electronic band structures and density of states along the principal symmetry direction in B_2 -phase is presented in Fig. 1(a)-1(b). The Fermi level is set at 0 eV. One can see from the Fig. 1(a) that the bands are crossing from valence band to conduction band, indicating the metallic character of RuZr. The total and projected density of state (Fig. 1(b)) provides an explicit understanding of interaction among different orbitals of atoms. It is seen that the valence region is mainly occupied with 'd' like state of Ru atom whereas in the conduction band the peaks are mainly due to 'd' like state of Zr atom in the energy range 1 eV to 6 eV. The metallic behaviour in RuSc is noticed mainly due to hybridized 'd' like states of Ru with 'd' like states of Zr at the Fermi level. The DOS value of RuZr at Fermi level is found to be finite i.e. 0.48 states/eV/F.U. (see Table 1) which verifies the metallic nature of these compounds.

The phonon dispersion curve (PDC) for RuZr in the Brillouin zone i.e. $\Gamma \rightarrow X \rightarrow M \rightarrow \Gamma \rightarrow R \rightarrow M$ is presented with total and partial phonon density of states in Fig. 2(a)-2(b). The present compound contain two atoms per primitive cubic unit cell, due to the symmetry the distinct number of branches is reduced along the high symmetry directions $\Gamma \rightarrow X$ and $\Gamma \rightarrow R \rightarrow M$. As one can notice from this Fig. that at 0 GPa there is no frequency gap between optical and acoustic phonon modes, indicating that these compounds are ductile in nature. The frequency gap can be directly associated with the mass ratio of the constituent atoms. Higher mass ratio indicates larger frequency gap. In case of our compound this ratio is found to be the lowest. The frequency of phonon modes is positive throughout the BZ, which clearly shows the dynamical stability of RuZr in B_2 -type (CsCl) crystal structure. The optical phonon modes look more dispersive. These modes are degenerated at zone centre Γ point and again split in LO and TO branches from zone centre, this splitting indicates the long range coulomb interaction [17]. The highest frequencies of optical and acoustic modes are found to be 51.06 THz and 30.6 THz respectively for RuZr. For acoustic branch the softening of LA and TA modes are observed from Γ -M point. A clear splitting of TA1 and TA2 branches is seen at X point, which again degenerate at zone centre Γ point. The phonon density of states is associated with phonon dispersion curve. There are mainly two prominent peaks are observed in its PhDOS profile. The first sharp peak is located nearly 30 THz which is due to the transverse acoustic (TA) phonon modes. This peak is created by the vibration of Ru atoms. The next peak is situated between 40-45 THz is due to longitudinal optical (LO) phonon modes which occurs due to the contribution of Zr atoms whose mass is lighter as compare to Ru atom. The study of thermodynamic properties of materials under high pressure and high temperature environment is essential in order to extend our knowledge about their specific behavior. The thermodynamic properties like volume, bulk modulus, heat capacity at constant volume and pressure, entropy, Debye temperature, Gruneisen parameter and thermal expansion are determined in the temperature range 0-2000 K, where the quasi-harmonic Debye model remains fully valid [14].

	a_0 (Å)	B (GPa)	B'	N(E_F) (States/eV)	C₁₁ (GPa)	C₁₂ (GPa)	C₄₄ (GPa)	v_l (m/s)	v_t (m/s)	v_m (m/s)
Pre.	3.275	186	4.24	0.48	338	109	64	5721	3043	3400
Exp.	3.25 ^a	-	-	-	-	-	-	-	-	-
O. T. LDA	3.22 ^b	228 ^b	3.6 ^b	-	375	154	78	-	-	-

Pre – Present, Exp. – Experimental, O. T. – Other Theory
^aRef [16], ^bRef [6]

V (Bohr³)		B (GPa)		C_v (J/molK)		C_p (J/molK)		S (J/molK)		Θ_D (K)		ζ		α (10⁻⁵K⁻¹)	
0 K	300K	0 K	300K	0 K	300K	0 K	300K	0 K	300K	0 K	300K	0 K	300K	0 K	300K
238	239	184	179	0	45	0	46	0	50	442	438	2.07	2.08	0	2.45
237	-	186	-	-	-	-	-	-	-	400	-	-	-	-	-

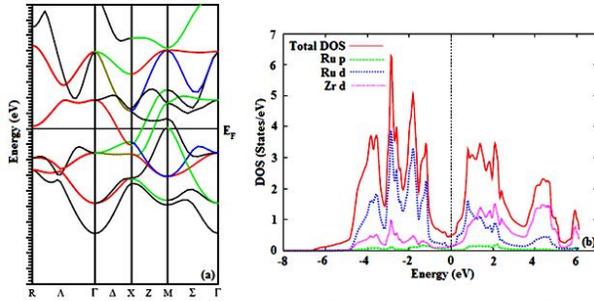


Fig. 1(a)-1(b) Electronic Band Structure and Density of States for RuZr

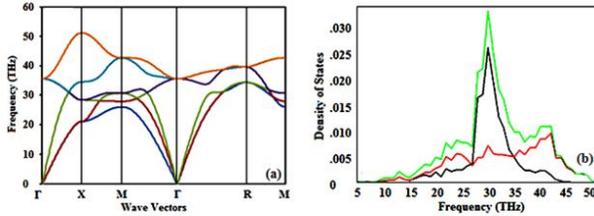


Fig. 2(a)-2(b) Phonon Dispersion Curves and Phonon Density of States for RuZr

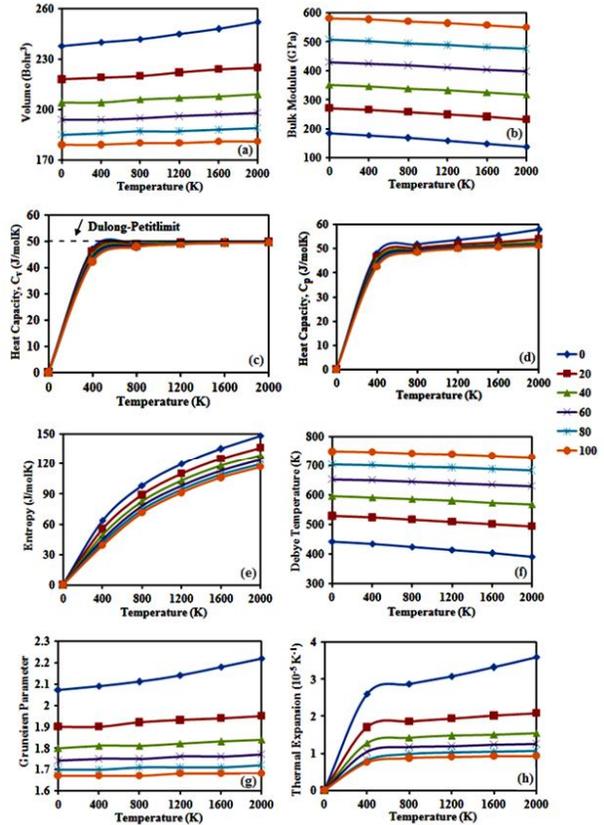


Fig. 3(a)-3(h) Variation of Volume (a), Bulk Modulus (b), Heat Capacity at Constant Volume (C), Heat Capacity at Constant Pressure (d), Entropy (e), Debye Temperature (f), Gruneisen Parameter (g) and Thermal Expansion (h) with Temperature for RuZr

The pressure effect is also taken into account in the 0-100 GPa range. We have also presented these thermodynamic properties in Table 2 at ambient pressure and room temperature. The variation of unit cell volume with temperature range at different pressure is presented in Fig. 3(a) for RuZr. It is seen that volume slightly increases in accordance with temperature. But when higher pressure is applied, it decreases. Fig. 3(b) shows the temperature dependence of bulk modulus at different pressure 0, 20, 40, 60, 80, 100 GPa. The effect of temperature on isothermal bulk modulus B_S is expected as very small while the values of bulk modulus is obtained larger at highest pressure. In Fig. 3(c) and Fig. 3(d), we demonstrated the variation of heat capacities at constant volume (C_v) and pressure (C_p) at different

ranges of temperature and pressure defined above. At low temperature $< 500\text{K}$, the shapes of curves for C_v and C_p are similar but at higher temperatures C_v reaches close to Dulong-Petit limit [18]. The saturation value of C_v at higher temperature is might be due to superposition of harmonic effect. While C_p deviates from the trend of C_v , and it becomes linear at higher temperature range. Fig. 3(e) depicted the variation of entropy, S with temperature at different pressure value. One may notice that entropy increases with increasing temperature. This Fig. also provides a clear understanding that it decreases as pressure increases. In Fig. 3(f), one can see that as the temperature increases, Debye temperature decreases with a moderate pace, and this decrease found a linear fashion. The variation of our calculated Gruneisen parameter (ζ) with temperature in Fig. 3(g) is in such a way that at lower temperature its value remains almost constant and then slightly increases with increasing temperature. On the other hand one can notice a decrease in the values of ζ with pressure. Further, In Fig. 3(h), we have plotted the variation of thermal expansion coefficient, α with temperature and pressure. Preliminary α increases with fast pace at low temperature and at higher temperature it increasing rate gradually decreases. On the other side it decreases with the increasing value of pressure, and it takes the highest values at all temperature ranges at lowest ($P = 0$ GPa) pressure.

CONCLUSION

In conclusion, we have studied the ground state, electronic, phonon and thermodynamic properties of RuZr using FP-LAPW method in DFT. PBE-GGA is used as exchange correlation scheme. The calculated ground state parameters are in good agreement with available data. The electronic band structure and density of states reveals the metallic nature of RuZr. The phonon dispersion curve and phonon density of states confirm the dynamical stability of this compound in B_2 phase. There is no frequency gap observed between optical and acoustic branches, which emphasize on the ductile character. The phonon density of states at high frequencies is mainly observed from Zr states. The temperature dependence of various quantities like volume, bulk modulus, heat capacity at constant volume and pressure, entropy, Debye temperature, Gruneisen parameter and thermal expansion is computed and discussed.

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