

Exploration of Structural, Mechanical and Valence variation of YbP under high Pressure at room Temperature

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Abstract- We have studied pressure-volume relationship and pressure induced structural phase transformation in YbP compound for the first time by using realistic interaction potential approach which considers Coulomb interaction; three body interaction and short range overlap repulsive interactions up to next nearest neighbor including temperature effects. The compound YbP found to undergo from their initial rocksalt phase to CsCl phase at high pressure. We have also studied the trivalent and intermediate valence in present compound and predicted the phase transition pressures, volume drop for two different valences. We have also studied the elastic properties of present compound and found that our results are in good agreement with experimental and other theoretical data.

Keywords – Pressure, three body interactions, transition pressure, temperature.

I. INTRODUCTION

Monopnictides of rare-earth elements (LnY, where Ln are lanthanides; Y = N, P, As, Sb, Bi) [1] have attracted attention of researchers due to their vast technological applications. The rare- earth pnictides have low carrier, strongly correlated systems and they show dense Kondo behavior and heavy fermion state [2, 3]. Most of the properties of ytterbium compounds are characteristics of valence variance and have completely filled 4f electron. These pnictides are considered as the trivalent compounds with the effective valences varied in intermediate values 2.69 and 2.63 for YbP, YbAs respectively [4]. YbP is found to have six- fold coordinated rock salt structure (Yb: 0,0,0; P : 1/2,1/2,1/2; space group Fm-3m under ambient conditions. Hayashi et al. [5] reported the pressure induced phase transition in YbP by using powder X-Ray diffraction (synchrotron radiation). Mendik et al. [6] studied the elastic, optical and phonon properties of ytterbium pnictides using reflectivity measurements and Raman spectroscopy. They have reported that these compounds are weakly intermediate-valent and are semi-metallic nature. Jha et al. [7] have reported the B₁–B₂ transition in ytterbium pnictides by using rigid ion model.

As fewer researches have been reported on YbP and no work have been done on present compound including the effects of temperature and valence variation. So, we have developed a realistic interaction potential approach. The present model incorporates coulomb interaction; three body interaction, and short range overlap repulsive interactions up to next nearest neighbor including temperature effects. We have computed the transition pressure, volume drop and elastic properties of present compounds and found results well suited with available experimental and theoretical data. To know the wider applicability of our model we have also computed the Blackman's parameter and the Every's parameter.

The rest of the paper is organized as follows. Method of computation is explained in section II. Results and discussion is presented in section III. Concluding remarks are given in section IV.

II. METHOD OF COMPUTATION

Application of pressure directly results in compression leading to the increased charge transfer due to the deformation of overlapping electron shell of the adjacent ions (or non rigidity of ions) in solids [8]. These effects have been incorporated in the Gibbs free energy ($G = U+PV-TS$) as a function of pressure and three body interaction which are the most dominant among the many body interactions. Here, U is the internal energy of the system, T is temperature and P is pressure. The Gibbs free energies for NaCl (B₁) and CsCl (B₂) are given by:

$$G_{B_1}(r) = U_{B_1}(r) + PV_{B_1} - TS_1$$

$$G_{B_2}(r') = U_{B_2}(r') + PV_{B_2} - TS_2$$

With U_{B_1} and U_{B_2} are the cohesive (lattice) energies, V_{B_1} (=2.00r³) and V_{B_2} (=1.54r'³) are the unit cell volumes for B₁ and B₂ phases respectively. The expressions for cohesive energies are as follows:

$$U_{B_1}(r) = \left[\frac{-(\alpha_m e^2 z^2)}{r} \right] - \left[\frac{(12\alpha_m e^2 z f(r))}{r} \right] + 6b\beta_{ij} \exp\left(\frac{r_i + r_j - r}{\rho}\right) + 6b\beta_{ij} \exp\left(\frac{2r_i - 1.414r}{\rho}\right) + 6b\beta_{ij} \exp\left(\frac{2r_j - 1.414r}{\rho}\right)$$

$$U_{B_2}(r') = \left[\frac{-(\alpha'_m e^2 z^2)}{r'} \right] - \left[\frac{(16\alpha'_m e^2 z f(r'))}{r'} \right] + 8b\beta_{ij} \exp\left(\frac{r_i + r_j - r'}{\rho}\right) + 3b\beta_{ii} \exp\left(\frac{2r_i - 1.154r'}{\rho}\right) + 3b\beta_{jj} \exp\left(\frac{2r_j - 1.154r'}{\rho}\right)$$

with α_m and α'_m as Madelung constants for B_1 and B_2 structures respectively, e as charge of electron and r and r' as interionic separation for NaCl (CsCl). β_{ij} ($=1+(z_i/n_i) + (z_j/n_j)$) is Pauling coefficient, where z_i (z_j) and n_i (n_j) are the valence and the number of electrons of the i (j) th ion, b is hardness parameter and ρ is range parameter. The first term in equations (5) and (6) are long-range Coulomb energy, second terms are three body interaction forces for B_1 and B_2 phases and remaining terms are due to overlap repulsive forces extended up to next nearest neighbor ions within Hafemeister and Flygare approach [9].

The present RIP approach contains three model parameters are range (ρ), hardness (b) and three-body force parameter ($f(r)$). Their values have been estimated from the knowledge of lattice parameter, cohesive energy and by solving the first and second derivatives of cohesive energy U .

Now, the entropy differences in the last term of Eqns-1 and 2 can be by the relations used earlier [10].

In order to explore the elastic behavior of YbP, we have calculated temperature dependent second order elastic constants (SOEC's). It is well known that the elastic constants are functions of first and second order derivatives of short range potential, so their calculation will give perception about the effect of short range forces on these materials. There are three independent SOECs namely, C_{11} , C_{12} and C_{44} in cubic system. It is well known that C_{11} is length related elastic constant and C_{12} and C_{44} are shape related elastic constants. For calculating SOECs, we have used the expressions stated in our earlier paper [10].

Another set of parameters which demonstrate the stability of the crystals are F_{12} and F_{44} , known as Blackman's parameters [11]. They are also based on SOECs and contain the ratio of elastic constants ($F_{12} = C_{12}/C_{11}$ and $F_{44} = C_{44}/C_{11}$). In order to characterize cubic elastic media we have used another set of parameters viz. s_1 , s_2 and s_3 introduced by Every [11]. The parameter s_1 depicts the phase and group velocities of sound; Young's and shear moduli as well as surfaces of constant energy of long wavelength acoustic phonons. The parameter s_3 depicts the acoustic and elastic anisotropies.

III. RESULTS AND DISCUSSION

The relative stability of the two phases were obtained by minimizing the Gibbs free energies $G_{B_1}(r)$ and $G_{B_2}(r')$ energies at different pressures corresponding to equilibrium inter-ionic separation $r(r')$ using the model parameters as listed in table 1. The condition of minimization is $\Delta G = G_{B_2}(r') - G_{B_1}(r)$. The pressure at which ΔG approaches zero is known as phase transition pressure (P_t). At P_t both the phases coexist. After phase transition system becomes stable in B_2 phase. We have also computed the P_t and associated relative volume drop V_p/V_0 which are given in Table 2.

Table 1. Input and model parameters

Compound	Valency	Input parameters		Model parameters		
		$r(\text{\AA})$	B_T (GPa)	b (10^{-12} erg)	$\rho(\text{\AA})$	$f(r)$
YbP	$z=3$	2.768 ^a	190.36 ^a	14.2010	0.2605	-0.0122
	$z=2.69$	2.768 ^a	190.36 ^a	13.5102	0.2605	-0.0092

a. Ref [6]

Table 2. Calculated transition pressures and volume drops

Compound	valency	Temperature (K)	Transition pressure (GPa)			Volume drop (%)		
			present	exp	other	present	exp	other
YbP	$z=3$	0	51.8	-	115 ^b	11.75	-	12 ^b
		300	50.9	51 ^a	-	11.82	-	-
	$Z=2.69$	0	48	-	-	11.17	-	-
		300	47	-	-	11.22	-	-

a. Ref [5], b. ref [7]

The variations of ΔG against pressure at $T=0\text{K}$ and $T=300\text{K}$ are depicted in Fig.1 and Fig.2 for YbP. The variations of V_p/V_o against pressure at $T=0\text{K}$ and $T=300\text{K}$ are depicted in Fig.3 and Fig.4 for YbP.

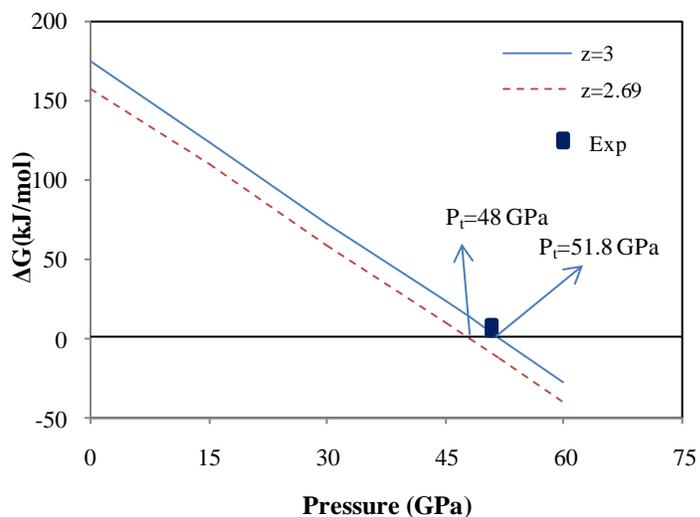


Fig.1 Variations of ΔG against pressure at $T=0\text{K}$

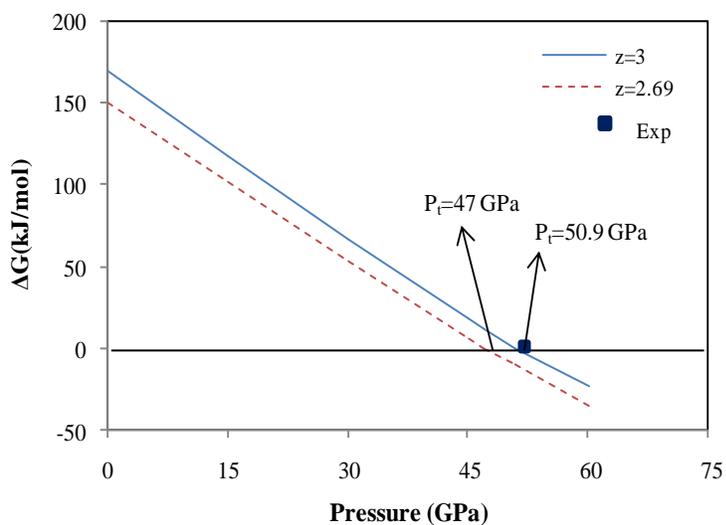
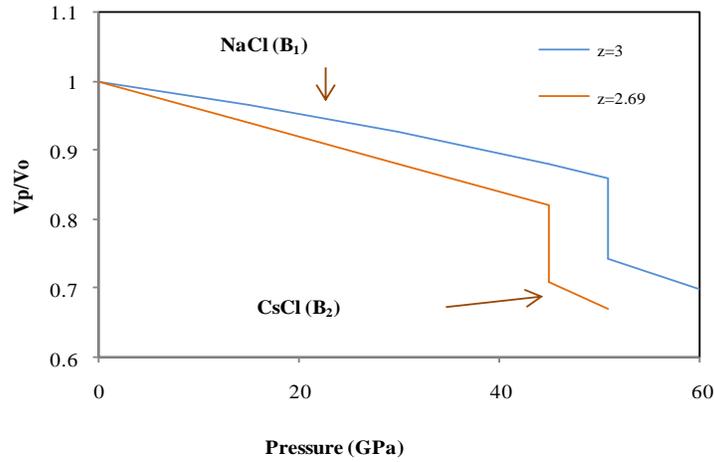
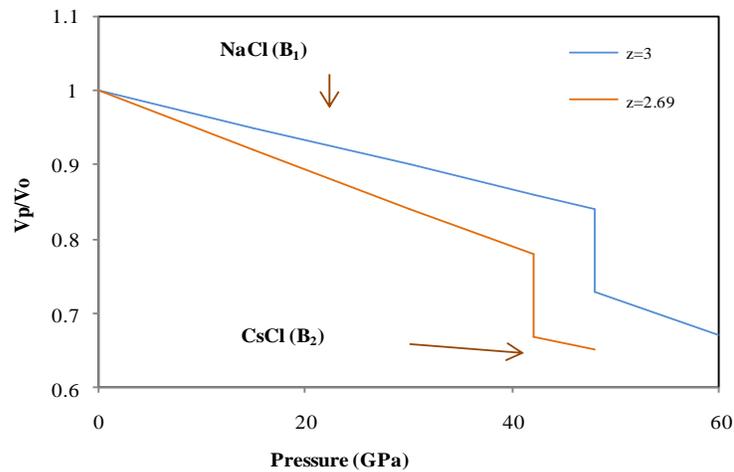


Fig.2 Variations of ΔG against pressure at $T=300\text{K}$


 Fig.3 Variations of V_p/V_o against pressure at $T=0K$

 Fig.4 Variations of V_p/V_o against pressure at $T=300K$

We have computed the second-order elastic constants (SOECs), Blackman's parameters and Every's parameter at different temperatures (0-300 K) which are shown in Table 3. The variation of SOECs against pressure is plotted in fig. 5.

 Table 3. Calculated SOECs and their combinations (10^{12} dyne/cm²)

Compound	Temperature (K)	C_{11}	C_{12}	C_{44}	F_{12}	F_{44}	s_1	s_2	s_3	Ref
YbP	0	3.12	1.65	1.20	0.528	0.384	5.52	0.347	-	Present
	300	2.79	1.52	1.05	0.544	0.376	4.89	0.355	-	Present
		2.7 ± 0.49	$1.5 \pm .30^a$	0.62 ± 0.05^a					0.16	exp

a. Ref [6]

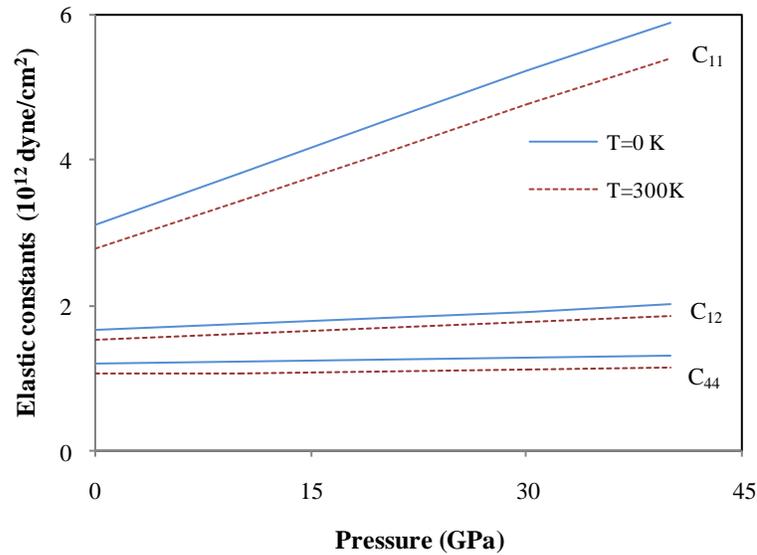


Fig. 5 Variations of SOECs against pressure

IV. CONCLUSION

Finally, we can conclude that our present RIP approach is suitable for predicting the structural and mechanical behavior of YbP at room temperature. We have taken two different valences ($z=3$ and intermediate) and got better results with $z=3$. So the present pnictide are well described by the trivalency. Our calculated elastic constants obey the traditional mechanical stability conditions for cubic crystals. This approach may be applied to other rare earth compounds.

V. ACKNOWLEDGEMENTS

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V. REFERENCE

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