

# High Pressure Phase Transition and Elastic Properties of AnAs (An = Th, U, Np, Pu) Compounds

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We have investigated the structural phase transition and higher order elastic constants of actinide mono-arsenides (AnAs; An = Th, U, Np, Pu) by using a two body interaction potential with modified ionic charge. This method has been found quite satisfactory in the case of other Rare-Earth compounds. The calculated compression curves of actinide mono-arsenides have been compared with high pressure X-ray diffraction data. The theoretically predicted phase transition pressure and other structural properties for these compounds agree reasonably well with the measured values. We have also reported the second and third order elastic constants and second order pressure derivatives, for the first time.

(Received April 13, 2009; accepted April 23, 2009)

*Keywords:* Phase transition, Elastic properties, High pressure, Actinide arsenides

## 1. Introduction

High pressure structural studies of Rare-earth materials are quite interesting because of the discovery of new crystal structures, soft mode transition and many geophysical and technical applications. Most of the actinides compounds exhibit the f.c.c. NaCl (B1) type structure at ambient pressure [1]. The contribution of the 5f electrons to the chemical bond in solids containing an actinide element is central to understanding the physical properties of these materials. In this regard many studies have been carried out in actinide compounds to understand the role of their 5f electrons during the application of pressure. The actinides mono-arsenide series (AnAs; An = Th, U, Np, Pu) display numerous allotropic structures and properties, which can be interpreted in term of valence fluctuation arising from the hybridization of the unstable 'f' band [2]. In case of thorium compounds, the thorium ion has essentially no 5f electrons. A comparison between other actinide compounds should therefore, give some information on the influence of the 5f electrons on their structural and elastic properties. The structural properties of the actinide mono-arsenides (AnAs) at high pressure have been investigated by using the experimental technique such as X-ray diffraction [3-6]. However, very few theoretical attempts have been made [7], to reveal the nature of bonding, ion-ion and ion-electron interactions etc. in these compounds. Most of these studies show that the degree of 5f electron localization is a factor, which determines the crystal structure, lattice constants and elastic properties of these compounds. These compounds crystallize in the NaCl (B1) structure at ambient condition and undergo a first order crystallographic phase transition from NaCl (B1) to CsCl (B2) structure under high pressure. Gerward [3] has measured structural properties

of ThAs such as equation of state and phase transition pressure for the B1-B2 transition using synchrotron X-ray diffraction at high pressure. Leger et al [4] have reported structural phase transition in UAs at around 18.5 GPa with volume collapse of 10.8%. In the Plutonium arsenide (PuAs) structural phase transition from B1 to B2 phase undergoes around 35 GPa with 9% volume reduction for both phases [6]. The electronic structure of Plutonium compounds have been investigated by Petit et al [8] using SIC-LSD scheme with the tight-binding linear muffin-tin orbitals (TB-LMTO) method. In the present paper we report the calculated results on structural phase transitions at high pressure and elastic properties using a theoretical model based on two body potential approach with modified ionic charge under the frame work of rigid ion model [9]. The present approach has been quite successful in predicting the high pressure behavior of several transition metal compounds [10]. In section 2, we present the brief outline of the method of calculation for predicting the structural and elastic properties and section 3, deals with the results and discussion.

## 2. Method of calculation

The inter-ionic potential for the actinide mono-arsenide (AnAs) compounds in the framework of the rigid ion model is expressed as [9-11]

$$U(r) = \sum_{ij} Z_i Z_j e^2 / r_{ij} + \sum_{ij} b \beta_{ij} \exp[(r_i + r_j - r_{ij}) / \rho_{ij}] + \sum_{ij} C_{ij} r_{ij}^{-6} + \sum_{ij} D_{ij} r_{ij}^{-8} \quad (1)$$

which includes long-range Coulomb (first term), Hafemeister and Flygare form of short-range repulsive (second term) and van der Waals multipole interactions

(third and fourth terms).  $Z_m e$  is the modified ionic charge due to Coulomb screening effect. The short range parameters  $\rho$  and  $b$  of the crystal energy are determined from the knowledge of lattice parameters, bulk modulus and the equilibrium condition

$$\left. \frac{dU(r)}{dr} \right|_{r=r_0} = 0 \quad (2)$$

where  $r_0$  is the equilibrium lattice constant. The input constants and model parameters for the AnAs compounds are presented in Table 1. Thermodynamically a phase transition is said to occur when changes in the structural details of the phase are caused by a variation of the free energy. The AnAs compounds transform from their initial NaCl (B1) to CsCl (B2) structure under pressure. The stability of a particular structure is decided by the minima of the Gibbs free energy, given by

$$G = U + PV - TS \quad (3)$$

where  $U$  is the internal energy (Eq. (1)), which at 0 K corresponding to cohesive energy,  $S$  the vibrational entropy at absolute temperature  $T$ , pressure  $P$ , volume  $V$ . The Gibbs free energies  $G_{B1}(r) = U_{B1}(r) + 2Pr^3$  for NaCl (B1) and  $G_{B2}(r) = U_{B2}(r) + (8/3\sqrt{3})Pr^3$  for CsCl (B2) phases become equal at the phase transition pressure  $P_t$  at temperature 0K. Such a theoretical approach has been found to predict most of the crystal properties of transition metal mono- nitrites compounds [10, 11] satisfactorily. In the present paper, we have also calculated the second order elastic constants (SOEC) from the following expressions, derived from the interionic potential (Eq. 1) [10]

$$C_{11} = \alpha [-5.112 Z_m^2 + A_1 + \frac{1}{2} (A_2 + B_2)] \quad (4)$$

$$C_{12} = \alpha [0.226 Z_m^2 - B_1 + \frac{1}{4} (A_2 - 5B_2)] \quad (5)$$

$$C_{44} = \alpha [2.556 Z_m^2 + B_1 + \frac{1}{4} (A_2 + 3B_2)] \quad (6)$$

Here,  $\alpha = e^2/4r_0^4$ ,  $A_1 = A_{12}$ ,  $B_1 = B_{12}$ ,  $A_2 = (A_{11} + A_{22})$  and  $B_2 = (B_{11} + B_{22})$ , and are expressed as:

$$A_{ij} = 2V/e^2 (d^2\Phi_{ij}(r)/dr^2) \quad (7)$$

$$B_{ij} = 2V/e^2 (1/r_{ij} (d\Phi_{ij}(r)/dr)) \quad (8)$$

where  $\Phi_{ij}(r)$  is the short-range potential in Eq.(1) and  $V$  is the unit cell volume. The expressions for the third order elastic constants (TOEC) can be derived as follows

$$C_{111} = \alpha [37.556 Z_m^2 + C_1 - 3A_1 + \frac{1}{4} (C_2 - 3A_2 - 9B_2)] \quad (9)$$

$$C_{112} = C_{166} = \alpha [-4.786 Z_m^2 + 1/8 (C_2 - 3A_2 - 3B_2)] \quad (8)$$

$$C_{123} = C_{144} = C_{456} = \alpha (2.717 Z_m^2) \quad (9)$$

with  $C_{1(2)} = A_{1(2)}^2 / B_{1(2)}$ . The expressions for the pressure derivatives of second order elastic constants can be derived from the combination of SOEC and TOEC constants for NaCl structure using their standard relations [10]

$$(dB_0/dP) = -(1/3)(C_{111} + 6C_{112} + 2C_{123}) / (C_{11} + 2C_{12}) \quad (10)$$

$$(dC_{44}/dP) = -(C_{11} + 2C_{12} + C_{44} + C_{144} + 2C_{166}) / (C_{11} + 2C_{12}) \quad (11)$$

$$(dS'/dP) = -1/2 (3C_{11} + 3C_{12} + C_{111} - C_{123}) / (C_{11} + 2C_{12}) \quad (12)$$

The expression for the bulk modulus ( $B_0$ ) and tetragonal shear modulus  $S'$  are

$$B_0 = (C_{11} + 2C_{12})/3$$

$$S' = (C_{11} - C_{12})/2$$

The Young modulus ( $E$ ) and Poisson's ratio ( $\sigma$ ) are calculated from

$$E = (C_{11} - C_{12})(C_{11} + 2C_{12}) / (C_{11} + C_{12}) \quad (15)$$

$$\sigma = C_{12} / (C_{11} + C_{12}) \quad (16)$$

### 3. Results and discussion

The required data and derived model parameters for actinide mono-arsenides (AnAs; An = Th, U, Np, Pu) compounds are given in Table 1. We have presented the phase transition properties of these compounds and compared our results with the available experimental and other theoretical data [3-6, 12-15] in Table 2. It is seen from Table 2 that the present model has correctly predicated the stability of competitive phases in all the cases as the value of  $\Delta U (= U_{B2} - U_{B1})$  are positive, which is a required criterion [16]. Also, the values of the equilibrium separation ( $r_0$ ) obtained by us from minimization technique are in good agreement with their experimental data [3-6].

In Fig. 1-4 (a), we have plotted the energy difference ( $\Delta G$ ) with pressure which have zero value at the phase transition pressures 18.1, 20.2, 30.5 and 38 GPa for ThAs, UAs, NpAs and PuAs respectively. These values are in better agreement with their corresponding measured data [3-6]. The equations of states for these mono-arsenides have been calculated up to various pressure ranges are plotted in Fig. 1- 4 (b). The volume discontinuity at phase transition pressure with associated volume collapse 10%, 9.4%, 6.9%, 5.6% for these compounds showing the compression of the lattice due to which the NaCl structure becomes unstable at high pressure and transforms to a denser 8-fold coordinated phase.

Table 1. Input data and model parameters of actinide mono-arsenide compounds.

Solids	Input data					Model parameter	
	$r_+$ (Å)	$r_0$ (Å)	$r_0$ (Å)	$B_0$ (GPa)	$Z_m^2$	$b(10^{-19}\text{J})$	$\rho$ (Å)
ThAs	0.94	1.20	2.9890 <sup>a</sup>	118 <sup>a</sup>	3.9204	19.694	0.271
UAs	0.91	1.20	2.8883 <sup>b</sup>	98 <sup>b</sup>	3.2761	13.626	0.272
NpAs	0.88	1.20	2.9183 <sup>c</sup>	70 <sup>c</sup>	3.097	11.935	0.311
PuAs	0.85	1.20	2.9282 <sup>d</sup>	68.6 <sup>d</sup>	3.027	11.865	0.328

<sup>a</sup>Ref.[3], <sup>b</sup>Ref.[4], <sup>c</sup>Ref.[5], <sup>d</sup>Ref.[6].

Table 2. Cohesive and phase transition properties of actinide mono-arsenide compounds.

Solids	Equilibrium interionic separation (Å)		Cohesive energy (KJ/mole)		Change in cohesive energy in KJ/mole	Phase Trans. Pres. (GPa)	Relative volume change in %
	$R_1$ (B1)	$R_2$ (B2)	$U_1$ (B1)	$U_2$ (B2)			
ThAs	Pres 3.000	3.110	-2929.46	-2861.83	67.63	18.1	10
	Theo. 2.9951 <sup>f</sup>	3.110 <sup>f</sup>	-2978.62 <sup>f</sup>	-2912.40 <sup>f</sup>	66.22 <sup>f</sup>	16.4 <sup>f</sup>	10.5 <sup>f</sup>
	Exp. 2.989 <sup>a</sup>	-	-	-	-	26.2 <sup>e</sup>	-
						18 <sup>a</sup>	10 <sup>a</sup>
UAs	Pres 2.900	3.020	-2525.36	-2461.40	63.96	20.2	9.4
	Theo. 2.8986 <sup>g</sup>	3.065 <sup>g</sup>	-2978.93 <sup>g</sup>	-2883.36 <sup>g</sup>	95.57 <sup>g</sup>	19.75 <sup>g</sup>	-
	Exp 2.8883 <sup>b</sup>	-	-	-	-	18.5 <sup>b</sup>	10.8 <sup>b</sup>
NpAs	Pres. 2.9200	3.070	-2330.63	-2255.29	75.34	30.5	6.9
	Theo. 2.9300 <sup>h</sup>	3.070 <sup>h</sup>	-2924.57 <sup>h</sup>	-2847.34 <sup>h</sup>	77.23 <sup>h</sup>	28.2 <sup>h</sup>	8.6 <sup>h</sup>
	Exp 2.9183 <sup>c</sup>	-	-	-	-	25-40 <sup>c</sup>	9 <sup>c</sup>
PuAs	Pres. 2.9300	3.090	-2255.76	-2175.56	80.20	38	5.6
	Theo. 2.9400 <sup>i</sup>	3.110 <sup>i</sup>	-1680.00 <sup>i</sup>	-1614.21 <sup>i</sup>	65.79 <sup>i</sup>	35 <sup>i</sup>	8.6 <sup>i</sup>
	Exp. 2.9280 <sup>d</sup>	-	-	-	-	36.2 <sup>d</sup>	9 <sup>d</sup>

<sup>a</sup>Ref.[3], <sup>b</sup>Ref.[4], <sup>c</sup>Ref.[5], <sup>d</sup>Ref.[6], <sup>e</sup>Ref.[7], <sup>f</sup>Ref.[12], <sup>g</sup>Ref.[13], <sup>h</sup>Ref.[14], <sup>i</sup>Ref.[15], Pres.→Present, Theo.→Theory

Table 3. Second and third order elastic constants of actinide mono-arsenides in GPa.

Solids	$C_{11}$	$C_{12}$	$C_{44}$	$C_{111}$	$C_{112}^=$ $C_{166}$	$C_{123}^=$ $C_{144}^=$ $C_{456}$
ThAs Pres	230.84	39.88	40.13	-2066.66	-136.98	76.90
ThAs Theo.	246.24 <sup>f</sup>	41.46 <sup>f</sup>	40.46 <sup>f</sup>	-5177.57 <sup>f</sup>	-114.79 <sup>f</sup>	78.54 <sup>f</sup>
UAs Pres.	208.26	38.58	38.87	-1740.47	-131.28	73.76
NpAs Pres	145.06	35.50	36.60	-869.16	-119.10	66.91
NpAs Theo.	115.85 <sup>h</sup>	47.93 <sup>h</sup>	47.93 <sup>h</sup>	-165.10 <sup>h</sup>	-175.50 <sup>h</sup>	86.41 <sup>h</sup>
PuAs Pres.	134.92	28.24	29.63	-1121.07	-91.14	51.20
PuAs Theo.	152 <sup>i</sup>	25 <sup>i</sup>	25 <sup>i</sup>	-	-	-

<sup>f</sup>Ref.[12], <sup>h</sup>Ref.[14], <sup>i</sup>Ref.[15]

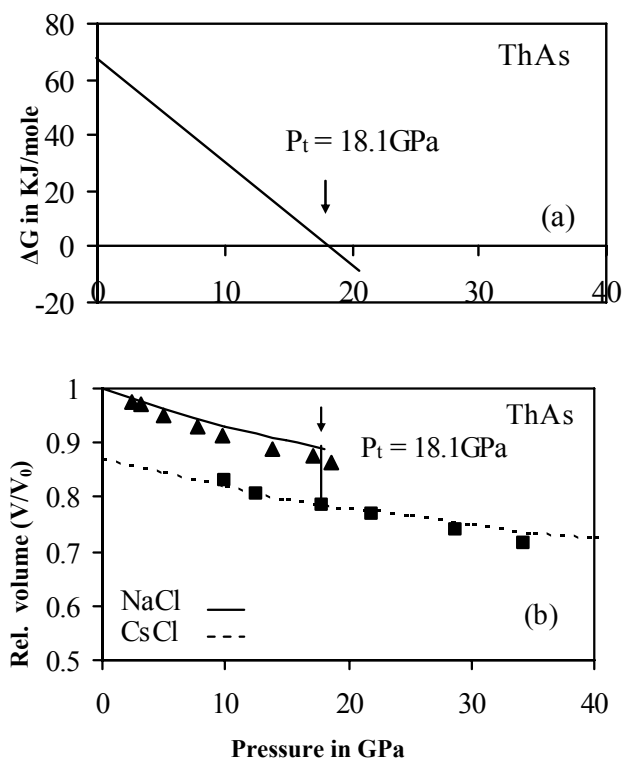


Fig.1(a) Variation of  $\Delta G$  with pressure for ThAs. (b) Compression curve for ThAs with expt. Points (▲, ■) are taken from ref. [3].

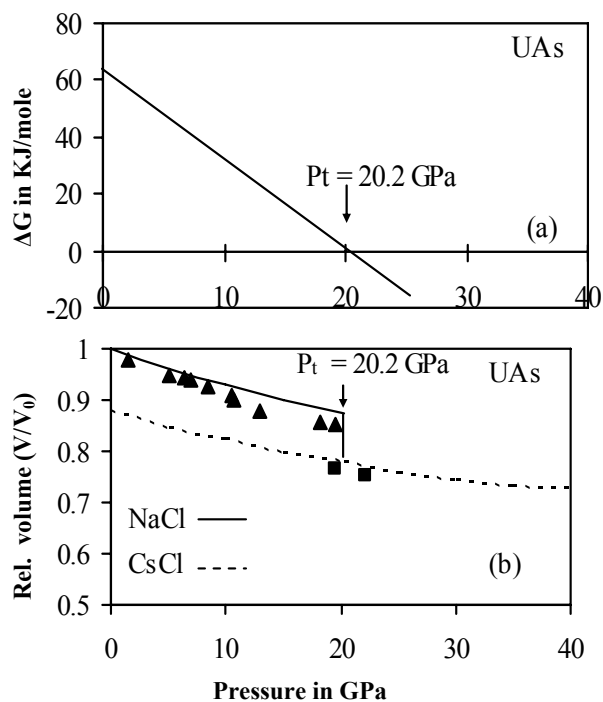


Fig. 2 (a) Variation of  $\Delta G$  with pressure for UAs. (b) Compression curve for UAs with expt. points (▲, ■), are taken from ref. [17].

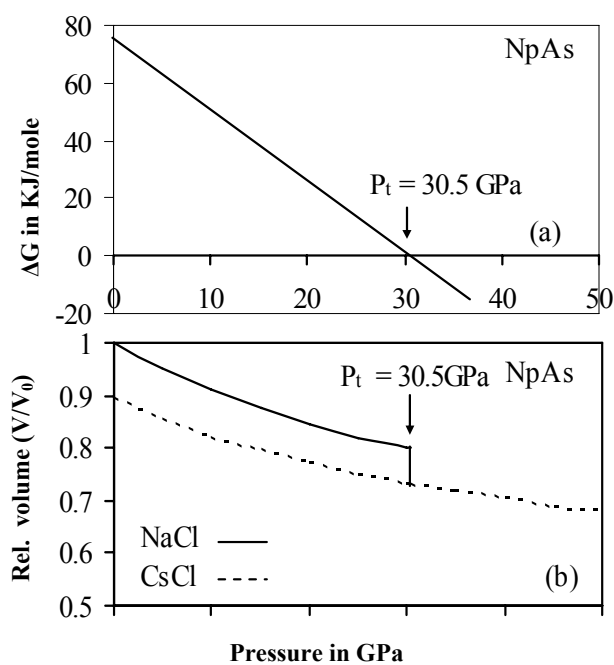


Fig.3. (a) Variation of  $\Delta G$  with pressure for NpAs. (b) Compression curve for NpAs

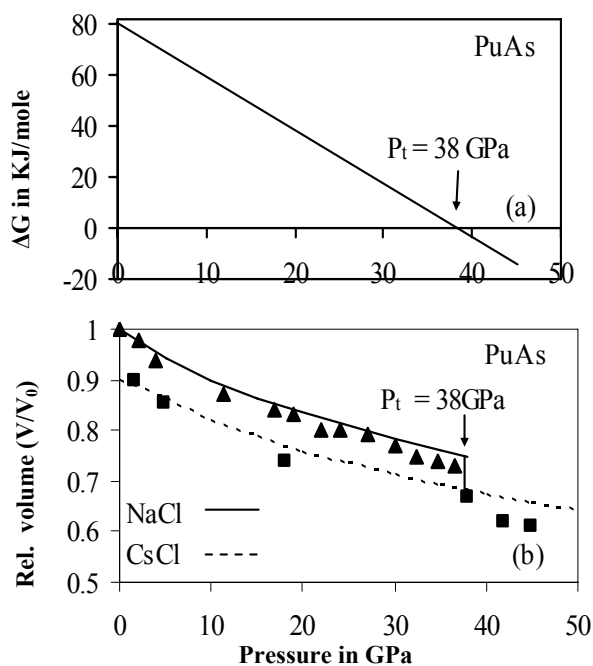


Fig. 4. (a) Variation of  $\Delta G$  with pressure for PuAs. (b) Compression curve for PuAs with expt. points (▲, ■) taken from ref. [6].

The trend of variation of transition pressure and volume in these compounds dictates that these compounds are moderately ionic and the f-electrons in these compounds are mostly localized and as such they do not interact with the lattice.

In order to study the high pressure behavior of the AnAs, we have estimated the pressure variations of the SOEC ( $C_{11}$ ,  $C_{44}$ ) and depicted them in Figures 5(a) and 5(b). It is noted from these figure that  $C_{11}$  increases linearly up to phase transition pressure. The decrease of  $C_{44}$  with applied pressure reflects the strong weakening of the bonding force constant in these compounds. This weakening of bonding force constants may be an indication that the crystals are becoming ionic with decreasing lattice separation. In Table 3, we have also reported the calculated values of second and third order elastic constants and compared them with theoretical data [12-15]. In Table 4, we have presented Bulk modulus, Shear modulus, Young's modulus, Poisson ratio and pressure derivatives of SOEC of these compounds and these results are compared with experimental and available theoretical data which show good agreement. In Table 5, we have presented variation of interionic distance at phase transformation and

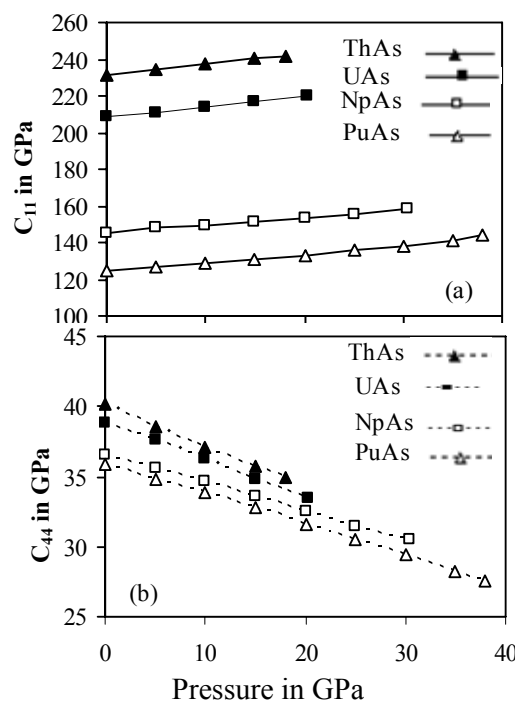


Fig.5 (a, b): Variation of second order elastic constants  $C_{11}$  and  $C_{44}$  with pressure for AnAs compounds.

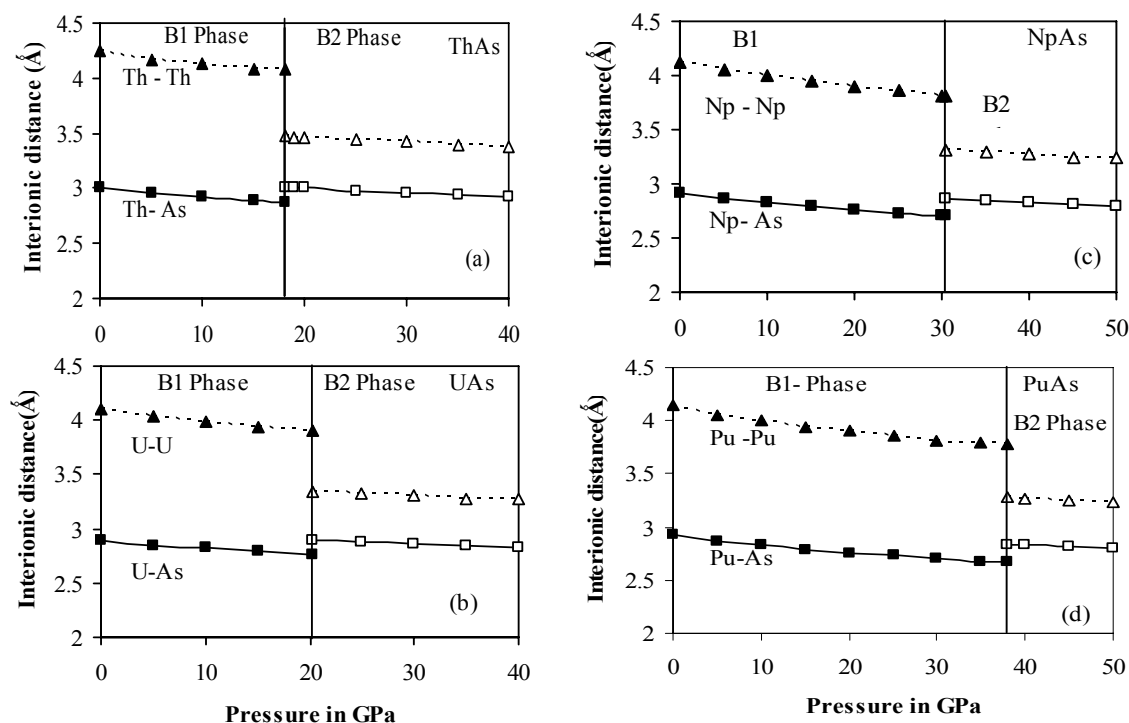


Fig. 6. Variation of interionic distance with pressure for (a) ThAs, (b) UAs, (c) NpAs and (d) PuAs

Fig.6 (a, b, c, d) shows the variation of cation - anion and cation - cation distance with pressure in ThAs, UAs, NpAs and PuAs compounds, respectively. The calculated

values of Pu-As ion distance in the NaCl type structure is 2.930Å at ambient pressure. This distance decreases on compression and at phase transition pressure reaches the

value of 2.67Å in the NaCl (B1) phase and 2.84Å in CsCl phase at ambient pressure also decreases with increase of structure phase. Pu-Pu ion distance is 4.143Å in NaCl pressure become 3.7754Å at phase transformation

Table 4. Calculated Bulk modulus ( $B_0$ ), Shear modulus ( $S'$ ), Young's modulus ( $E$ ), Poisson's ratio and Pressure derivatives of AnAs compounds.

Solids	$B_0$ (GPa)	( $dB_0/dP$ )	( $dS'/dP$ )	( $dC_{44}/dP$ )	$S'$ (GPa)	$E$ (GPa)	$\sigma$
ThAs Pres	103.54	5.40	5.91	-0.43	95.48	219.09	0.147
Theo.	109 <sup>f</sup>	5.98 <sup>f</sup>	6.67 <sup>f</sup>	-0.46 <sup>f</sup>			
Expt.	118 <sup>a</sup>	3.4 <sup>a</sup>	-	-			
UAs Present	95.15	5.28	5.70	-0.38	84.69	195.86	0.156
Expt.	98 <sup>b</sup>	-	-	-			
NpAs Present	72.02	4.83	4.85	-0.22	54.78	131.10	0.196
Theo.	70.12 <sup>h</sup>	4.18 <sup>h</sup>	3.34 <sup>h</sup>	-0.023 <sup>h</sup>			
Expt.	70 <sup>c</sup>	-	-	-			
PuAs Present	64.49	4.67	4.51	-0.14	53.34	125.14	0.173
Theo.	67	-	-	-			
Exp.	69 <sup>d</sup>	3.3 <sup>d</sup>	-	-			

<sup>a</sup>Ref.[3], <sup>b</sup>Ref.[4], <sup>c</sup>Ref.[5], <sup>d</sup>Ref.[6], <sup>e</sup>Ref.[5], <sup>f</sup>Ref.[12], <sup>h</sup>Ref.[14]

Table 5. Variation of interionic distance with pressure in AnAs compounds

Pressure	Interionic distance in ThAs		Interionic distance in UAs		Interionic distance in NpAs		Interionic distance in PuAs	
	$d_{\text{cat-an}}$	$d_{\text{cat-cat}}$	$d_{\text{cat-an}}$	$d_{\text{cat-cat}}$	$d_{\text{cat-an}}$	$d_{\text{cat-cat}}$	$d_{\text{cat-an}}$	$d_{\text{cat-cat}}$
Ambient pressure (NaCl)	3.0	4.242	2.9	4.1006	2.92	4.128	2.93 2.91 <sup>d</sup>	4.14 4.14 <sup>d</sup>
Phase transition pressure NaCl	2.88	4.072	2.76	3.9026	2.7	3.817	2.67 2.63 <sup>d</sup>	3.775 3.72 <sup>d</sup>
Phase transition pressure CsCl	3.01	3.475	2.90	3.3486	2.87	3.313	2.84 2.79 <sup>d</sup>	3.279 3.22 <sup>d</sup>

<sup>d</sup>Ref.[6], cat → cation, an → anion

and 3.2793 Å for CsCl phase. The calculated values have been compared with measured data and show a good agreement [6]. Thus it is observed that the cation-anion distance is slightly larger in B2 phase as compared to B1 phase. However cation-cation distance is lower in B2 phase as compared to B1 phase at the phase transformation. This variation of interionic distance under high pressure predicts structural phase transition from NaCl to CsCl phase is accompanied by an increase in the coordination number from six to eight, in accordance with pressure coordination rule [6]. The same analysis has been carried out for other three compounds (UAs, NpAs and ThAs) found the similar variation in the interionic distances with increasing pressure.

### Acknowledgement

The authors are grateful to Madhya Pradesh Council of Science and Technology (MPCST), Bhopal for funding this work.

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