Elastic and Structural Properties of Plutonium Pnictides

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Abstract
The structural phase transitions of plutonium pnictides (PuAs and PuSb) have been investigated. The Extented Interaction Potential (EIP) model has been developed (including the zero point energy effect in three body interaction potential model). The phase transition pressures and associated volume collapses obtained from present model show in general in good agreement with available experimental data than others. The elastic constants and modulus of elasticity are also reported.
Keywords: High pressure, Crystal structure, Elastic properties, Phase transition.

1. Introduction

Binary compounds formed by plutonium have attracted much attention owing to their unique physical and chemical properties. These properties make them interesting from the fundamental point of view, as well as for a variety of technical applications. The study of solid state properties of actinide compounds have been limited because of the care needed in handling the radioactive materials. The very small quantities of these actinides are available. Less attention has been paid on neptunium and plutonium compounds. The studies on transplutoniums are rather seldom because of the consequence of the high activity of Np and Pu and transplutonium elements [1-7]. The 5f electrons of these compounds show variable behaviour [8-10]. Plutonium pnictides are also related to the localized state of the 5f electrons.

Previously, the high pressure structural and elastic properties of plutonium compounds by using simple inter-atomic potential approach have been reported by Srivastava et. al. [11]. Electronic structures of plutonium compounds have been investigated by Petit et al. [12] using SIC-LSD scheme within the Tight-Binding Linear-Muffin-Tin Orbitals (TB-LMTO) method. The phonon dynamics of the plutonium compounds (PuX; X = S, Se, Te, As, and Sb) by using rigid ion (RIM) and breathing shell models (BSM), later includes breathing motion of the electrons of the Pu-atoms due to f–d hybridization have been investigated by Arya et. al.[13]. Present plutonium pnictides crystallize in NaCl-type structure (B1) at normal conditions with space group *Fm3m* (225). Under pressure, the present compounds undergo a first-order phase transition from the sixfold-coordinated NaCl structure to the eightfold-coordinated CsCl-type structure (B2) with the space group symmetry *Pm3m* (221).

Motivated from the fact that the earlier works have not been reported using the model calculation, we have applied our extended interaction potential (EIP) model for plutonium compounds. The necessitate inclusion of three body interaction forces was accentuated by many workers for the better corresponding of results [14-17]. Their calculations for B1-B2 transitions were stand on two-body potential mainly. They concluded that possible reason for disagreements include the failure of the two body potential model. Because these studies were based on two body potentials and could not explain Cauchy violations ($C_{12} \neq C_{44}$). They observed that results could be better by including the effect of non-rigidity of ions in the model. To overcome these inconsistencies we have incorporated the charge transfer and zero point energy effect in our model for better comparison of results. In this paper, we have investigated the structural and elastic properties of actinide pnictides.

1.1 Potential Model and Method of Calculation

Application of pressure directly results in compression leading to the increased charge transfer (or three body interaction effect [18]) due to the deformation of the overlapping electron shell of the adjacent ions (or non-rigidity of ions) in solids. Also we have considered zero point energy effects, which, is the lowest possible energy that the compound may possess. The energy of the compound is ($\varepsilon = (h\upsilon)/\{e^{h\upsilon/kt}-1\} + (h\upsilon)/2$), here υ, h, t, and k are the frequency, plank constant, temperature and Boltzaman constant of the compound. It is clear from the above expression that even at absolute zero the energy of the compound cannot be zero but at least h   . Hence there arises a need to include the zero point energy term in TBP approach for better agreement with experimental approaches.

These effects have been incorporated in the Gibbs free energy (G = U+PV-TS) as a function of pressure

and three body interactions (TBI) [13], which are the most dominant among the many body interactions. Here, U is the internal energy of the system equivalent to the lattice energy at temperature near zero and S is the entropy. At temperature T=0K and pressure (P) the Gibbs free energies for rock salt (B1, real) and CsCl (B2, hypothetical) structures are given by:

$$G_{B1}(r) = U_{B1}(r) + PV_{B1}(r) \qquad (1)$$
$$G_{B2}(r') = U_{B2}(r') + PV_{B2}(r') \qquad (2)$$

With $V_{B1}(=2.00r^3)$ and $V_{B2}(=1.54r'^3)$ as unit cell volumes for B_1 and B_2 phases respectively. The first terms in (1) and (2) are lattice energies for B_1 and B_2 structures and they are expressed as:

$$
\begin{aligned}
U_{B_1}(r) = {} & \frac{-\alpha_m z^2 e^2}{r} - \frac{(12\alpha_m z e^2 f(r))}{r} - \left[\frac{C}{r^6} + \frac{D}{r^8}\right] \\
& + 6b\beta_{ij}\exp[(r_i + r_j - r)/\rho] + 6b\beta_{ii}\exp[(2r_i - 1.414r)/\rho] \\
& + 6b\beta_{jj}\exp[(2r_j - 1.414r)/\rho] + (0.5)h\langle\omega^2\rangle^{1/2}{}_{B_1}
\end{aligned}
\qquad (3)
$$

$$
\begin{aligned}
U_{B2}(r') = {} & \frac{-\alpha'_m z^2 e^2}{r'} - \frac{(16\alpha'_m z e^2 f(r'))}{r'} - \left[\frac{C'}{r'^6} + \frac{D'}{r'^8}\right] \\
& + 8b\beta_{ij}\exp[(r_i + r_j - r')/\rho] + 3b\beta_{ii}\exp[(2r_i - 1.154r')/\rho] \\
& + 3b\beta_{jj}\exp[(2r_j - 1.154r')/\rho] + (0.5)h\langle\omega^2\rangle^{1/2}{}_{B_2}
\end{aligned}
\qquad (4)
$$

With α_m and α'_m as the Madelung constants for NaCl and CsCl structure respectively. C(C') and D(D') are the overall Vander Waal coefficients of B1 (B2) phases, β_{ij} (i,j=1,2) are the Pauling coefficients. Ze is the ionic charge and b (ρ) are the hardness (range) parameters, r (r') are the nearest neighbour separations for NaCl (CsCl) structure $f(r)$ is the three body force parameter.

The term $\langle\omega^2\rangle^{1/2}$ as the mean square frequency related to the Debye temperature (θ_D) as

$$\langle\omega^2\rangle^{1/2} = k\theta_D/h \qquad (5)$$

Here, θ_D can be expressed as [13,14]

$$\theta_D = (h/k)[(5rB_T)/\mu]^{1/2}$$

With B_T and μ as the Bulk modulus and reduced mass of the compounds.

These lattice energies consists of long range Coulomb energy (first term), three body interactions corresponding to the nearest neighbour separation r (r') (second term), vdW (van der Waal) interaction (third term), energy due to the overlap repulsion represented by Hafemeister and Flygare (HF) type potential and extended up to the second neighbour ions (fourth, fifth and sixth terms), and last term indicates zero point energy effect term.

1.1.1 Results and Discussion
1.1.2 Structural properties

The Gibbs free energies in eq. (1) and (2) contain three model parameters [b, ρ, $f(r)$]. The values of these model parameters have been computed using the following equilibrium conditions.

$$\left[\frac{dU}{dr}\right]_{r=r_0} = 0 \qquad (6)$$

and the bulk modulus

$$\left[\frac{d^2U}{dr^2}\right] = 9kr_0B \qquad (7)$$

Using these model parameters and the minimization technique, phase transition pressures of present compounds have been computed. The input data of the crystal and calculated model parameters are listed in Table-1.

We have followed the technique of minimization of Gibbs free energies of real and hypothetical phases. Then we have calculated the Gibbs free energy change (ΔG) of B1 and B2 phases. The phase transition occurs when ΔG approaches zero ($\Delta G \rightarrow 0$). At phase transition pressure (P_t) these compounds undergo a (B1-B2) transition associated with a sudden collapse in volume showing a first order phase transition. The values of ΔG with pressure have been plotted in Fig. 1. It is clear from this figure that our present computed phase transition pressure for B1-B2 structure transition in PuAs at 35.5 GPa, and PuSb at 21.0 GPa respectively. The present phase transition pressures have been illustrated by arrows in Fig. 1. The computed phase transitions pressures (P_t), obtained from the present model, and are given in Table-2.

At high pressures, the materials undergo structural phase transition associated with an abrupt change in the volume. The discontinuity in volume at the transition pressure is obtained from the phase diagram. We have computed the relative volume changes V/V_0 at different pressures. The values of volume change (%) have been tabulated in Table-2. The values of V/V_0 have been plotted against the pressure in Fig. 2 for PuAs and in Fig. 3 for PuSb. The variations of V/V_0 with pressure for NaCl and CsCl phases have been studied in these graphs and compared with experimental results for both PuAs and PuSb. It is clear from this graph that when we increase the pressure the values of V/V_0 decrease. It is obvious from Table-2 that the computed values of phase transitions and volume collapses have been compared with available experimental and theoretical results. Our values shows better comparisons with experimental than other theoretical results.

1.1.3 Elastic properties

Elasticity is the fundamental property of a material. When an elastic material is deformed due to an external force, it experiences internal forces that oppose the deformation and restore it to its original state if the external force is no longer applied. To study the elastic properties of present compounds the calculations of second order elastic constants is needed. The knowledge of second order elastic constants (SOECs) and their pressure derivatives are important for the understanding of the interatomic force in solids. The expressions of second order elastic constants are given in our earlier works [15-20].

The expressions of second order elastic constants are as follows:

$$C_{11} = (e^2/4a^4)[-5.112Z(Z+12f_m(r)) + A_1 + (A_2+B_2)/2 + 9.3204zaf_m'(r)] \quad (7)$$

$$C_{12} = (e^2/4a^4)[0.226Z(Z+12f_m(r)) - B_1 + (A_2-5B_2)/4 + 9.3204zaf'_m(r)] \quad (8)$$

$$C_{44} = (e^2/4a^4)[2.556Z(Z+12f_m(r)) - B_1 + (A_2+3B_2)/4 \quad (9)$$

Using model parameter (b, ρ, $f(r)$), pressure derivatives of bulk modulus have been computed whose expressions are as follows:

$$\frac{dB}{dp} = -(3\Omega)^{-1} \begin{bmatrix} 13.980Z(Z+12f_m(r)) + C_1 - 3A_1 + C_2 - 3A_2 \\ -167.7648zaf_m'(r) + 41.9420za^2f_m(r)] \end{bmatrix} \quad (10)$$

$$B = \frac{1}{3}(C_{11} + 2C_{12}), \quad S = \frac{1}{2}(C_{11} - C_{12})$$

and

$$\Omega = -2.330Z(Z+12f_m(r)) + A_1 + A_2 + 21.9612zaf_m'(r)$$

The values of A_i, B_i, and C_i (i =1, 2) have been evaluated from the knowledge of b, ρ and vdW coefficients.

We have calculated the values of the second order elastic constants (SOEC's) of the materials under study. Also, we could reproduce the correct sign of the elastic constants (C_{11}-C_{12}). The study of SOEC's under pressure is important as C_{11} represents elasticity in length and C_{12} and C_{44} are shape related elastic constants. The second order elastic constants (SOEC's) and pressure derivatives of plutonium pnictides have also been calculated by using eq. (7-10). The computed values of SOEC's are given in Table-3. We have compared our results with available experimental [12] and theoretical results [11]. It is clear from this table that our values show a better agreement with experimental results compared with theoretical results.

In the overall attainment, it may be concluded that there is reasonably good agreement of the present extended interaction potential (EIP) model with the results of other theoretical data. The charge transfer effect seems to be of great importance at high pressure when the inter-ionic separation reduces considerably and the coordination number increases.

Finally, it may be concluded that the present model is adequately suitable for describing the phase transition phenomena and elastic properties of PuAs and PuSb under high temperature and pressure. The

inclusion of three body interactions and zero point energy effect has improved the prediction of phase transition pressures.

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Table-1 Input data and calculated model parameters for PuAs and PuSb.

Solid	Input Parameters		Model Parameters		
	r_0 (Å)	B (GPa)	b(10^{-12} ergs)	ρ(Å)	f (r)
PuAs	2.92[a]	69[b]	12.0748	0.198	0.1023
PuSb	3.12[a]	68[b]	10.9256	0.212	0.1147

a-ref [6], b-ref [12]

Table-2 Phase transition and volume change of plutonium pnictides.

Solid	Phase Transition Pressure (GPa)			Volume Collapse %		
	Present	Expt.	Others	Present	Expt.	Others
PuAs	35.5	35-38[a]	35.0[b]	8.7	9.0[a]	8.6[b]
PuSb	21.0	20[a],40[a]	20.8[b]	7.2	4.0[a], 9.0[a]	6.9[b]

a-ref [2], b-ref [11]

Table-3 Calculated values of second order elastic constants (SOEC's) (in GPa), bulk modulus (in GPa), and pressure derivative of bulk modulus of plutonium pnictides.

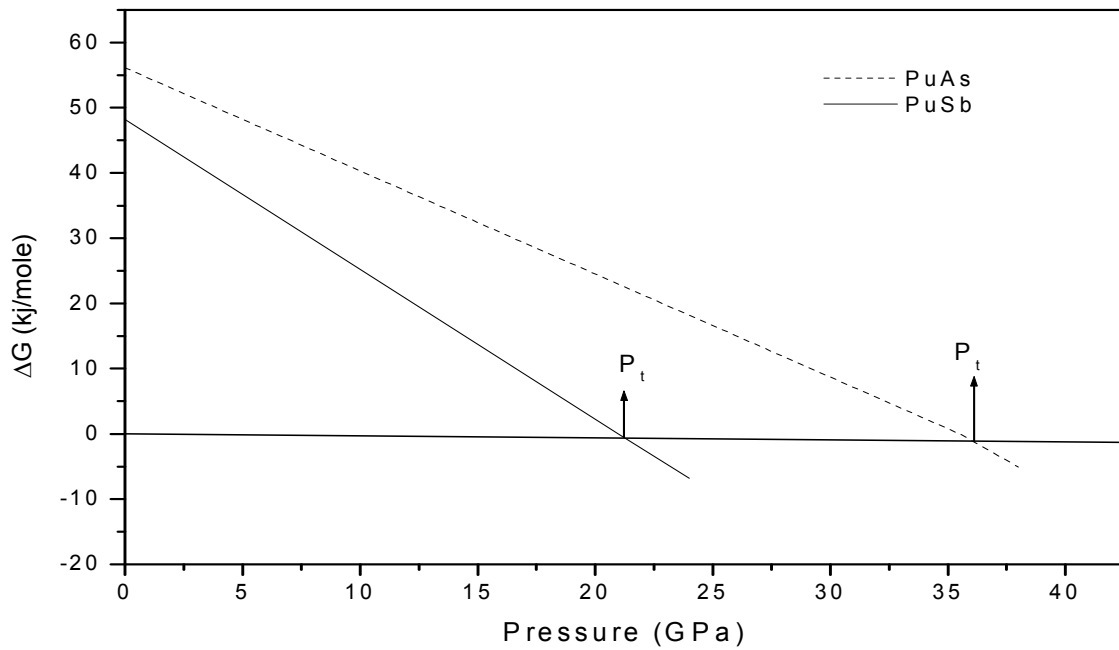| Solid	C_{11}	C_{12}	C_{44}	B	dB/dP
PuAs	150	27	31	68	2.01
Others	152[a]	25[a]	25[a]	67[a]	-
Expt.	-	-	-	69[b]	-
PuSb	155	25	29	68.33	1.91
Others	158[a]	21[a]	21[a]	67[a]	-
Expt.	-	-	-	68[b]	-

a-ref [11], b- ref [12]

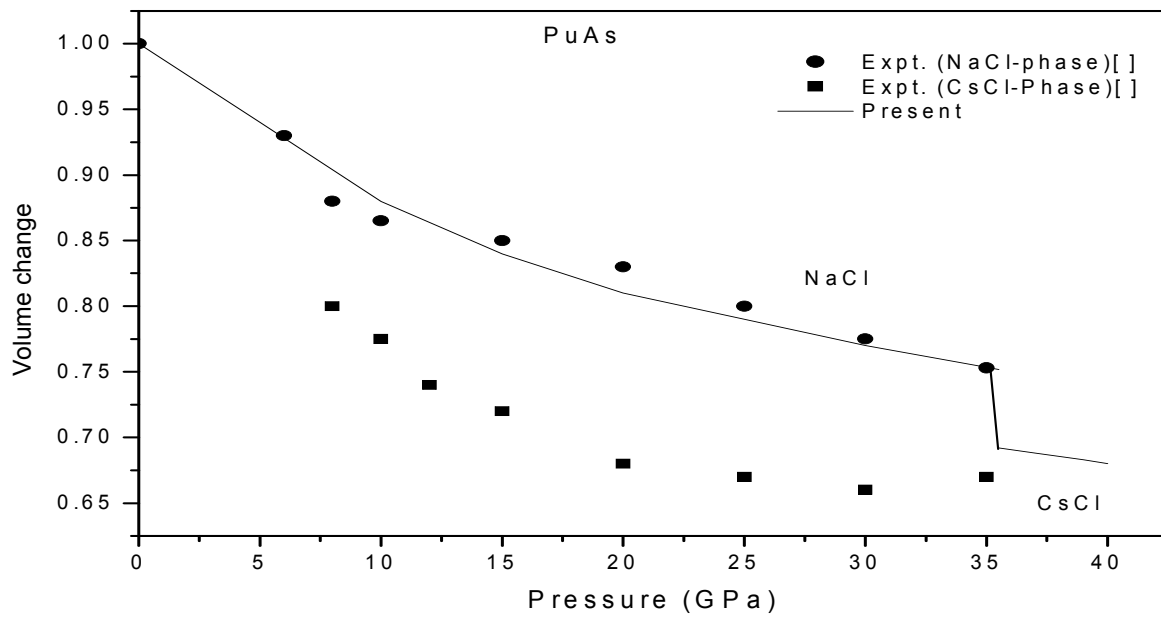Figure 1. The variation of Gibbs free energy change with pressure.

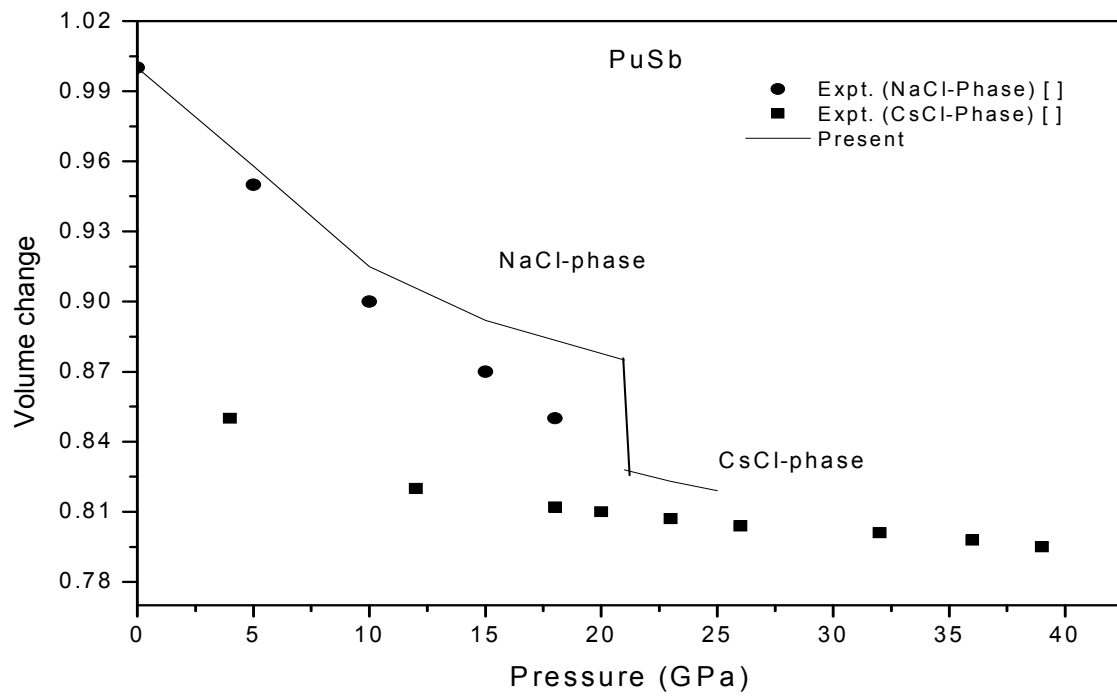Figure 2. The variation of volume change with pressure for PuAs.

Figure 3. The variation of volume change with pressure for PuSb.

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