

High Pressure Structural and Elastic Properties of Neptunium Arsenide

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Abstract. High pressure structural and elastic properties of neptunium arsenide (NpAs) have been studied using three body interaction potential (TBIP). The three body interaction arises from the electron-shell deformation when the nearest –neighbor ions overlap. The equation of state of NpAs has been calculated and compared with high pressure X-ray diffraction data. The theoretically predicted phase transition pressure and other structural properties agree reasonably well with the measured values. The second and third order elastic constants, second order pressure derivatives and variation of second order elastic constants (SOEC) with pressure is also presented.

Key words: Phase transition, Elastic properties, High pressure.

INTRODUCTION

Over few decades, high pressure structural and elastic behavior of the actinide mono-chalcogenides and pnictides have been studied by many theoretical and experimental researchers because of their diverse structural, transport, magnetic and phonon properties. They crystallize in NaCl –type structure at ambient pressure and their f -electrons are localized [1]. The $5f$ electrons in the actinide elements show variable behavior, depending on the particular element, the material and the specific conditions being considered [2]. High pressure X- ray diffraction studies have been performed by S. Dabos et al [3] at room temperature on NpAs up to 53 GPa. This compound undergoes a structural phase transition from NaCl structural phase (B1) to CsCl structural phase (B2) at 37GPa with volume collapse 9%. In neptunium metal, $5f$ electrons are itinerant. In some of its compounds they are close to itinerancy, which can sometimes be induced by applying moderate pressure. Other neptunium compounds, in contrast, are quite far from the Hill limit which separates neptunium compounds with localized $5f$ states from itinerant systems [4]. Prafulla K. Jha et al [5] have reported high pressure structural and elastic properties of neptunium compounds (NpSe, NpTe and NpAs) by using a two body interionic potential approach. Devraj et al [6] have been investigated mechanical and thermophysical properties of neptunium mono-pnictides using Coulomb and Born-Mayer potential up to second nearest neighbor in the temperature range 0-300K. However, very little theoretical attempts have been made to reveal the nature of bonding, ion-ion and ion-electron interactions, elastic properties in NpAs. The two body potential leads to the Cauchy relation ($C_{12} = C_{44}$), which is strongly violated by the experimental values of the elastic constants used by Catlow et al and Ghosh and Dasgupta [7-8]. In order to eliminate this drawback from the two body potential, one is compelled to incorporate the effect of many-body interactions, which take proper account of the Cauchy violation and existence from quantum [9]. The three body interaction potential (TBIP) has yielded somewhat more realistic predictions of the phase transition and high-pressure structural behavior as compared to those derived from the usual two-body potential based on phenomenological [5, 6]. In the present paper, we report the calculated results on structural phase transitions and elastic properties using a theoretical model based on three body interaction potential approach in the frame work of rigid ion model at high pressure [10-11]. As the study of elastic behavior under pressure is well to provide useful information about changes in the nature of ionic forces

induced in the crystal as it subjected to the phase transformation, we, therefore, have calculated the pressure variation of C_{11} and C_{44} [11]. We have expressed the brief outline of the method of calculation for predicting the structural and elastic properties and the results and discussions in the following sections.

THE THEORETICAL MODEL

The three body inter-ionic potential (TBIP) for the neptunium arsenide (NpAs) in the framework of the rigid ion model is expressed as [12]

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

which includes long-range Coulomb (first term), three body interaction (2nd term), Hartee –Fock (H.F.) form of short-range repulsive (3rd term) and van der Waals multipole (4th and 5th terms) interactions energies, respectively. Where β_{ij} (i,j=1,2) are the Pauling coefficients. Ze is ionic charge. This potential has three model parameters b(hardness), ρ (range) and $f(r_{ik})$ (three body force interaction). The TBI parameter $f(r_{ik})$ is a measure of the overlap between the adjacent ions. They can be determined from the knowledge of lattice parameters, bulk modulus, second order elastic constants 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 required expressions for the second order and third order constants for NaCl phase are reported elsewhere [12-13]. The TBI parameter has the functional form

$$f(r) = f_0 \exp(-r_{ij} / \rho_{ij}) \quad (3)$$

The higher order derivatives of $f(r)$ can be evaluated by assuming the above functional form. Moreover, this parameter has been considered structure dependent.

The neptunium arsenide 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

$$G = U + PV - TS \quad (12)$$

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

$$G_{B1}(r) = U_{B1}(r) + 2Pr^3 \quad (13)$$

for NaCl (B1) and

$$G_{B2}(r') = U_{B2}(r') + (8/3\sqrt{3})Pr^3 \quad (14)$$

for CsCl (B2) phases become equal at the phase transition pressure P_t at temperature 0K, i.e. $\Delta G = (G_{B1} - G_{B2})$ becomes zero. Such a theoretical approach has been found to predict most of the crystal properties of barium chalcogenides [12] satisfactorily. 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 used by us are reported elsewhere [11,12]. The expression for the bulk modulus (B_0), tetragonal shear modulus S, Young modulus (E) and Poisson's ratio (σ) are

$$B_0 = (C_{11} + 2C_{12})/3, \quad S = (C_{11} - C_{12})/2 \\ E = (C_{11} - C_{12})(C_{11} + 2C_{12}) / (C_{11} + C_{12}); \quad \sigma = C_{12} / (C_{11} + C_{12}) \quad (15)$$

RESULTS AND DISCUSSION

The structural and elastic properties of neptunium arsenide have been calculated at high pressure using the methodology outlined above. The required input data and derived model parameters for NpAS are presented in Table 1. We have presented the phase transition properties of NpAs and compared our results with the available

experimental [3] and other theoretical data [5] in Table 2. It is seen from Table 2 that the present model has correctly predicated the stability of competitive phases as the value of $\Delta U (= U_{B2} - U_{B1})$ is positive, which is a required criterion of stability of structure [14]. Also, the value of the equilibrium separation (r_0) obtained by us from minimization technique is in good agreement with their experimental data [3]. In Fig.1 (a), we have plotted the energy difference (ΔG) with pressure graph, which has zero value at phase transition pressures 34GPa for NpAs compound. In Fig.1 (b), we have plotted the equation of states for NpAs at various pressures and compared with the experimental data [3] shows reasonably good agreement. We have calculated the volume discontinuity at phase transition pressure with associated volume collapse 7%, and compared them with experimental data [3].

Table1: Input data and model parameters of neptunium arsenide (NpAs)

Solids	Input data				Model parameter		
	$r_+(\text{Å})$	$r_-(\text{Å})$	$r_0(\text{Å})$	$B_0(\text{GPa})$	$f(r)$	$b(10^{-19}\text{J})$	$\rho(\text{Å})$
NpAs	0.91	1.20	2.9183 ^a	70 ^a	-0.0376	11.94	0.311

^aRef.[3],

TABLE 2: Cohesive energy and phase transition properties of neptunium arsenide(NpAs).

Solids		Equilibrium interionic separation (Å)		Cohesive energy (KJ/mole)		Change in cohesive energy in (KJ/mole)	Phase Trans. Pres. (GPa)	Relative volume change in %
		$R_1(B1)$	$R_2(B2)$	$U_1(B1)$	$U_2(B2)$	ΔU	P_T	$\Delta V/V_0$
NpAs	Pres	2.9200	3.070	-2339.03	-2256.29	82.74	34	7
	Exp	2.918 ^a	-	--	-	-	37 ^a	9 ^a
	Theo	2.930 ^b	3.070	-2924.57	-2847.34	77.23 ^b	28.2 ^b	8.6 ^b

^aRef.[3], ^bRef.[5],

TABLE 3: Second order elastic constants and bulk modulus (K) in GPa and pressure derivatives of neptunium arsenide (NpAs).

Solids		C_{11}	C_{12}	C_{44}	B_0	dB_0/dP	dS/dP	dC_{44}/dP
NpAs	Pres	144.02	34.4	36	70.94	4.84	486	-0.2220
	Exp	-	-	-	70 ^a	-	-	-
	Theo	47.0 ^c	12.7	12.7 ^c	-	-	-	-
	Theo	-	-	-	70.12 ^b	4.18 ^b	3.34 ^b	-0.023 ^b

^aRef.[3], ^bRef.[5], ^cRef.[6]

In order to study the high pressure elastic behavior of the NpAs, we have estimated the pressure variations of the SOEC (C_{11} , C_{44}) and depicted them in Figure 3. It is noted from this 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. The trend of variation of C_{11} , C_{44} with pressure are same as result predicted by Singh et al [13]. In Table 3, we have also reported the calculated values of second order elastic constants, bulk modulus and pressure derivatives and compared them with experimental and theoretical data [3, 5, 6].

TABLE 4: Third order elastic constants (TOEC), Young Modulus (E) in GPa and Poisson's ratio (σ) of neptunium arsenide (NpAs).

Solids		C_{111}	$C_{112}=C_{166}$	$C_{123}=C_{144}=C_{456}$	E	σ
NpAs	Pres	- 1107.68	- 104.42	58.66	130.75	0.1928
	Theo.	-165.10 ^b	-175.50 ^b	-86.41 ^b	-	-

^bRef.[5]

In Table 4, we have presented third order elastic constants, Young's modulus, Poisson's ratio of these compounds. We have compared our predicted values which are more close to experimental than other theoretical

data. Therefore TBIP model is more suitable to explain the structural and mechanical properties of these compounds as compared to two body interionic potential rigid ion model.

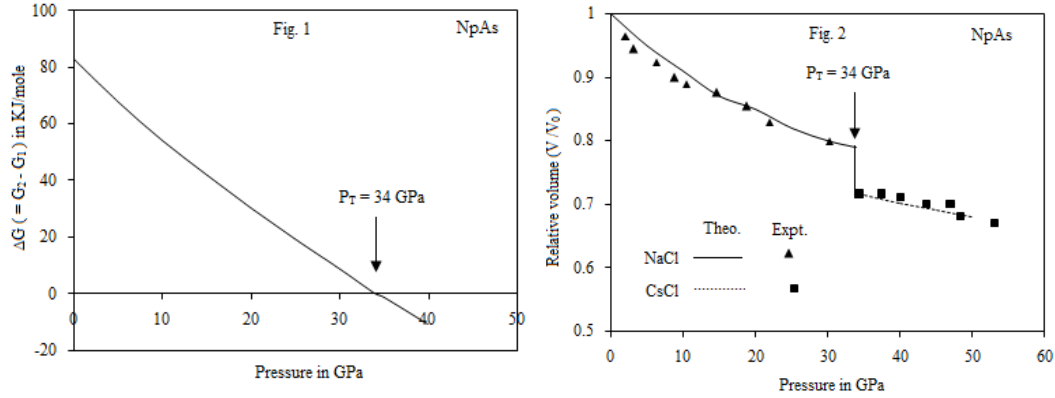


FIGURE 1. Variation of ΔG with pressure of NpAs. **FIGURE 2.** Equation of states of NpAs. (\blacktriangle), (\blacksquare), are the experimental data [3] corresponding to B1 and B2 phases, respectively.

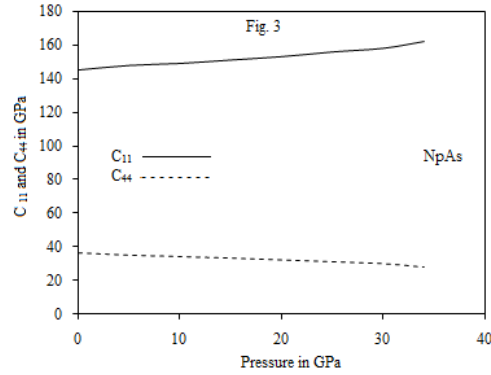


FIGURE 3. Variation of second order elastic constants (C_{11} and C_{44}) with pressure of NpAs

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