

STRUCTURAL PHASE STABILITY AND HALF-METALLIC BEHAVIOUR OF ACTINIDE BISMUTHIDES (UBi and NpBi)

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Abstract

The structural phase stability and mechanical properties of two mono-bismuthides (UBi and NpBi) are investigated by using an improved interaction potential model (IIPM), employing the minimization technique of Gibbs free energy expressed as a function of pressure. These compounds undergo phase transition from rocksalt type (B1) to tetragonal (distorted CsCl-type, P4/mmm) structure. The calculated values of phase transition pressure and associated volume collapse are found to be well suited with experimental values. We have also calculated the mechanical and thermophysical properties of UBi and NpBi.

Keywords: phase transition; three body interaction; volume collapse; elastic properties.

Introduction

The uniqueness of rare-earth (RE) has been interesting in theoretical and experimental studies of rare-earth compounds (REX) with NaCl (B1) structure [1]. The study of actinide compounds (AnY) with NaCl (B1) structure are very interesting in theoretical and experimental work. These compounds exhibit a rich variety of electronic and magnetic properties, which can be interpreted in terms of mixed valence or valence fluctuations that come from the partially filled 5f electrons in An-atom of rare earth ions [2]. The phase transition of CuBi and UBi from B1 to BCT transition around 8.5 GPa with volume collapse 12% and isothermal bulk moduli (BT) also observed to be 145 GPa at ambient pressure are reported experimentally by using X-ray diffraction method [3]. The phase transition and volume collapse of PuBi is studied by Petit et. al. [4] using SIC-LSD scheme technique. The structural study of PuBi from NaCl to body centered tetragonal structure using X-ray diffraction technique is reported by Meresse et. al. [5]. Structural, mechanical and thermal properties of NpBi and PuBi is investigated by Ahirwar et. al. [6] using modified inter-ionic potential theory (MIPT). Benedict et. al. [7]. calculated the lattice parameter ($a_0=6.3732\text{\AA}$) of NpBi. Using two body potential model Pagare et. al. [8] determined the phase transformation of four bismuthides (CeBi, PrBi, UBi and PuBi).

It is interesting to study effect of pressure on actinide bismuthides. In the present study we have investigated the phase transition in uranium and neptunium bismuthides which

crystallize in NaCl to distorted CsCl structure. From the survey of various literatures it is clear that no study is done on UBi and NpBi using the improved interaction potential model (IIPM). Consequently, the main purpose of this work is to provide additional information to the existing data on the mechanical and thermal properties of UBi and NpBi by using improved interaction potential model (IIPM) for the betterment of the results[9].

Computational Methods

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. 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. At temperature $T = 0\text{K}$ and pressure P the Gibbs free energies for NaCl (B1) and BCT structures are given by:

$$G_{B1}(r) = U_{B1}(r) + PV_{B1} \quad (1)$$

$$G_{BCT}(r') = U_{BCT}(r') + PV_{BCT} \quad (2)$$

with V_{B1} and V_{BCT} as the unit cell volumes for B1 and BCT phases, respectively. The first terms in the R.H.S of equation (1) and (2) are lattice energies for B1 and BCT structures.

$$U_{B1}(r) = [-(\alpha_m z^2 e^2)/r] - [(12\alpha_m z e^2 f(r))/r] + (e^2 \alpha_c)/r^4 + 6b\beta_{ij} \exp[(r_i + r_j - r)/\rho] + 6b\beta_{ij} \exp[(2r_i - 1.41r)/\rho + 6b\beta_{ij} \exp [(2r_j - 1.41r)/\rho] \quad (6)$$

$$U_{BCT}(r') = [-(\alpha'_m z^2 e^2/r')] - [(16\alpha'_m z e^2 f(r'))/r'] + (e^2 \alpha_c)/r'^4 + 8b\beta_{ij} \exp [(r_i + r_j - r')/\rho] + 2b\beta_{ii} \exp [(2r_i - r')/\rho] + b\beta_{ii} \exp [(2r_i - r'')/\rho] + 2b\beta_{ij} \exp [(2r_j - r')/\rho] + b\beta_{ij} \exp[(2r_j - r'')/\rho] \quad (7)$$

Here, ze is the ionic charge, r_i (r_j) is the ionic radii of i (j) ions, ρ is the range parameter, b is the hardness parameter, $f(r)$ is the three body interaction parameter, r is nearest neighbor (nn) separation for NaCl phase and r' and r'' are the nearest neighbour distances corresponding to lattice parameters a and c in tetragonal structure and β_{ij} is the Pauling coefficients defined as

$$\beta_{ij} = 1 + \frac{z_i}{n_i} + \frac{z_j}{n_j}$$

where, z_i (z_j) and n_i (n_j) denote the valence and number of electrons in the outermost orbit of cations (anions). These lattice energies consist of long-range Coulomb energy (first term), three body interactions (second term), the electronic polarizability (third term) and the short range overlap repulsive interaction (fourth term). To calculate these parameters, we have employed the following equilibrium conditions.

$$[dU / dr]_{r=r_0} = 0 \quad \text{and} \quad [d^2 U / dr^2] = 9k r_0 B_T \quad (8)$$

To understand elastic properties of these mono-pnictides, we have calculated second order elastic constants (SOEC) C_{11} , C_{12} and C_{44} and their pressure derivatives at 0 K, since these elastic constants are functions of first and second order derivatives of short range potential, so their calculation will provide knowledge about the effect of short range forces on these materials following Shankar et al. [10]. The expression for SOEC is given as:

$$C_{11} = e^2/4r_0^4 [- 5.112z \{z+12f(r)\} + A1 + (A2 + B2)/ 2] + 9.30z \quad (9)$$

$$C_{12} = e^2/4r_0^4 [1.391z \{z + 12f(r)\} + (A2 - B2)/4 + 9.30z \quad (10)$$

$$C_{44} = e^2/4r_0^4 [2.556z \{z+12f(r)\} + B1 + (A2 + 3B2)/ 4] \quad (11)$$

The Zener anisotropy factor A , Poisson ratio ν , Young's modulus Y and Kleinman parameter ξ , which are the most interesting elastic properties for technological applications, are also calculated in terms of the computed data using the following relations :

$$A = \frac{2C_{44}}{(C_{11} - C_{12})} \quad (12)$$

$$\nu = \frac{1}{2} \left[\frac{(B - \frac{2}{3}G)}{(B + \frac{1}{3}G)} \right] \quad (13)$$

$$Y = \left[\frac{9GB}{G + 3B} \right] \quad (14)$$

$$\xi = \frac{C_{11} + 8C_{12}}{(7C_{11} + 2C_{12})} \quad (15)$$

where $G = (G_V + G_R) / 2$ is the isotropic shear modulus, G_V is Voigt's shear modulus corresponding to the upper bound of G values, and G_R is Reuss's shear modulus corresponding to the lower bound of G values, and can be written as $G_V = (C_{11}-C_{12} + 3C_{44})/5$, and $5/G_R = 4/(C_{11}-C_{12})+ 3/ C_{44}$. Kleinman parameter describes the relative positions of the cation and anion sublattice under volume conserving strain distortions for which positions have not fixed by symmetry. Harrison [11] defines the internal displacement parameter slightly differently from Klein man. However, the physical meanings of the ξ depend to each other. Instead of a uni-axial strain, a pure shear strain applied to the crystal. The total energy is a contribution of bond stretching term and bond bending term. The

derived in terms of crystals elastic parameters, C_{11} and C_{12} . According to Harrison the range of ξ is from $-1/2$ to 1 . if $\xi = -1/2$, when there is no energy cost associated with bond stretching and if $\xi = 1$ when there is no energy cost for bond

Table 1: Input parameters and model parameters

Compounds	Input Parameters		Model Parameters		
	r_0 (Å)	B_T (GPa)	b (10^{19} J)	ρ (Å)	$f(r)$
UBi	3.1813	91 ^a	19.559	0.583	0.06217
NpBi	3.186	145 ^b	32.637	0.745	0.08138

a. Ref. [3], b. Ref. [7]

Table 2: Calculated transition pressures and volume collapses of UBi and NpBi

Compounds	Transition Pressure (GPa)		Volume Collapses (%)	
	Present	Exp. and other	Present	Exp. and other
UBi	9.7	10 ^a and 10 ^b	11	11 ^a and 13.7 ^b
NpBi	8.7	8.5 ^c and 9 ^d	10	12 ^c and 12 ^d

a. Ref. [3], b. Ref. [8], c. Ref. [7], d. Ref. [6]

bending. Our values are also in above limit. The calculated Zener anisotropy factor (A), Poisson ratio (ν), Young’s modulus (Y), and Shear modulus (S) are given in Table 3.

The thermo physical properties provide us the interesting information about the compounds. We have calculated thermo physical properties of UBi and NpBi compounds and listed them in Table 4. The Debye characteristic temperature (θ_D) reflects its structure, stability, the bond strength between its separate elements, structure defects availability and its density. We have also computed molecular force constant (f), infrared absorption frequency (ν_0), Gruneisen parameter (γ) and ratio of volume expansion coefficient (α_v) to specific heat (C_v) at constant volume which are directly derived from the cohesive energy U(r). The expressions have been given in earlier paper [12]. In terms of molecular force constants

$$f = \frac{1}{3} \left[U_{kk'}^{SR}(r) + \frac{1}{2} U_{kk'}^{SR}(r) \right]_{r=r_0}$$

(16)

Result and Discussion

Pressure induced phase transition

To examine the stableness of the B1 (NaCl) structure and body-centred tetragonal (BCT) structure, we have followed the technique of minimization of Gibbs free energies of real and hypothetical phases. When ΔG approaches zero ($\Delta G \rightarrow 0$) then the phase transition arises. The compound transform from B1 (NaCl) structure to body-centred tetragonal (BCT) structure associated with a volume collapse at a phase transition pressure (Pt), showing a first-order phase transition. Using the measured values of the equilibrium lattice constant (r_0) and bulk modulus (B_T) with $K=2$ for B1 phase, the model parameters thus calculated are given in Table 1. and are used to compute the results presented and discussed below. For simplicity, we have taken account of only a single set [ρ , b , $f(r)$] in B1-phase and the same set is used in BCT phase. Then we have plotted ΔG against pressure as shown in Fig.1. for UBi and NpBi. The present phase transition pressure is illustrated by arrow in Fig.1. The calculated values of phase transition pressure 9.7 GPa & 8.7 GPa and volume collapse are 11% & 10 % for UBi and NpBi are listed in Table 2 and compared with their experimental and other theoretical results. It is interesting to note from Table 2 and Fig.2. that the phase transition pressures (Pt), obtained from our model, are in general in closer agreement with experimental data [3, 7] and match equally well with other theoretical results[8, 6].

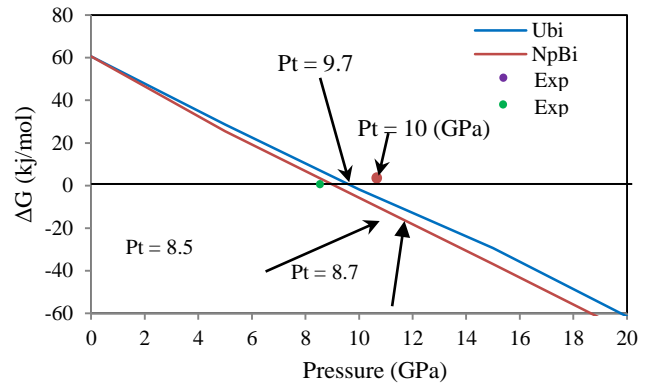


Fig.1. Variation of ΔG with Pressure

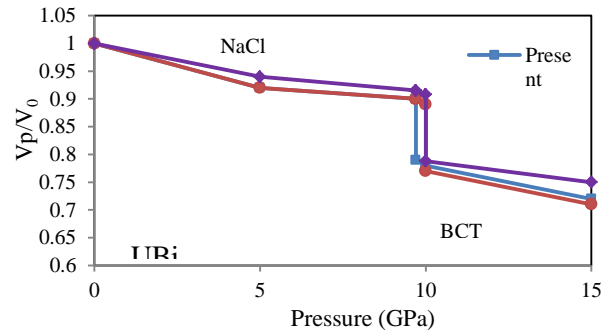


Fig.2. Variation of V_p/V_0 with Pressure

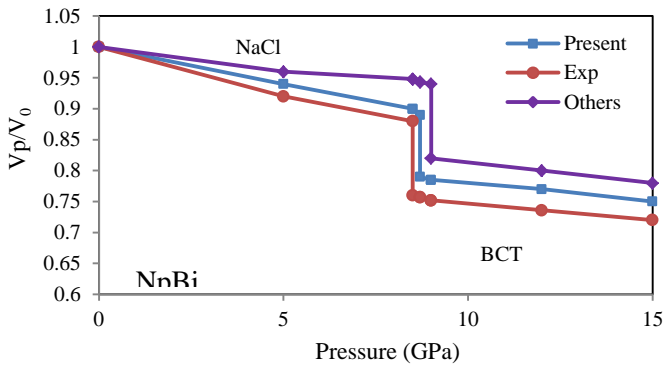


Fig.3. Variation of V_p/V_0 with Pressure

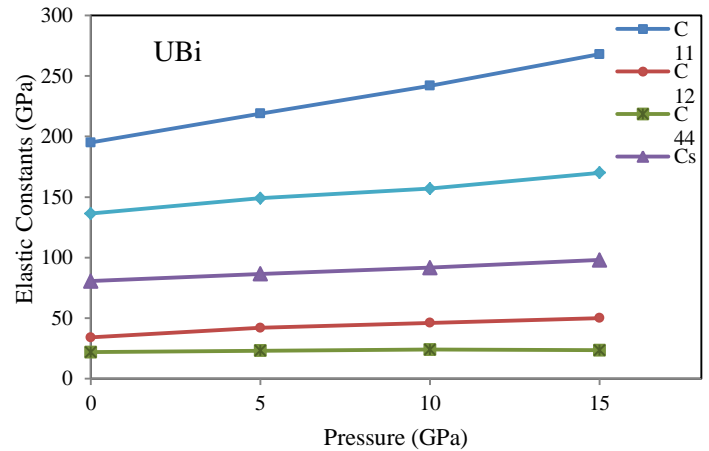


Fig.4. Variation of Elastic constants with pressure

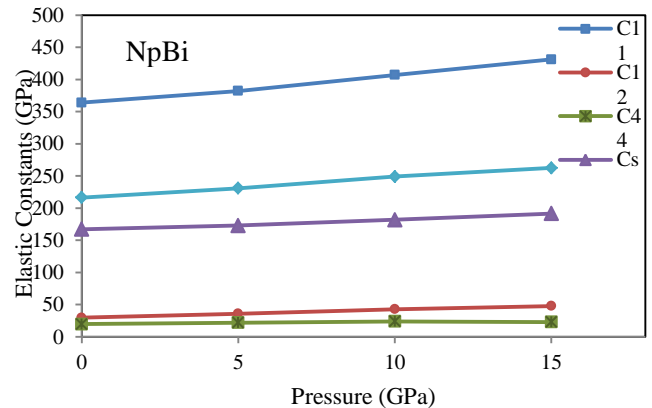


Fig.5. Variation of Elastic constants with pressure

Elastic Properties

We have used theoretical study of second-order elastic constants (SOECs) of cubic crystals by the method of homogeneous finite deformation. The potential is independent of temperature and entropy, so the mechanical elastic constants depend only on the configuration of the crystal. The only condition is that the known potential must be in an analytical form, i.e. it must be a function of relative positions of the ions in the crystal. The knowledge of SOECs are important for the understanding of the inter atomic forces in solids. The calculated elastic constants and elastic properties are given in Table 3. We have also calculated the SOECs with variation of pressure and plotted them in Fig.4. and Fig.5. for UBi and NpBi.

Table 3: Calculated elastic constants, Zener anisotropy factor (A), Poisson ratio (ν) and Young's modulus (Y) of UBi and NpBi in (GPa)

Compound s	C_{11}	C_{12}	C_{44}	C_{44}/B_T	A	ν	Y
UBi	19 5	34	21.8	0.248 6	0.7 4	0.3 3	176.4 3
NpBi	36 4	29. 7	19.6 7	0.139 4	0.5 9	0.3 7	349.1 9

Thermophysical properties

Thermophysical properties of any material are important as they provide us interesting information about the substances. We have calculated thermo physical properties of UBi and NpBi and listed them in Table 4. The Debye characteristic temperature (θ_D) reflects its structure stability, the bond strength between its separate elements, structure defects availability and its density [11]. We have also computed molecular force constant (f), infrared absorption frequency (ν_0), Gruneisen parameter (γ) and ratio of the volume expansion coefficient (α_v) to specific heat (Cv) at constant volume which are directly derived from the cohesive energy U(r).

Table 4: The calculated value of molecular force constants (f), infrared absorption frequency (ν_0), the ratio of thermal expansion coefficient of specific heat (α_v/C_v), Debye temperature (Θ_D), Kleinman parameter (ξ) and Gruneisen parameter (γ) for UBi and NpBi in B1 phase.

Compounds	f (10^4)	ν_0 (10^{12} Hz)	α_v/C_v (10^3J)	Θ_D (K)	ξ	γ
UBi	1.86	2.31	3.975	378.94	0.671	2.017
NpBi	1.47	1.83	2.419	362.76	0.509	1.367

Conclusions

We can conclude that the Improved Interaction Potential model (IIPM) successfully estimates the phase transition and volume collapse of UBi and NpBi at high pressure. The outcomes are:

- I. UBi and NpBi crystallize in six fold coordinated NaCl-type structure (B_1) at ambient conditions and under pressure, it transforms to the distorted CsCl-type structure (BCT).
- II. The calculated value of phase transition pressure and volume collapse agrees well with available experimental and theoretical results and at P_t , the discontinuity in volume represents that the transition is of first order.
- III. The calculated values of mechanical and thermophysical properties are serves as a guide for the experimental and theoretical work.

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