High Pressure Behavior of PuBi and NpBi Compounds

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Abstract-The structural phase transition properties of two mono-bismuthides (NpBi, PuBi) are investigated by using a modified inter-ionic potential theory (MIPT), employing the minimization technique of Gibbs free energy expressed as a function of pressure. We have also presented the equation of state, which shows an appreciable volume collapse at the phase transition pressure and associated volume collapse are generally in good agreement with their experimental findings. We have also reported the elastic and thermal properties for these compounds, for the first time.

1. Introduction
In recent years, there has been considerable interest in theoretical and experimental studies of actinide compounds (AnX) with NaCl (B1) structure. These compounds exhibit a rich variety of electronic and magnetic properties. One of the common problem observed in these compounds, the degree of localization and itinerancy of the 5f electrons in An-An atom [1,2,4]. This property depends on the bonding distance between An atoms and consequentially on the lattice parameter of the compounds. It is therefore, interesting to note that, by applying pressure the lattice parameter can be changed appreciably, and thereby reveling the effect of electron localization on structural, mechanical, thermal and elastic properties of actinides compounds [3,5]. The structural at high pressure properties for NpBi have been investigated by Genesini et. al. [6] using high pressure X-ray diffraction method. It has been reported that it undergoes first order structural phase transitions from NaCl structure (B1) to body centered tetragonal structure (BCT) around 8.5 GPa with volume collapse 12% and isothermal bulk moduli (B1) also observed to be 145 GPa at ambient pressure. The lattice parameter (a0) of NpBi was determined to be 6.3732 Å by Benedict et.al. [7]. The high pressure behavior in PuBi has been studied by Meresse et. al. [8] using X-ray diffraction method. It was found that PuBi undergoes a NaCl type structure to body centered tetragonal structure (BCT) at 10 GPa with volume change 12%. Petit et.al. [10] have also reported first principles calculations on plutonium compounds using SIC-LSD scheme technique.

2. Methodology
In the present analysis, we have considered three types of interionic forces that are responsible for cohesion in crystals with NaCl structure, viz. long range Coulomb, Flygare form of short range repulsive and van der Wall multipole interaction. Accordingly, the crystal energy can be expressed as

\[ U(r) = \sum \frac{Z_m^2 e^4}{r_{ij}} + \sum b_{ij} \exp \left( \frac{(r_i + r_j - r_{ij})}{\rho_{ij}} \right) + \sum c_{ij} r_{ij}^{-6} + \sum D_{ij} r_{ij}^{-8} \]
Where the first term represents the usual Coulomb energy with $r_{ij}$ as the interionic separation. The second term corresponds to Flygare form of short range repulsive while third and fourth terms in equation (1) represent the van der Wall’s dispersive forces due to dipole-dipole and dipole-quadrupole interactions, with $C_{ij}$ and $D_{ij}$ as coefficients. $Z_m$ is the modified ionic charge due to Coulomb screening effect, $\beta_{ij}$ are the Pauling coefficients, $b$ and $\rho$ are the short range parameters, which can be determined from the equilibrium condition and bulk modulus ($B_T$). Details of the method of calculation of elastic and thermal properties are given in our earlier paper [3].

3. Result and Discussion

In the present paper, we have investigated the structural phase transition, elastic and thermal properties of NpBi and PuBi compounds using the methodology outlined in section 2. The input data and output parameters are given in Table 1 and the cohesive and structural properties at high pressure are presented in Table 2. An inspection of the Table 2 reveals that the present MIPT has satisfactorily explained the structural stability, cohesive and phase transition properties of these compounds. It is also seen from Table 2 that $\Delta G$ is positive which implies that the zero pressure NaCl phase is stable. The table also contains the calculate values of structural phase transition pressure for NpBi and PuBi from NaCl (B1) phase to body centered tetragonal (BCT) phase which are 9 Gpa and 11 GPa with 12% and 10% volume collapse respectively. These results are good agreement with experimental and other theoretical results [6-8].

Table 1. input and output model parameters for NpBi and PuBi compounds.

| Solid | Solid $r_0$ (Å) | $r_0$ (Å) | $r_0$ (Å) | $B_T$ (GPa) | $Z_m^2$ | $b$ (10$^{-19}$J) | $\rho$ (Å) |
|-------|----------------|-----------|-----------|-------------|---------|-------------------|-------------|
| NpBi  | 0.80           | 1.03      | 3.186$^a$ | 145$^b$     | 3.90    | 425.11            | 0.185       |
| PuBi  | 0.89           | 1.03      | 3.179$^c$ | 61$^c$      | 2.755   | 50.24             | 0.290       |

$^a$Ref. [7], $^b$Ref.[6], $^c$Ref.[8].

Table 2. Cohesive energy, Phase transition pressure and Volume collapse for NpBi and PuBi.

| Solid | Equilibrium constant(R) | Cohesive energy | $\Delta U$ | $P_T$ | V/V$_0$ |
|-------|-------------------------|-----------------|------------|-------|---------|
|       | Solid                      | (Å)            | (KJ/mole)  | (KJ/mole) | (GPa) | (%)     |
|       | R$_{B1}$ | RBCT | $U_{B1}$ | $U_{BCT}$ |          |         |
| NpBi  | Pre.      | 3.199 | 3.334 | -2855.15 | -2803.04 | 52.1 | 9 | 12 |
|       | Exp.      | 3.186$^a$ | - | - | - | 8.5$^b$ | 12$^b$ |
| PuBi  | Pre.      | 3.055 | 3.231 | -1953.03 | -1904.01 | 49.02 | 11 | 10 |
|       | Exp.      | 3.179$^c$ | - | - | - | 10$^c$ | 12$^c$ |

$^a$Ref. [7], $^b$Ref.[6], $^c$Ref.[8].

It is obvious that the energy differences ($\Delta G$) have attained their values to be zero at the phase transition pressure ($P_T = 9$ &11 GPa) for NpBi and PuBi respectively. These values are in better agreement with their measured data [6-8]. Also, there is an abrupt change in Figures (1) – (2) of volume discontinuity at the phase transition pressures showing the compression of the lattice due to which the NaCl structure becomes unstable at high pressure and transforms to body centered tetragonal (BCT) phase.
At this point it can be emphasized that at high pressure the short range forces for these compounds increase significantly, which are responsible for change in the coordination number and phase transformation.

![Figure 1. Equation of state for NpBi](image1)

![Figure 2. Equation of state for PuBi](image2)

The elastic properties are important parameters for crystals. They provide valuable information about the nature of the forces and bonding characteristics of solids. The calculated values of second order elastic constant (SOEC) for NpBi and PuBi at ambient as well as high pressure, by using present approach are obtained by using the methodology as described in section 2. To the best of our study no experimental and theoretical measurement on elastic constant have been reported so far, for NpBi. There are some useful information about the second order elastic constants of PuBi observed by Srivastava et. al [9]. A look at from Figure-3, that the $C_{11}$ increase linearly with pressure and $C_{44}$ decreases with pressure up to 18 GPa. This similarity has also been observed in other rare earth compounds [3,5,13]. Our results for second order elastic constants (SOEC) satisfy the stability condition criteria for cubic crystal, $C_{11}-C_{12} > 0$, $C_{44} > 0$, $B_0 > 0$, by using elastic constants namely $C_{11}$, $C_{12}$ and $C_{44}$. Due to absence of any earlier work, we could not compare our calculated values.

![Figure 3. variation of elastic constants with pressure.](image3)

![Figure 4. variation of Debye temperature with pressure.](image4)

The Debye temperature is an important fundamental parameter of solid. The calculated values of debye temperature for these compounds are 281 K and 179 K at ambient pressure.
We have also calculated the variation of $\theta_D$ with respect to pressure for these compounds and predicted them in Figure 4. It is clear from the figure that $\theta_D$ increases as pressure increases for both the compounds, which show quite normal behavior in this type of compounds.

4. Conclusions
We present the results of our investigation, employing the modified inter-ionic potential theory (MIPT). Our calculation on structural phase transition pressure, bulk modulus and volume collapse agree well with the available experimental data for NpBi and PuBi compounds. We have also analyzed the elastic, mechanical, thermal properties for both the compounds for first time. Our theory is adequately suitable for explaining the structure stability and nature of inter-atomic forces for both the compounds.

5 References
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