

# A First Principle Study of Pressure Induced Structural and Electronic Properties in Neptunium Bismuthide

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## Abstract

We have examined the pressure induced structural and electronic properties of neptunium monobismuthides. The total energy as a function of volume is obtained by means of self-consistent tight binding linear muffin-tin-orbital (TB-LMTO) method within the local density approximation (LDA). It is found that NpBi is stable in NaCl – type structure under ambient pressure. We predict a structural phase transition from NaCl-type ( $B_1$ -phase) structure to CsCl-type ( $B_2$ -phase) structure for NpBi in the pressure range of 11 GPa. We also calculate the lattice parameter ( $a_0$ ), bulk modulus ( $B_0$ ), band structure and density of states. From energy band diagram it is observed that NpBi exhibit metallic behaviour. The calculated equilibrium lattice parameters and bulk modulus are in general good agreement with available experimental data.

**Keywords:** Structural phase transition; Electronic band structure; Metallic.

## 1. Introduction

The actinide based compounds are endowed with several physical properties due to the presence of  $f$ -electrons. The  $f$ -electrons are generally less localised than in the corresponding lanthanides, which explains the itinerant behaviour at the beginning of the series, but for elements beyond Pu the increased nuclear charge causes the  $f$  orbitals to overlap less, and crossover from itinerant to localised  $f$  electron behaviour occurs [1-3]. Considerable theoretical but few experimental studies on plutonium binary compounds have been reported during the last few years. Gensini et al. [4] have studied the high pressure behaviour of NpBi by using anvil cell and high pressure X-ray diffraction measurements and reported that NpBi exhibit first order crystallographic phase transition from NaCl ( $B_1$ ) to CsCl ( $B_2$ ) structure at high pressure. It is well known that with increasing atomic number, the  $f$ -shells become smaller and thus are more localized implying a smaller band width [5]. This localization is also favoured from lighter (e.g. P) to heavier anions (e.g. Bi). In this context, it will be interesting as well to investigate the structural phase transition in NpBi. In the present study we have investigated, for the first time, the high pressure structural and electronic properties of neptunium monobismuthides (NpBi) at ambient and high pressure using *ab initio* Tight Binding-LMTO with LDA. In the section 2, we briefly describe the method of total energy calculation which will be followed by results and discussion on structural and electronic properties in section 3.

## 2. Method of Calculation

The total energy, structural stability, electronic band structure (BS) and density of states (DOS) of neptunium monobismuthides is calculated by using tight binding LMTO (TB-LMTO) method [6] within local density approximation (LDA) [7]. The Von – Barth and Hedin parameterization scheme [8] has been used for exchange correlation potential. NpBi crystallize in  $B_1$ -type (NaCl) structure with Space group Fm-3m (no. 225) at ambient pressure. In  $B_1$  structure, Np atoms occupy at (0, 0, 0) and Bi atoms at (0.5, 0.5, 0.5) positions respectively. The calculations were performed for 8000  $k$ - points ( $20 \times 20 \times 20$   $k^3$  grids) in the Brillouin zone for both  $B_1$  and  $B_2$  structures. The E and  $k$  convergence were checked subsequently. The total energies were calculated by changing the volume from 1.1 to 0.70 $V_0$ , where  $V_0$  is the equilibrium cell volume at ambient pressure. The calculated total energies as a function of volume for NpBi in  $B_1$  and  $B_2$  structures were fitted to Birch equation of state to obtain pressure – volume (P-V) and pressure-enthalpy (P-H) relation, finally leading to equilibrium lattice constants ( $a_0$ ) and bulk modulus ( $B_0$ ).

## 3. Result and discussion

### 3.1. Structural properties

The structural stability of NpBi has been examined by calculating the total energy as a function of volume in ambient (NaCl phase) and at the high pressure (CsCl phase) structures and the results are shown in Fig. 1. The NpBi, as is seen from Fig.1. transform to CsCl structure on compression. The calculated value of equilibrium lattice constant in the NaCl Structure is 6.00Å for NpBi, which agree fairly well with the experimental and theoretical data [5] shown in table 1. The structural phase transition is determined by calculating the Gibbs free

energy ( $G$ ) for two phases ( $B_1$  and  $B_2$ ), which is given by  $G = E_{tot} + PV - TS$ . Since the theoretical calculations are performed at  $T = 0K$ , Gibbs energy becomes equal to enthalpy ( $H$ ) ( $H = E_{tot} + PV$ ). For a given pressure, a stable structure is one for which enthalpy has lowest value and the transition pressure ( $P_t$ ) is determined at which the enthalpies of two structures are the same. Following such a procedure, the phase transition pressures ( $P_t$ ) for NpBi is calculated for a  $B_1 - B_2$  transition. The phase transition pressures have been estimated as 11 GPa NpBi, with volume collapse of 7%. The pressure – volume relationship or equation of states for NpBi is shown in Fig. 2.

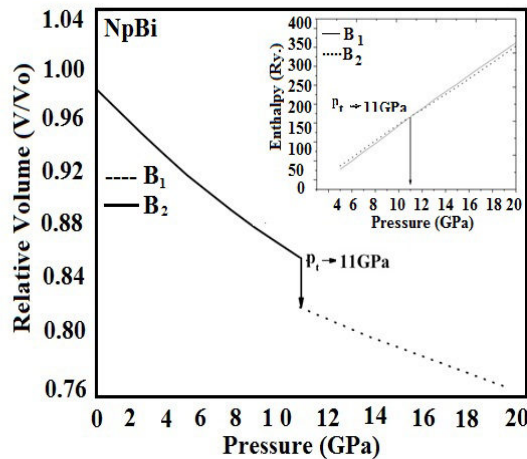


Fig. 2. Equation of states (P-V) and P-H relation (in the inset) for NpBi. Solid line represents  $B_1$  and dotted line represents  $B_2$  phases.

The insets show the variation enthalpy as a function of pressure for respective compounds. In the  $B_2$  phase the corresponding lattice parameter is  $3.60\text{\AA}$ . In addition to the above structural properties, the values of bulk modulus ( $B_0$ ), calculated by using Birch equation of state, which has been shown in Fig.1. (for energy as a function of pressure). The calculated results are presented in Table 1 for NpBi [5].

Table 1: Calculated ground state properties of NpBi

| Solid           | Lattice Constant( $\text{\AA}$ ) |       | Bulk Modulus(GPa) |       | Phase Transition Pressure(GPa) |
|-----------------|----------------------------------|-------|-------------------|-------|--------------------------------|
|                 | $B_1$                            | $B_2$ | $B_1$             | $B_2$ |                                |
| Solid NpBi Pre. | 6.00                             | 3.60  | 82                | 141   | 11                             |
| Exp.            | 6.438 <sup>a</sup>               | ----- | -----             | ----- | -----                          |

<sup>a</sup>Ref. [5]

### 3.2 Electronic Properties

An exact understanding of the electronic structure of NpBi is an extremely challenging problem, because of the itinerant behaviour of their 5- $f$  electrons. However a qualitative picture of their electronic properties can be drawn by comparing these properties for NpBi.

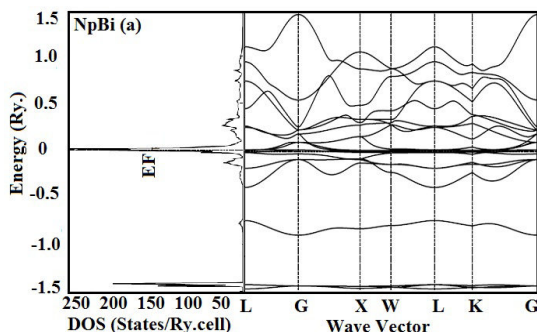


Fig. 3. Electronic band structure (BS) and Total density of states (DOS) for NpBi in  $B_1$  phase.

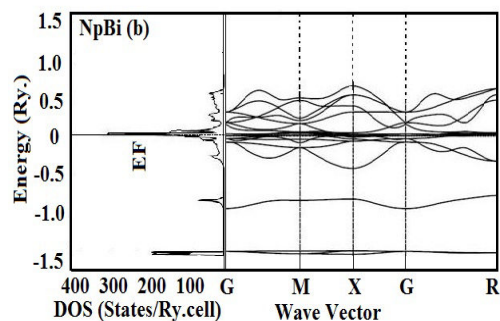
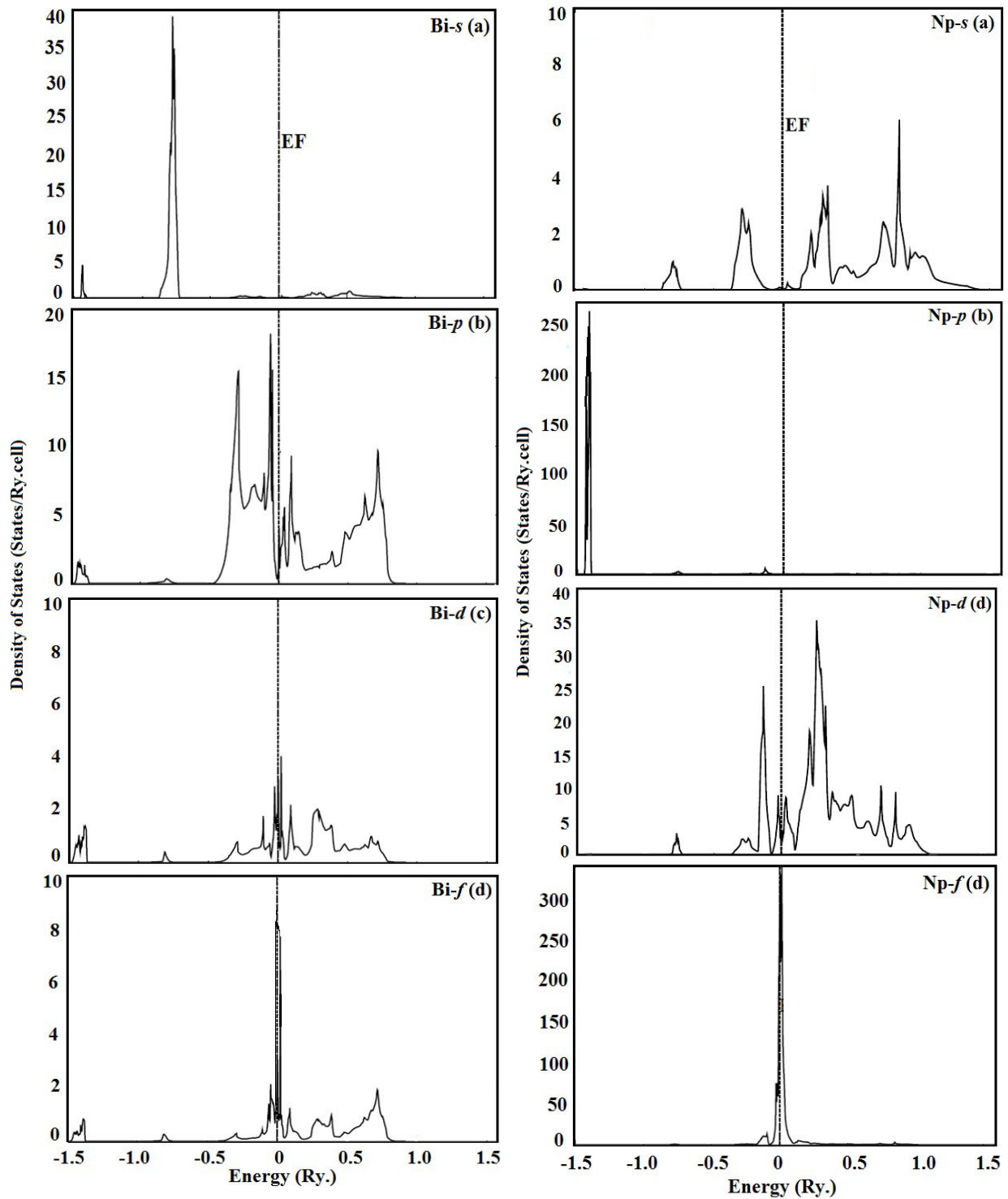


Fig. 4. Electronic band structure (BS) and Total density of states (DOS) for NpBi in  $B_2$  phase.

We have, therefore, calculated the electronic band structure (BS) and density of states (DOS) of this compound in  $B_1$  and  $B_2$  phases and plotted them in Figs. 3(a-b). It is seen from Fig.3. that both this compound are metallic in nature in  $B_1$  phase at ambient pressure.



**Fig. 5. Partial density of states for NpBi, in B<sub>1</sub> Phase**

To understand the band structure of NpBi qualitatively in Figs. 5, we have plotted the partial density of states (PDOS). Highly localised Np-*f* band stays above the Fermi level at ambient, and moves marginally towards Fermi level on application of pressure.

#### 4. Conclusion

The structural phase transition due to high pressure and electronic properties of NpBi has been studied using the TB-LMTO method. This compound undergoes a structural phase transition to B<sub>2</sub> structure at 11 GPa and is found to be metallic in both the phases.

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