Structural phase transition and elastic properties of neptunium compounds at high pressure

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The high pressure behaviour and pressure induced structural phase transition of three neptunium compounds have been investigated by using a two body interionic potential approach. The calculated compression curves and the values of different high pressure properties for NpSe, NpTe and NpAs are presented and compared with the experimental values wherever available. The calculated values of elastic properties show predominantly ionic nature of these compounds. For NpSe, NpTe and NpAs, the phase transition pressures for structural transition from NaCl to CsCl phase have been predicted at 23.4, 12.9 and 28.2 GPa, respectively.

1 Keywords: Structural phase transition, Elastic properties, Neptunium compounds

1 IPC Code: G01D

1 Introduction

The monohalogenides and mononitrides of neptunium (Np) pose striking similarities and differences in their physical properties as compared to those of the other rare earth series. But due to the difficulties encountered in handling these radioactive materials, relatively little is known about their structural and mechanical properties as compared to the technologically important elements like uranium and plutonium. One of the most intriguing questions faced with actinides is the problem of the degree of localization and itinerancy of the 5f electrons in Np atom. This property strongly depends on the binding distance of the involved atoms and consequently on the lattice constant of the compounds. It is therefore interesting to note that by applying high pressure, the lattice constants can be changed appreciably thereby revealing the effect of electron localization on structural, mechanical and elastic properties etc.

The structural properties of the mononitrides and monohalogenides of neptunium at high pressure have been investigated by using the experimental techniques such as high pressure X-ray diffraction, optical reflectivity measurements etc. However, very little fewer theoretical efforts have been made, so far to reveal the nature of bonding, ion-ion and ion-electron interactions etc. in the compounds. Most of these studies show that the degree of 5f localization is a factor which determines the crystal structure, lattice constants and elastic properties compounds. These compounds crystallize in the NaCl type (B1) structure at ambient condition and undergo a first order crystallographic phase transitions from NaCl (B1) to CsCl (B2) structure under high pressure. Genisini et al have from high pressure X-ray diffraction (HPXRD) studies have reported that the NpSe undergoes a transition from B1 to B2 at about 23 GPa with a volume collapse of 9%. Dabos et al have reported, such a transition in NpTe around 12-20 GPa with volume reduction of 7%. The electronic band structure, based on TBLMTO method has recently been reported by Rajagopal who has also predicted 10 GPa as phase transition pressure for NpTe. Though the conclusions obtained by this author is quite reasonable but a relatively large difference in magnitude of phase transition pressure is observed experimentally.

In the present paper we report the calculated results on structural phase transition at high pressure and elastic properties using suitable interionic potential theory based on ionic model. In section 2, we present the brief outline of the methodology for calculating the structural properties and section 3, deals with the results.

2 Methodology

The interatomic potential for the rare-earth compounds in the framework of the rigid ion model can be expressed as

$$ U(r) = \sum Z_i Z_j e^2/r_{ij} + \sum b_i \exp \left( \frac{r_{ij} - r_{ij}^-}{\alpha} \right) $$

$$ + \sum C_i \left( r_{ij}^- \right)^2 + \sum D_i \frac{1}{r_{ij}^-} \cdots \cdots \text{(1)} $$

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which includes the long-range Coulomb (first term), Hafemeister and Flygave form of short-range repulsive (second term) and the van der Waals (third and fourth terms) energies. This potential has only two parameters $b$ and $p$ which are determined from bulk modulus and the following equilibrium condition

$$
\left. \begin{array}{ll}
\frac{b}{r_0} & \exp(r_{-} + r_{-})/p + 2 \beta_{-} \exp(2r_{-} - 2r_{-})/p + 2 \beta_{-} \exp(2r_{-} - 2r_{-})/p
\end{array} \right\}
= (2a/ \beta) Z^{n/2} + (3 \beta) Z^{n/2} + 6 C_{r} r_{-}^{3} + 8 D_{r} r_{-}^{3} + 0.75 \left(C_{r} r_{-}^{6} + 0.5 \left(D_{r} + D_{r} \right) r_{-}^{6}\right)
$$

(2)

The input constants and model parameters for neptunium compounds are presented in Table 1. The neptunium compounds transform from their initial B1 (NaCl) to B2 (CsCl) structure under pressure. The stability of a particular crystal structure is decided by the minima of the Gibbs free energy

$$
G = U + PV - TS
$$

(3)

Where, $U$ is the internal energy, at 0 K, $S$ is the vibrational entropy at absolute $T$, pressure $P$ and volume $V$.

The Gibbs free energies $G_{n}(r) = U_{n}(r) + 2 P r_{-}$ for NaCl (B1) phase and $G_{n}(r) = U_{n}(r) + (8/3) P r_{-}^{3}$ for CsCl (B2) phase become equal at the phase transition pressure $P$ and temperature 0 K, i.e., $\Delta G = \Delta G_{n} = G_{n} - G_{m}$ becomes zero.

<table>
<thead>
<tr>
<th>Solids</th>
<th>Input parameters</th>
<th>Output parameters</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$r_{+}$ ($\AA$)</td>
<td>$r_{-}$ ($\AA$)</td>
</tr>
<tr>
<td>NpSe</td>
<td>0.8114</td>
<td>1.1914</td>
</tr>
<tr>
<td>NpTe</td>
<td>0.814</td>
<td>1.2441</td>
</tr>
<tr>
<td>NpAs</td>
<td>0.814</td>
<td>1.054</td>
</tr>
</tbody>
</table>

Table 1 - Input crystal and Model parameters for Neptunium compounds

Here the abbreviations $U_{n1}$ and $U_{n2}$ represent cohesive energies for the phases B1 and B2, respectively, and are written as

$$
U_{n1}(r) = -1.7475 \varepsilon^{2} r_{-}^{2} + 6 V_{00}(r) + 6 V_{01}(r)
$$

(4)

And

$$
U_{n2}(r) = -1.7627 \varepsilon^{2} r_{-}^{2} + 8 V_{00}(r) + 3 V_{01}(r)
$$

(5)

Here $r$ and $r_0$ are nearest-neighbor (nn) separations corresponding to NaCl and CsCl phases, respectively. The short-range potential $V(r)$ for both the phases between the ions are written as

$$
V_{00}(r) = b_{0} \exp(-r_{0}) - C_{0} r_{-}^{6} P r_{-}^{6}
$$

(6)

where $b_{0}$ and $p_{0}$ are short-range parameters. For predicting the transition pressure, we have minimized the Gibbs free energies with respect to interatomic separations. The cohesive properties and stability of the structure for Neptunium compounds are presented in Table 2.

In the present paper, we have calculated the second order elastic (SOE) and third order elastic (TOE) constants and pressure derivatives of SOE from the following expressions, derived from the interionic potential (Eq. 1) Ref 11-13,

$$
C_{pi} = \alpha [5.112Z^{2} + A_{p} + \frac{1}{2} \left(A_{p} + B_{p}\right)]
$$

(7)

$$
C_{pi} = \alpha [0.226Z^{2} - B_{p} + \frac{1}{4} \left(A_{p} - 5B_{p}\right)]
$$

(8)

$$
C_{pi} = \alpha [2.556Z^{2} + B_{p} + \frac{1}{4} \left(A_{p} + 3B_{p}\right)]
$$

(9)

With

$$
\alpha = \varepsilon^{2}/4 \eta^{2}
$$

and, $A_{p} = A_{p1}B_{1} + B_{p1}A_{2} = (A_{p1} + A_{p2})$ and $B_{p} = (B_{p1} + B_{p2})$, and are expressed as:

$$
A_{p} = 2 \varepsilon^{2} (dV_{00}(r)/dr) |_{r_{0}}
$$

Table 2 - Cohesive and Phase transition properties of Neptunium compounds
\[ \frac{\partial V}{\partial V} = 2V/\epsilon (U_\epsilon (dV_\epsilon (r) /dr) \] 

where \( V_\epsilon (r) \) is the short-range potential, defined by Eq. (6). The expressions for the third order elastic constants (TOEC) can be derived as follows:

\[ C_{11} = \alpha / 37.556 Z^2 + C_{ij} - 3A_i + \frac{1}{2} \left( C_{ij} - 3A_i - 9B_i \right) \] 

\[ C_{12} = C_{11} = \alpha \left[ 1 - 4.786 Z^2 \right] + \frac{1}{8} \left( C_{ij} - 3A_i - 9B_i \right) \] 

\[ C_{44} = C_{11} = \alpha (2.717 Z^2) \] 

With \( C_{11} = A_{ij}/B_{ij} \) 

The expressions for the pressure derivatives of second order elastic constants can be derived from the combination of SOE and TOE constants for NaCl structure, using their standard relations.

3 Results and Discussion

The input constants and derived model parameters for Neptunium compounds are given in Table 1. In Table 2, we have presented the phase transition properties of three neptunium compounds and compared our results with the available experimental and other theoretical results. We have also presented the calculated values of second and third order respectively. The compression characteristics along with the variation of Gibbs energy (\( \Delta G \)) with pressure of these solids have been presented in Figs. 1-3.

An inspection of the Table 2 reveals that the present two body potential has satisfactorily explained the structural stability, cohesive and phase transition properties of all the three neptunium compounds, NpSe, NpTe and NpAs. The relative stability of crystal structure at ambient pressure has been correctly reproduced to be free as the present theory predicts lower value of cohesive energy in B1 phase as compared to that in B2 phase. In the present investigation, we have also obtained, the value of phase transition pressures for NpSe, NpTe and NpAs as 23.4, 12.9 and 28.2 GPa respectively, which are close to the experimental results (see Table 2). The transition pressure for NpSe is slightly higher than that of ThSe, emphasizing that the bonding in NpSe is predominantly ionic. Moreover, the relative change of volume at B1-B2 transition obtained from present calculation are in excellent agreement with their measured values. It is seen from Figs 1-3 that the pressure-volume characteristics for this series is nicely reproduced by the present ionic and two body interaction potential model. The trend of variation of transition pressure and volumes in NpSe, NpTe and NpAs dictates that these compounds are moderately ionic, and apparently non-inclusion of electronic effects does not lead to any appreciable change in interpreting their structural properties. Though the experimental result on transition pressure predicts a large range of pressure (25-40 GPa) for NpAs, we predict it at 28.2 GPa, with 8.6% change in relative volume. These results are also consistent with the theoretical results on phase transition of ThAs (Ref. 11).

In Table 3, we have reported the calculated values of SOE constants, while those for TOE constants and pressure derivatives are presented in Table 4, and are compared with experimental data for bulk modulus only. To the best of our knowledge, no measurement on elastic constants has been reported so far, except the bulk modulus and its pressure derivatives. However, the trend of variation of the elastic
(both SOE and TOE) seems reasonable, in view measured values of \( B_I \). In conclusion, we have the structural properties of three Np-compound elastic interionic potential, and their elastic, which need further experimental support. We observed any appreciable effect of \( f \)-electrons in structural properties as is seen in the case of cerium.

Variation of Gibbs free energy \( (\Delta G) \) with pressure for (a) Equation of state for NpTe. Solid circles and cross represent experimental values ref.\(^5\).

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**Table 4 - Third order elastic constants (GPa) and Pressure derivatives**

<table>
<thead>
<tr>
<th>Constants and Pressure derivatives</th>
<th>NpSe</th>
<th>NpTe</th>
<th>NpAs</th>
</tr>
</thead>
<tbody>
<tr>
<td>( C_{11} )</td>
<td>-213.12</td>
<td>-513.35</td>
<td>-165.10</td>
</tr>
<tr>
<td>( C_{11} = C_{33} )</td>
<td>-183.86</td>
<td>-139.91</td>
<td>-175.50</td>
</tr>
<tr>
<td>( C_{12} = C_{13} )</td>
<td>88.37</td>
<td>67.95</td>
<td>86.41</td>
</tr>
<tr>
<td>( dV/dP )</td>
<td>3.90</td>
<td>4.34</td>
<td>4.18</td>
</tr>
<tr>
<td>( dV/dP )</td>
<td>(2.50)</td>
<td>(1.80)</td>
<td>(6.20)</td>
</tr>
<tr>
<td>( dC_{12}/dP )</td>
<td>2.49</td>
<td>4.13</td>
<td>3.34</td>
</tr>
<tr>
<td>( dC_{12}/dP )</td>
<td>0.260</td>
<td>-0.105</td>
<td>-0.023</td>
</tr>
</tbody>
</table>

\( (\cdot) \) indicates Experimental value.\(^5\)
compounds. The measured values of bulk modulus for NpSe and NpTe are nearly equal, and thus it is different to assess the accuracy of calculated values of elastic constants. Nevertheless, they fit reasonably well to the measured values of $B_T$ and $dB/dP$.

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**References**