Journal of Molecular Structure 1068 (2014) 20–26

Contents lists available at ScienceDirect

Journal of Molecular Structure

journal homepage: www.elsevier.com/locate/molstruc

An investigation on the structural transition and stability of some actinide nitrides under pressure

Faisal Shareef M. *, Purvee Bhardwaj, Sadhna Singh

High Pressure Research Lab, Department of Physics, Barkatullah University, Bhopal 462026, India

HIGHLIGHTS

- The present study gives the improved results after the inclusion of covalency in TBI effect for actinides.
- It predicts the phase transition pressure, volume discontinuity and elastic properties at high pressure.
- The inclusion of vander Waal effect is important as it is difficult in DFT and other ab intio calculations.
- To explain the stability of the materials the Every's and Blackman's diagrams are analyzed.
- The newly obtained values can consider as a future reference to the experimentalists.

ARTICLE INFO

Article history:
Received 10 January 2014
Received in revised form 26 February 2014
Accepted 20 March 2014
Available online 29 March 2014

Keywords:
Phase transition
Covalency
Stability
Elastic constants

ABSTRACT

A theoretical study of the structural and related properties of some actinide nitrides under high pressure has been carried out using three-body interaction (TBI) potential model. The present TBI model constitutes the long range Coulombic, three body interaction forces with inclusion of covalency effect, van der Waals' interaction and short range overlap repulsive forces operative up-to next nearest neighbor ions. The covalency effect is introduced to explain the partial covalent nature of the present compounds. Using this static simulation technique we have investigated the phase transition pressures, volume collapses and elastic behaviour of ThN, NpN and CmN at high-pressures. A detailed discussion of stability criteria using various theories has also been done. The results found are well agreed with available experimental and other data.

© 2014 Elsevier B.V. All rights reserved.

Introduction

The actinide nitrides have a fascinating attraction like other actinide monochalcogenides and monopnictides from materials scientists. This is because of their unusual properties due to the valance fluctuations arising from instability of 5f electrons. The understanding of 5f electron system in these compounds reveals the numerous allotropic properties such as chemical bonding, magnetic ordering etc. and the vibrational properties of the compounds [1,2]. The actinide compounds possess a vital role in the nuclear energy and relevant applications. The actinide nitrides have a possible advantage as advanced fuels, over present oxide fuels in fourth generation nuclear reactors because of their desired attributes like superior thermophysical properties, higher burn up, higher density, etc. [3,4]. The behaviour of several actinide monopnictides and monochalcogenides under pressure has been studied substantially in recent years. But fewer attempts have been made from experimental or theoretical grounds on actinide nitrides to reveal their unusual peculiar properties under pressure. It is materially mentioned that all the present nitrides of the actinides (ThN, NpN and CmN) exhibit NaCl-type (B1) crystal structure at ambient pressure and temperature [5,6].

Modak et al. [1] conducted the first principles study of ThN up to a pressure of 100.0 GPa to investigate its electronic, vibrational, elastic and structural properties. Their generalized-gradient approximation (GGA) study predicted a phase transition in ThN from B1 structure to B2 structure at 72.5 GPa with a volume reduction of 11.0%. They have also reported the bulk modulus values for ThN as 211.5 GPa and 180.8 GPa in LDA and GGA respectively. The experimental high-pressure X-ray diffraction study reveals the bulk modulus of 175.0 GPa [5] for it. Aynyas et al. [7] have studied the structural phase transition and elastic properties of thorium pnictides under pressure using two body interaction potential in the frame work of the rigid ion model. They predicted a first order phase transition in ThN from B1 structure to B2 structure at 77.5 GPa with a relative volume change 6.5% and bulk modulus to be 167.0 GPa.

---

* Corresponding author. Tel.: +91 9827232948.
E-mail address: fm.shareef@gmail.com (F. Shareef M.).

http://dx.doi.org/10.1016/j.molstruc.2014.03.056
0022-2860/© 2014 Elsevier B.V. All rights reserved.

Singh et al. [8] have studied the structural phase transition and electronic structure of NpN using self-consistent tight-binding linear muffin tin orbital (TB-LMTO) method within the local density approximation (LDA). They observed a phase transition from B1 structure to B2 structure at 79.7 GPa for NpN with a relative volume collapse of 5.0% and bulk modulus of 229.4 GPa. The ground state electronic structure of actinide carbides and nitrides has been studied by Petit et al. [9] using self-interaction corrected local spin-density approximation. They reported the bulk modulus of NpN to be 228.0 GPa. The fully relativistic full-potential calculation, based on density functional theory within the local spin density approximation, announces a bulk modulus of 230.0 GPa for NpN [10].

Damien et al. [11] has performed the X-ray powder diffraction technique to measure the lattice parameters of the curium pnictides. The ground state properties and the electronic structure of CmN have been studied by Petit et al. [9] using LMTO method within self-interaction corrected local spin-density approximation (SIC-LDA). They obtained the bulk modulus value of 154.0 GPa for this nitride. Most recently Singh et al. [12] have studied the structural phase transition and electronic structure of curium pnictides using TB-LMTO method within the local density approximation (LDA). They reported a structural change from B1 structure to B2 structure at a transition pressure of 50.9 GPa for CmN with a relative volume collapse 5.0%. The bulk modulus gives a value of 154.4 GPa.

The literature on three body interaction (TBI) potential model introduced by Singh et al. [13,14] has been successfully employed in several ionic and semiconducting crystals to explore their different properties like structural, elastic, phonon, etc. Following the successful application of the TBI model, various effects (van der Waals', zero point energy, etc.) have been included by many researchers [15,16] for the better prediction of phase transition and related properties of several crystals under pressure. Also the inclusion of three body interactions makes the model suitable to explain the Cauchy violation ($C_{12} \neq C_{44}$) in elastic constants which is a challenge in two body potential models. In the present TBI model we included the covalency effect to predict the same. The partial covalent natures exhibited by the present compounds encourage us to consider this effect. The importance of covalence effect in the rare-earth pnictides has already been pointed out by Pagare et al. [17] and Vaitheeswaran et al. [18] in their recent studies. It is already mentioned that the present actinide nitrides undergo a transformation to close-packed structures under high pressure and therefore this effect becomes remarkable in the present study. To accomplish the need we included the covalency effect in the three body force parameter $f(r)$ following the lines of Motida [19]. This must be a captivating and powerful approach as atoms are brought closer under pressure. More over the effect plays a major role when interionic separation reduces and the overlapping of ions occurs. This modified model has been applied effectively in some rare-earth monopnicties [20] and divalent metal oxides [21]. Over all the present investigation spreads more light on the structural properties (particularly the elastic properties) of the actinide nitrides under pressure which was not greatly explained by the previous studies.

Potential model and method of calculation

During the lattice vibrations, the ions experience an appreciable overlap and consequently their electron shells go through deformation. This mechanism causes a transfer of charge between the overlapping ions and these transferred charges interact with all other charges of the lattice giving rise to many body interaction. This model has a parameter $f_m(r)$ which furnishes with the overlap between the adjacent ions. The physical concept underlying the mechanism of charge transfer can be understood from the following fact. When the shells of neighbouring ions are displaced with respect to each other an extra charge is transferred between the shells which depend on the variation in the overlapping.

These effects have been incorporated in the Gibbs free energy ($G = U + PV - TS$) as a function of pressure and three body interactions [13,14], which are the most dominant among the many body interactions. Here, U is the internal energy of the system equivalent to the lattice energy at temperature near zero and S is the entropy. At temperature $T = 0$ K and pressure (P) the Gibbs free energies for rock salt (B1, real) and CsCl (B2, hypothetical) structures are

$$G_{B1}(r) = U_{B1}(r) + \mathrm{PV}_{B1} \tag{1}$$

$$G_{B2}(r') = U_{B2}(r') + \mathrm{PV}_{B2} \tag{2}$$

where V_{B1} (=2.00r^3) and V_{B2} (=1.54r'^3) are unit cell volumes for B1 and B2 phases respectively. The terms, $U_{B1}(r)$ and $U_{B2}(r')$ are the lattice energies for B1 and B2 structures respectively and they can be expressed as:

$$U_{B1}(r) = U_C(r) + U_{TBI}(r) + U_{vdW}(r) + U_{HF}(r) \tag{3}$$

$$U_{B2}(r') = U_C(r') + U_{TBI}(r') + U_{vdW}(r') + U_{HF}(r') \tag{4}$$

Here U_C stands for the long range Coulomb energy, U_{TBI} for three body interactions corresponding to the nearest neighbor separation, U_{vdW} for van der Waals' interaction and U_{HF} for the energy due to the overlap repulsion represented by Hafemeister and Flygare (HF) type potential [24] and extended up to the second neighbor ions. These contributions can be obtained using the following expressions:

For B1 structure,

$$U_C(r) = \frac{-\alpha_m z^2 e^2}{r}$$

$$U_{TBI}(r) = \frac{-12\alpha_m z e^2 f_m(r)}{r}$$

$$U_{vdW}(r) = -\left[\frac{C}{r^6} + \frac{D}{r^8}\right]$$

$$U_{HF}(r) = 6b\beta_{ij}\exp[(r_i + r_j - r)/\rho] + 6b\beta_{ii}\exp[(2r_i - 1.414r)/\rho] + 6b\beta_{jj}\exp[(2r_j - 1.414r)/\rho]$$

and for B2 structure,

$$U_C(r') = \frac{-\alpha'_m z^2 e^2}{r'}$$

$$U_{TBI}(r') = \frac{-16\alpha'_m z e^2 f_m(r')}{r'}$$

$$U_{vdW}(r') = -\left[\frac{C'}{r'^6} + \frac{D'}{r'^8}\right]$$

$$U_{HF}(r') = 8b\beta_{ij}\exp[(r_i + r_j - r')/\rho] + 3b\beta_{ii}\exp[(2r_i - 1.154r')/\rho] + 3b\beta_{jj}\exp[(2r_j - 1.154r')/\rho]$$

In the above expressions α_m and α'_m are the Madelung constants for B1 and B2 structures respectively. C (C') and D (D') are the overall van der Waals' coefficients of B1 (B2) phases [22,23], β_{ij} (i,j = 1,2) are the Pauling coefficients defined as $\beta_{ij} = 1+(Z_i/n_i)+(Z_j/n_j)$ with Z_i (Z_j) and n_i (n_j) are the valence and the number of electrons of the i(j)th ion. Ze is the ionic charge and $b(\rho)$ are the hardness (range) parameters, $r(r')$ are the nearest neighbor separations for B1 (B2)

Download English Version:

https://daneshyari.com/en/article/1405529

Download Persian Version:

https://daneshyari.com/article/1405529

Daneshyari.com