Journal of Alloys and Compounds 504 (2010) 427–430

Contents lists available at ScienceDirect

Journal of Alloys and Compounds

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

Pressure-induced phase transition phenomena in NpSe and NpTe

A. Gour[a,*], Sadhna Singh[b]

[a] Govt. Polytechnic College, Indore Road, Harda, M.P. 461331, India
[b] High Pressure Lab, Physics Department, Barkatullah University, Bhopal, M.P. 462016, India

ARTICLE INFO

Article history:
Received 11 November 2008
Received in revised form 24 May 2010
Accepted 30 May 2010
Available online 11 June 2010

PACS:
61.50 Ks.
61.50 Lt.
61.66-f
62.20
64

Keywords:
High pressure
Phase transition
Equation of state

ABSTRACT

A three-body interaction potential (TBIP) has been formulated by incorporating the effects of long-range coulomb interaction, three-body interaction and short-range repulsive interactions effective up to second neighbor ions. The three-body interactions arise from the electron-shell deformation when the nearest-neighbor overlaps. This TBIP has been employed for detailed studies of pressure-induced phase transition and high-pressure behavior of NpSe and NpTe. The model has yielded fairly good description of the cohesive energy, compressibility, molecular force constant, reststrahlen frequency and Debye temperature in case of these actinide monochalcogenides.

1. Introduction

In recent past several monopnictides and monochalcogenides of neptunium (Np) have been studied experimentally using high-pressure X-ray diffraction and optical reflectivity measurements [1–5]. But due to the problem of handling these radioactive materials, less attention has been drawn about their structural, phonon and thermo-physical properties. Theoretical investigations [6–8] are made which reveal that *5f* unfilled electrons are mainly responsible for the structural and elastic properties of these compounds. These *5f* electrons have lower binding energies and less effective shielding by the outer electrons as compared to the *4f* electrons in case of lanthanides. Hill [9] has pointed that the distance between the actinide atoms is mainly responsible for many solid-state properties for instance, there is critical distance below which the compounds are non-magnetic and above which they are magnetic at low temperature. It is obvious that due to the application of high-pressure the lattice constants get changed, inducing many changes in the bond length, structure, optical and phonon properties.

At room temperature and pressure these neptunium chalcogenides crystallize with the rocksalt structure (B1) but undergo pressure-induced phase transition from rocksalt (B1) to cesium chloride (B2) structure. Gensini et al. [10] reported that the NpSe undergoes a transition from B1 to B2 structure at about 23 GPa with a volume change of 9%. Dabos et al. [11] investigated that the first-order phase transition in NpTe from B1 to B2 structure occurs at around 12–20 GPa with volume change of 7%.

In the recent past, extensive efforts have been made to reveal the phase transition and anharmonic properties of solids by means of different forms of cohesion. The inadequacy of two-body interactions is clearly indicated by its failure to explain the Cauchy violations in ionic crystals. Lowdwin [12] and Lundqvist [13] in terms of three-body interactions (TBI) argued an acceptable explanation of these violations, which have their origin in the non-orthogonality of electron wave function. The importance of TBI in potential model to improve results has also been emphasized by Sims et al. [15] and Froyen and Cohen [16]. Moreover inter-ionic potentials are developed including the TBI (many-body interaction) while studying α-AgI by Vashishta et al. [17]. Motivated from the remarks of Lowdin [12] and Lundqvist [13] and the versatility of many-body interactions approach [14] for the successful description of the high-pressure phase transition in neptunium chalcogenides, we thought it pertinent to make a comprehensive study of TBI effects on cohesive and thermo-physical properties of NpSe and NpTe compounds. We have employed three-body interaction potential (TBIP) model [14] which consists of long-range Coulomb interaction, three-body interaction and short-range

---

[*] Corresponding author at: Govt. Polytechnic College, Indore Road, Harda, M.P. 461331, India. Tel.: +91 07574 256286; fax: +91 0755 256286.
E-mail address: atul_gour@rediffmail.com (A. Gour).

0925-8388/$ – see front matter © 2010 Elsevier B.V. All rights reserved.
doi:10.1016/j.jallcom.2010.05.140

repulsive interactions. We have also studied the TBI effects in case of semiconductors [18] and more recently in case of rare-earth mono-tellurides [19]. Jha and Sanyal [7] have successfully investigated the high-pressure behavior of NpSe and NpTe using same set [$\rho, b, f(r)$] of model parameters in both B1 and B2 phases. More recently Kholiya and Gupta [8] employed the potential model taking different set of [ρ, b, $f(r)$] and shown the realistic approach to analyze the high-pressure phase transition and elastic properties of actinide-arsenides. They reported some weaknesses in the potential model developed by Jha and Sanyal [7] viz (a) They have used the same ionic radii in both phases and (b) They have used same model parameters for both the phases etc. Hence, we thought it pertinent to employ TBIP in case of NpSe and NpTe taking different sets of model parameters [ρ, b, $f(r)$] for both B1 and B2 phases in order to make TBIP approach more realistic. The proposed potential model and computed results are illustrated in Sections 2 and 3 respectively.

2. Potential model

It is well known that pressure causes a change in volume of the crystal and consequently it alters the charge distribution of electron shells. As a result of this, a deformation of the overlapping shell takes place that give rise to charge transfer. This transferred charge when interacts with other charges of the lattice via Coulomb's law gives rise to many-body interactions (MBI), the significant part of MBI is three-body interactions (TBI) [14]. This interaction becomes more important to consider due to the decrease in the inter-ionic spacing of the crystal when pressure gets increased. The transferred charge due to the overlap of electron shells, modifies the ionic charge which in turns enhances the coulomb energy. The increased effects of TBI, thus obtained, lead to an obvious necessity of their inclusion in the high-pressure phase transition studies. Thus, the expression for the modified Coulombic energy due to TBI is:

$$\phi_m(r_0) = \phi^C + \phi^{TBI} \tag{1}$$

$$\phi_m(r) = \left[\frac{-\alpha_M z^2 e^2}{r}\right]\left[1 + \left(\frac{2n}{z}\right) f(r)\right] \tag{2}$$

Here, α_M is the Madelung constant, which is 1.7476 (1.7629) for NaCl (CsCl) structure solids, r is the equilibrium nearest neighbor (nn) ion separation, n is the number of nearest neighbor (nn), z is the valence, e is the electronic charge and $f(r)$ is the TBI parameter which is dependent on the nearest-neighbor distance (r) as $f(r) = f_0 \exp(-r/\rho)$ [14].

The effect TBI is introduced in the expression of Gibb's free energy. Obviously, the stability of a particular lattice structure is decided by the minima of the Gibb's free energy ($G = U + PV - TS$). Here, U being the internal energy which at 0 K is equivalent to lattice energy. S is the vibrational entropy at absolute temperature T. Since the theoretical calculations are done at $T = 0$ K, hence the Gibbs's free energy is equivalent to enthalpy. As the temperature or pressure variable acting on the compounds is altered the free energy changes smoothly and continuously. The Gibb's free energy for the rock salt (B1) structure is:

$$G_{B1}(r) = U_{B1}(r) + 2r^3P \tag{3}$$

and for the cesium chloride (B2) structure is:

$$G_{B2}(r') = U_{B2}(r') + 1.54r'^3P \tag{4}$$

Here, V_{B1} (=2.00 r^3) and V_{B2} (=1.54 r^3) are the unit cell volumes for B1 and B2 phases respectively. The first terms in the energies expressed by Eqs. (3) and (4) are lattice energies for B1 and B2 structures and they are expressed as follows:

$$U_{B1}(r) = \frac{-\alpha_m z^2 e^2}{r} - \frac{12\alpha_m z e^2 f(r)}{r} + 6\,b\exp[(-r)/\rho] + 12\,b\exp[(-1.414r)/\rho] \tag{5}$$

$$U_{B2}(r^1) = \frac{-\alpha'_m z^2 e^2}{r^1} - \frac{16\alpha_m z e^2 f(r)^1}{r^1} + 8b^1\exp[(-r^1)/\rho^1] + 6\,b^1\exp[(-1.154r^1)/\rho^1] \tag{6}$$

Here, ρ (ρ^1), $b(b^1)$ and $f(r)$ [$f(r)^1$] are the range, hardness and TBI parameters for the B1(B2) structures. These lattice energies $U_{B1}(r)$ and $U_{B2}(r^1)$ consist of long-range Coulomb energy (first term), TBI corresponding to the nearest-neighbor separation $r(r')$ for B1 (B2) phases (second term), energy due to the overlap repulsion (third term) and extended up to the second neighbor ions (fourth terms).

The effective inter-ionic potential model described for NaCl (B1) and CsCl (B2) structures contain three model parameters [ρ, b, $f(r)$] for B1 structure and three model parameters [ρ^1, b^1, $f(r)^1$] for B2 structure. For B1 structure, these parameters are calculated by employing the equilibrium conditions:

$$\left[\frac{dU}{dr}\right]_{r=r_0} = 0 \quad \text{and} \quad \left[\frac{d^2U}{dr^2}\right]_{r=r_0} = 9kr_0B_T \tag{7}$$

Here B_T is isothermal bulk modulus and $K = 2$ for B1 phase. For B2 phase, we have followed Kholiya and Gupta [8] realistic approach, according to which the value of range parameter decreases from B1 to B2 structure up to 10% and the value of hardness parameter increases by the ratio 8/6 from B1 to B2 phase and hence written as:

$$b^1 = \frac{8}{6}b \tag{8}$$

Here, 8 and 6 are the coordination numbers for the B1 and B2 structures respectively. Also, the value of the range parameter ρ^1 in B2 phase is calculated by knowing the fact that the range parameter decreases as the inter-ionic separation (r) increases and can be written as:

$$\rho^1 = \frac{r}{r^1}\rho \tag{9}$$

Also, the TBI parameter [$f(r^1)$] is calculated by the minimum value of the Gibb's free energy for B2 phase whereas the inter-ionic separation(r^1) for B2 phase is calculated from the experimental relative volume change at the phase transition pressure. The expression for second-order elastic constants i.e. SOCE's (C_{11} C_{12} & C_{44}) and their pressure derivatives are well described in our earlier work [19].

Moreover, We have investigated various physical properties like Compressibility (β) force constant (f), Debye temperature (θ_D), Gruniesen parameter(γ), Reststrahlen frequency (ν_0) in order to assess the relative merit of TBIP. The relevant expressions used in our calculations are taken from Singh et al. [20].

In order to describe the anharmonic properties, we have calculated compressibility (β) of the compounds from the relation:

$$\beta = \frac{3Kr_0}{f} \tag{10}$$

which is written in terms of the molecular force constant and can be expressed as:

$$f = \frac{1}{3}\left[\Phi_{SR}(r) + \frac{2}{r_0}\Phi'_{SR}(r)\right] \tag{11}$$

where $\Phi_{SR}(r)$ is the short-range overlap repulsion energy and $\Phi'_{SR}(r)$ is the first-order derivatives of short-range overlap repulsion

Table 1
Input parameters used to calculate the model parameters.

Crystal	r_0 (A°)	Volume collapes (%)	B_T (GPa)
NpSe	2.902[a]	9[a]	60[a]
NpTe	3.099[b]	7[b]	62[b]

[a] Ref. [10].
[b] Ref [11].

Table 2
Calculated model parameters.

Crystal	B1-phase			B2-phase		
	ρ (A^o)	b (10^{-19} J)	$f(r)$	ρ^1 (A°)	b^1 (10^{-19} J)	$f(r)^1$
NpSe	0.55	1175.5	0.0329	0.521	1565.4	0.035
NpTe	0.575	1247.8	0.0332	0.54	1658	0.056

energy. This force constant is also used to calculate the infrared absorption (reststralhlen) frequency from the relation:

$$\nu_0 = \frac{1}{2\pi}\left[\frac{f}{\mu}\right]^{1/2} \tag{12}$$

The values of Debye temperature have been calculated from the Blackmann's relation [21] which is as follows:

$$\theta_D = \frac{\hbar}{k_B}\left(\frac{5r_0}{B_T\mu}\right)^{1/2} \tag{13}$$

Here, $\hbar = h/2\pi$ is the Planck's constant, k_B is the Boltzman's constant, μ is the reduced mass.

The Gruneisen parameter is calculated from the relation [20] as follows:

$$\gamma = \frac{-r_0}{6}\left[\frac{\Phi'''(r)}{\Phi''(r)}\right]_{r=r_0} \tag{14}$$

Here, $\Phi'''(r)$ and $\Phi''(r)$ are the third and second-order derivative of overlap energy with respect to inter-ionic separation respectively.

3. Results and discussion

The effective potential model described in the earlier section for B1 and B2 phases contain different set of model parameters viz [ρ, b, $f(r)$] and [ρ^1, b^1, $f(r^1)$]. Previous workers [7,18,19] have taken single set [ρ, b, $f(r)$] in B1 phase and same set of values was used in B2 phase. The reason for this was to maintain the simplicity in theoretical calculations with the single set. The necessity and validity for different set of parameters for both the phases are well illustrated by Kholiya and Gupta [8]. They suggested that while using minimization technique of cohesive energy for two different structures viz for B1 and B2 phase having different potential model their corresponding parameters should also be different. The utilization of different parameters for different structures in the present potential model enables to calculate theoretical cohesive energy more accurately than other [7]. The input data for calculating the model parameters are listed in Table 1 and the model parameters thus obtained are presented in Table 2. The cohesive energy and the phase transition pressures for NpSe and NpTe are tabulated in Table 3 along with the experimental and other work. In an attempt to reveal the structural phase transition of the test material, we minimize the Gibb's free energies $G_{B1}(r)$ and $G_{B2}(r^1)$, for the equilibrium inter-ionic separation (r) and (r^1). As the pressure is increased, ΔG decreases and approaches to zero at the phase transition pressure. Beyond this pressure, ΔG becomes negative as the phase B2 is more stable. The Gibbs free energy differences $\Delta G = (G_{B2}(r^1) - G_{B1}(r))$ have been plotted as the function of pressure (P) and are shown in Fig. 1(a) for NpSe and Fig. 2(a) for NpTe. The estimated value of phase transition pressure (P_t) for NpSe and NpTe are 24.4 and 12.2 GPa which are very close to experimental results of NpSe and NpTe. The compression curves from present model are shown in Figs. 1(b) and 2(b) indicating the first-order transition from B1 to B2 structures.

Table 3
Cohesive and phase transition properties of NpSe and NpTe.

Crystal	Cohesive energy (10^{-19} J)		Transition pressure (GPa)		
	$G_{B1}(r)$	$G_{B2}(r^1)$	Present	Exp	Others
NpSe	−96.26	−94.99	24.4	23[a]	22.4[b]
NpTe	−91.77	−90.57	12.2	(12–20.0)[c]	14.2[b]

[a] Ref. [10].
[b] Ref [7].
[c] Ref. [11].

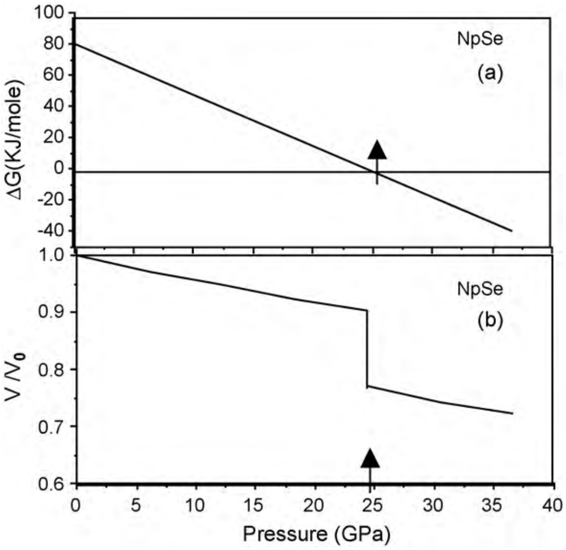

Fig. 1. (a) Variation of Gibbs free energy difference with pressures for NpSe and (b) variation of relative volume change with pressure for NpSe.

We have studied the anharmonic properties of these monopnictides by calculating SOEC's (C_{11} C_{12} & C_{44}) and the pressure derivative of the bulk modulii dB_T/dP as they provide physical insight into the nature of binding forces between the different con-

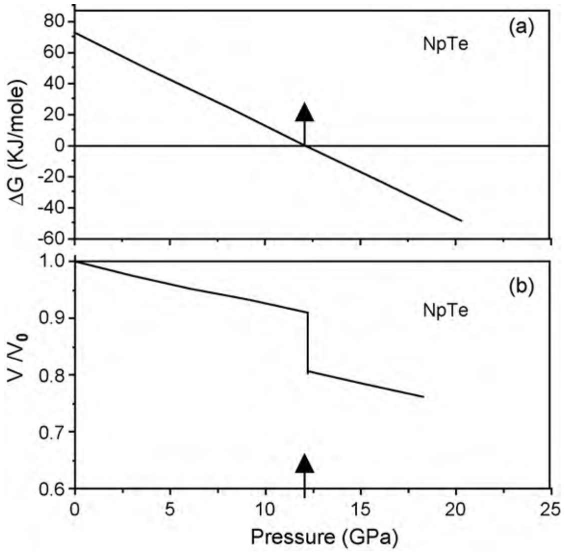

Fig. 2. (a) Variation of Gibbs free energy difference with pressures for NpTe and (b) variation of relative volume change with pressure for NpTe.

Table 4
Calculated elastic constants and their combinations (GPa).

Crystal	C_{11}	C_{12}	C_{44}	dB_T/dP
NpSe	1.11	0.618	0.638	4.45[a]
NpTe	1.52	0.638	0.68	2.35[a]

[a] Ref. [8].

Table 5
Calculated values of compressibility, force constant, Debye temperature, Gruneisen and reststrahlen frequency.

Crystal	$\beta\,(10^{-12}\,\mathrm{dyne^{-1}\,cm^2})$	$f\,(10^5\,\mathrm{dyne/cm})$	θ_D (K)	γ	$\nu_0\,(10^{12}\,\mathrm{Hz})$
NpSe	3.2	1.84	228	0.89	2.13
NpTe	3.15	1.85	203.68	0.91	6.11

stituents of a crystal. The methods for their calculations are same which we have reported in our earlier work [19]. The values of SOEC's are well tabulated in Table 4 which we are not able to compare due to the lack of available experimental data but their values are well suited with the values reported for actinide arsenide compounds [8] having NaCl-type structure. In addition, Vukcevich [22] proposed a high-pressure stability criterion for ionic solids, according to which the stable phase of a crystal is one in which the shear elastic constant $C_{44,}$ is nonzero at the phase transition pressure. Thus, it is inferred in Table 4 that the shear elastic constants from the present potential model is non-zero and this supports the above defined high-pressure stability criterion. Also, the values of dB_T/dP for NpSe (NpTe) are positive indicating that the bulk modulus increases on increasing the pressure, i.e. the elastic constants C_{11} and C_{12} also increase with pressure.

Apart from elastic constants, we have investigated various important physical properties like Debye temperature Θ_D, Gruneisen parameter (γ) and Anderson parameter(δ). The calculated values from the TBIP approach are well tabulated in Table 5. Quite generally, the Debye temperature is the function of temperature and varies technique to technique and also depends on sample quality with the standard deviation of about 15 K. Our values for the Debye temperature are calculated from well-known Blackmann's formula [21] and their values for NpSe and NpTe are 228 and 203.68 K respectively. The experimental data for the Debye temperature of solids under study is not known yet. Thus we do not claim the process to be rigorous, but a consistent agreement following TBIP is obtained on Debye temperature. Moreover, we have calculated the Gruneisen parameters which describe the alteration in crystal lattice vibrations frequency (phonon) based on the lattice increase or decrease in volume due to the temperature or pressure change. Also, our values of Gruneisen parameter (γ) seem to be realistic as they are close in magnitude to the measured values of alkali halides having NaCl-type structure [14]. Since the compounds under study are recently discovered, hence the direct comparisons of these properties are not possible. The present results on thermo-physical properties are however are of academic importance but they will also guide the experimental workers in future. A complete analysis of the dielectric and dynamical properties of the actinide monopnictides and monochalcogenides from the present TBIP model seems desirable and is in progress in our group.

4. Conclusion

In the present investigation, an effective inter-ionic interaction potential model is formulated for analyzing the structural and elastic properties as well as the quantitative description of thermo-physical properties in case of NpSe and NpTe. In the present TBIP model, we have used different sets of model parameters for B1 and B2 phases for the first time including the effects of three-body interactions. Previous workers have taken single set of parameter [ρ, b, $f(r)$] in B1-phase and same set was used in B2-phase which is not the realistic method because we are utilizing the minimization of Gibb's free energy for two different structures and their expressions are also different. Also, we have noticed that during the crystallographic phase transition from NaCl to CsCl structure, the volume discontinuity in pressure-volume phase diagram identifies the same trends as the experimental data. Moreover our calculated values of Compressibility, force constant, Debye temperature, Gruneisen and reststrahlen frequency are consistent with the alkyl halide compounds having the NaCl-type structure.

It is thus obvious from the overall achievements that the present TBIP model is adequately suitable for describing the phase transition pressure, relative stability and the thermo-physical properties of neptunium monochalcogenides. This model has promise for such successful descriptions in case of other actinide compounds also.

Acknowledgement

One of the authors (SS) is thankful to BRNS, Mumbai for financial support.

References

[1] S.S. Dabos, C. Dufor, U. Benedict, J.C. Spirlet, M. Pages, Physica B 144 (1986) 79.
[2] C. Abraham, U. Benedict, J.C. Spirlet, Physica B 222 (1996) 52.
[3] J. Schoences, Physica B 102 (1980) 1463.
[4] J. Schoences, J. Less-Common Met. 121 (1986) 87.
[5] M. Gensini, E. Gering, S. Healthmann, U. Benedict, J.C. Spirlet, High Pressure Res. 2 (1990) 347.
[6] C.H.U.M. Trinaddh, M. Rajagopalan, S. Natrajan, J. Alloys Compd. 274 (1998) 18.
[7] P.K. Jha, S.P. Sanyal, J. Phys. Chem. Solids 64 (2003) 127.
[8] K. Kholiya, B.R.K. Gupta, Physica B 387 (2007) 271.
[9] H.H. Hill, in: W.N. Winner (Ed.), Plutonium 1970 and Other Actinides, Metallurical Society of AMIE, New York, p. 2.
[10] M. Gensini, U. Benedict, J. Rebizant, J. Alloys Compd. 201 (1993) 35.
[11] S.S. Dabos, U. Benedict, J.C. Spirlet, M. Pages, J. Less-Common Met. 160 (1989) L19.
[12] P.O. Lowdin, Adv. Phys. 5 (1956) 1.
[13] S.O. Lundqvist, Ark. Fys. (Swedon) 12 (1957) 263.
[14] R.K. Singh, Phys. Rep. 85 (1982) 259.
[15] C.E. Sims, G.D. Barrera, N.L. Allan, Phys. Rev. B 57 (1998) 1164.
[16] S. Froyen, M.L. Cohen, J. Phys. C 19 (1983) 2623.
[17] P. Vashista, A. Rahman, Phys. Rev. Lett. 40 (1976) 1337.
[18] R.K. Singh, S. Singh, Phys. Rev. B 38 (1989) 76.
[19] A. Gour, S. Singh, R.K. Singh, J. Phys. Chem. Solids 69 (2008) 1669.
[20] R.K. Singh, N. Kumar, G.B. Varshney, Phys. Status Sol. B 136 (1986) 457.
[21] M. Blackman, Philos. Trans. R. Soc. (London) A236 (1936) 103.
[22] M.R. Vukcevich, Phys. Status Sol. B 54 (1972) 435.