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ANALYSIS OF STRUCTURAL AND ELASTIC PROPERTIES OF THN UNDER HIGH PRESSURE AND HIGH TEMPERATURE

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Abstract

We have developed a realistic interaction potential model (RIPM) approach for investigating the pressure induced phase transition and elastic properties of ThN. The present compound exhibits NaCl structure and transforms to CsCl structure under pressure. Probably this is the first time when the present compound has been studied by using the three body potential including the temperature effect. The results obtained from the present work are found to be in good agreement with the available theoretical results.

Keywords: Phase transition; three body interaction; pressure; temperature and volume collapse.

Introduction

Thorium pnictides are generally crystallize in a simple rock-salt type structure at ambient condition and are completely solid soluble in whole composition due to these properties, they are used as fuel materials [1]. These compounds have attracted huge attention of researchers because of their potential application in reactors. The binary compounds based on thorium formed with lighter nuclei such as ThC and ThN are currently being investigated due to their application in fast breeder reactors, owing to their high melting point, high thermal conductivity, high density and good compatibility with the coolant (liquid Na) [2-3].

ThN is less explored and there is little known about its structural and elastic properties under high pressure and no other study had been done for the same under high pressure and high temperature. Modak and Verma [4] investigated the high pressure behavior of ThN by using ab initio total energy calculations. It had been found that ThN is stable in B_1 structure up to 47 GPa, experimentally [5]. Gupta et al. [6] have used MCTP model for studying the high pressure properties of thorium pnictides.

Earlier studies related to structural phase transition and elastic properties under pressure were carried out by taking temperature as 0 K. For the realistic approach, studies should be done by taking temperature effects instead of taking it as zero temperature. Since there is no study available in literature in which effects of both pressures and temperatures are applied on ThN. So, we aimed to develop realistic interaction potential model (RIPM) approach to investigate the structural properties of present compound under high pressure including the effects of temperature. This model consists of Coulomb interaction, three body interaction and short range overlap repulsive interaction up to second neighbours and Van der Waal interactions including temperature effects. We have calculated the transition pressure, volume collapse, second order elastic constants (SOECs) and the combinations of SOECs for ThN and found results well suited with other available theoretical data. We have also found the nature of ThN.

Method of Computation

The pressure causes a compression in the crystal due to which the charge distribution of the electron shells get changed, which results in the deformation of the overlapping electron shells of the adjacent ions and leads to an increased charge-transfer (or three-body interaction (TBI)) [7]. This interaction becomes very significant to consider because the decrease in inter-ionic spacing of the lattice crystal when pressure gets increased, the anions experience sufficient overlap. Besides, the enhancement in overlap energy, the transferred charge due to the overlap in electron shells, varies the ionic charge which modifies the coulomb energy by $\{1+(2n/z)\}$, where n and z are the number of electrons in outermost shell and ionic charge of the compound. The *f(r)* is the TBI parameter and it depends on the nearest neighbour distance (r) [7] and can be expressed as:

$$f(r) = f_0 \exp(-r/\rho)$$

(1)

To obtain the stability condition for a crystal structure, the effect of TBI is introduced in the expression of Gibbs free energy, (G = U + PV -TS). Here U is the internal energy, which at T=0K is equivalent to the lattice energy, S is the vibrational entropy at absolute temperature. Since the theoretical calculation are done at T=0 K, hence the Gibbs free energy is equivalent to enthalpy (H). This is not a realistic approach because experiments are carried out at room temperature and not at T=0K. In order to get better comparability with experimental results we have taken account of the room temperature and elevated temperature in pressure induced theoretical calculations. The Gibbs free energies for rock salt (B_1, real) and CsCl (B_2, hypothetical) structures at room temperature T=300K is given by:

$$G_{B_1}(r) = U_{B_1}(r) + PV_{B_1} - TS_1 \qquad (2)$$

$$G_{B_2}(r') = U_{B_2}(r') + PV_{B_2} - TS_2 \qquad (3)$$

where, V_{B_1} (=2.00 r^3) and V_{B_2} (=1.54 r^3) as the unit cell volumes, S_1 and S_2 are the entropies for B_1 and B_2 phases, respectively.

The first terms in the energies (2) and (3) are lattice energies and the last terms are temperature effects, then the expressions of lattice energies are as follows:

$$U_{B_1}(r) = \left[\frac{-(\alpha_m e^2 z^2)}{r}\right] - \left[\frac{(12\alpha_m e^2 z f(r))}{r}\right] - \left[\frac{C}{r^6} + \frac{D}{r^8}\right] + 6b\beta_{ij}\exp\left(\frac{r_i + r_j - r}{\rho}\right) + 6b\beta_{ii}\exp\left(\frac{2r_i - 1.414r}{\rho}\right) + 6b\beta_{jj}\exp\left(\frac{2r_j - 1.414r}{\rho}\right)$$

(4)

$$U_{B_2}(r') = \left[\frac{-(\alpha'_m e^2 z^2)}{r'}\right] - \left[\frac{(16\alpha'_m e^2 z f(r'))}{r'}\right] - \left[\frac{C'}{r'^6} + \frac{D'}{r'^8}\right] + 8b\beta_{ij}\exp\left(\frac{r_i + r_j - r'}{\rho}\right) + 3b\beta_{ii}\exp\left(\frac{2r_i - 1.154r'}{\rho}\right) + 3b\beta_{jj}\exp\left(\frac{2r_j - 1.154r'}{\rho}\right)$$

(5)

Here, α_m and α'_m are the Madelung constants, r(r') are the nearest separation, C(C') and D(D') are the overall Van der Waal coefficients of B_1 and B_2 phases respectively, ρ (b) are the range(hardness) parameters, f(r) is three-body force parameter, β_{ij} = 1 ± ($n_i/z_i + n_j/z_j$) is the Pauling coefficient where z_i (z_j) and n_i (n_j) denote the valence and number of electrons in the outermost orbit of cations (anions) and r_i (r_j) is the ionic radii of *i (j)* ions.

The first term in equations (4) and (5) are long-range Coulomb energies, second terms are due to three body interaction forces for B_1 and B_2 phases, third terms are Van der Waal (vdW) interactions and remaining terms are the short range overlap repulsion represented by Born – Mayer potential for (i, j) ions extended up to second neighbours within Hafemeister and Flygare approach [8].

The essential condition for a phase transition is that the difference in free energies between two phases ($\Delta G = \Delta H - T\Delta S = 0$) approaches to zero (i.e. $\Delta G \rightarrow 0$). Now, the entropy differences in the last term of Eqns-2 and 3 can be calculated from the relation

$$\Delta S = S_1 - S_2 = \int_1^2 [(C_1 - C_2)/T]dT$$

(7)

Here, S_1 and S_2 are the entropies for the B_1 and B_2 phases, C_1 and C_2 are the specific heats of two phases at constant pressure and their values can be calculated by the knowledge of Gruneisen parameter (γ) and linear isothermal temperature coefficients (β) used by Shanker et al. [9] as:

$$C_i = \{\beta V_i(B_T)\}_i / \gamma_i$$

Here, Gruneisen parameter (γ) can be calculated by well known formula [10] as follows by

$$\gamma = \frac{-r_0}{6}\left[\frac{U'''(r)_0}{U''(r)_0}\right]$$

(8)

Here, $U'''(r)_0$ and $U''(r)_0$ are the third and second derivatives of lattice energy with respect to inter-ionic separation at zero pressure. The present RIPM approach contains three model parameters $[\rho, b, f(r)]$ and their values have been determined by solving the equilibrium conditions**.**

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

(9)

Now, we have evaluated the difference in Gibb's free energies ΔG = (G_{B_2}(r') - G_{B_1}(r)). The pressure at which ΔG approaches zero is known as phase transition pressure (P_t). At P_t the ThN undergo a collapse ($B_1 \rightarrow B_2$) in volume showing first-order phase transition. We have also calculated the P_t at high temperatures.

In order to explore the elastic behavior of ThN, we have calculated temperature dependent second order elastic constants (SOEC's). There are three independent SOEC namely, C_{11}, C_{12} and C_{44} in cubic system. Since these elastic constants are functions of first and second order derivatives of short range potential, so their calculation will provide knowledge about the effect of short range forces on this compound. We have also calculated the combination of SOECs viz. shear (C_S) and stiffness constants (C_L). They are calculated by using the relations followed by Dubey et al. [11].

Results and Discussions

The B_1 structure is most stable in these compounds and at high pressure they transform to body centred B_2 structure. As the stable phase is associated with minimum free energy of the crystal, we have followed the technique of minimization of Gibbs free energies of real and hypothetical phases. The phase transition occurs when ΔG approaches zero ($\Delta G \rightarrow 0$). At phase transition pressure (P_t) these compounds undergo a ($B_1 \rightarrow B_2$) transition associated with a sudden collapse in volume showing a first order phase transition.

The input parameters and model parameters for present compound is given in table 1. In order to study the temperature behavior of phase transition pressure we have computed the values of phase transition pressure in the temperature range 0-600K for present compound. The phase transition pressure and volume collapse for present compound is given in table 2. We have plotted ΔG against pressure (P) in fig.1 and Vp/Vo against pressure (P) in fig 2. It is clear from fig 1 that the phase transition pressure decreases monotonically with increasing temperature. The calculated values of SOECs and their combinations viz. shear (C_S) and stiffness constants (C_L) and δ are listed in table 3 and we have plotted SOECs against pressure in fig.3. It is clear from fig.3 that the unidirectional elastic constant C_{11}, related to the unidirectional compression along the principal crystallographic direction, varies largely under the effect of pressure than C_{12} and C_{44} in present compound. Their Knowledge facilitates us to understand, characterize and predict mechanical properties of materials. We have obtained the same trends which were reported earlier by Karki et al [12]. The deviation from the Cauchy violation ($\delta = C_{12} - C_{44}$) is a measure of the contribution from the non central many-body force. Our present model is able to explain the Cauchy violation better than other model [13]. The negative value of δ indicates that ThN is brittle in nature.

Table 1. Input and Model parameters [a]Ref [5]

Solid	**Input Parameters**		**Model parameter**		
	r_0 (Å)	**B_T (GPa)**	**b(10^{-12} ergs)**	**ρ (Å)**	**f(r)**
ThN	2.583[a]	175 [a]	8.2376	0.2682	-0.0114

Table 2. Calculated transition pressure and Volume collapse

Solid	**Temperature (K)**	**Transition Pressure (GPa)**		**Volume collapse (%)**	
		Present	other	Present	other
ThN	0	70.90	70.54 [a]	6.12	6.35 [a]
	300	66.80	-	6.40	-
	600	63.02	-	6.70	-

[a]Ref [6]

Table 3. Calculated Second order elastic constants (GPa)

Solid	**Property**	**Temperature (K)**	**Pressure (GPa)**			
			0 (Present)	0 (other)	25 (Present)	50 (Present)
ThN	C_{11}	0	342.4	344.9[a],372.8[b]	358.2	372.6
		300	337.3		352.3	366.3
		600	327.0		342.5	360.9
	C_{12}	0	70.3	77.8[a], 72.87[b]	72.4	77.2
		300	69.5		71.3	73.4
		600	67.6		70.0	72.6
	C_{44}	0	82.3	77.8[a],98.9[b]	83.8	86.7
		300	82.1		83.3	84.5
		600	81.2		82.5	84.0
	C_S	0	136.0	148.4 [b]	143.1	157.5
		300	130.4		140.4	146.4
		600	129.6		136.3	144.0
	C_L	0	288.7	323.3[b]	299.4	321.4
		300	285.4		295.2	304.4
		600	278.6		288.6	300.8
	δ	0	-12.0	0[a*],-26.2 [b*]	-11.4	-9.5
		300	-12.6		-12.0	-11.1
		600	-13.6		-12.5	-11.4

[a]Ref [12], [b]Ref [6], *calculated

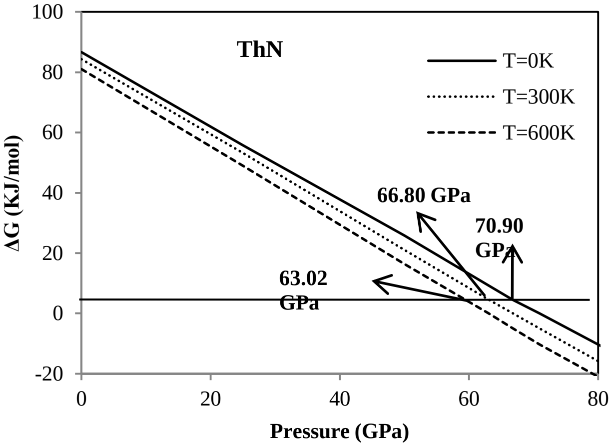

Figure 1. Variation of ΔG with pressure

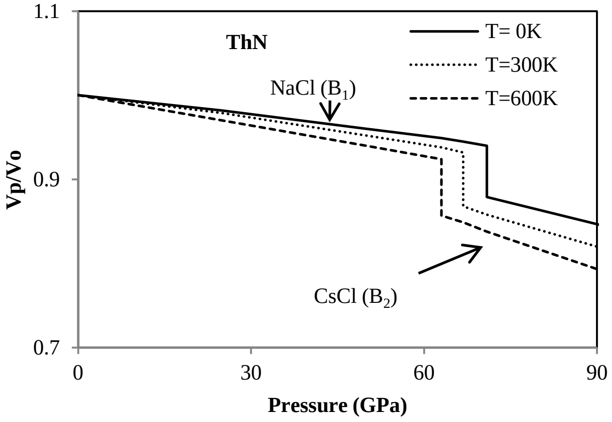

Figure 2. Variation of Vp/Vo with pressure

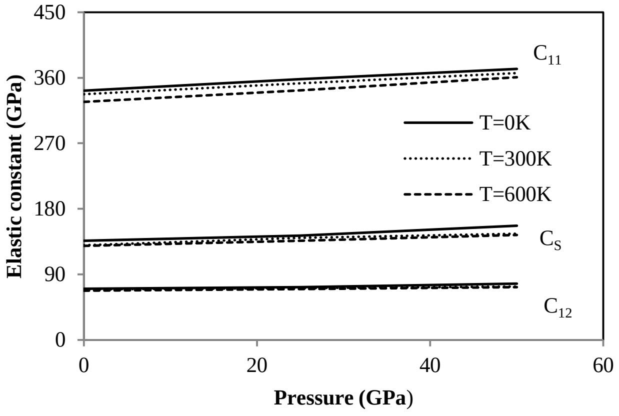

Figure 3. Variation of elastic constants with pressure

Conclusions

We can conclude that

1. The present RIPM approach is suitable for studying the crystallographic pressure induced phase transition from NaCl to CsCl at room temperature rather than at T= 0K and further higher temperatures.
2. We obtained reasonable results regarding the phase transition pressure and the volume collapse with the other theoretical data. The temperature variation of phase transition pressures show the same behaviour as reported previously [14].
3. The computed values of SOECs and their combinations are well matched with other available data.
4. The present study is successful in explaining Cauchy violation and its calculated value shows that ThN is brittle in nature.

This approach can be applicable for other actinide compounds.

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