

## Structural phase transition and elastic properties of thorium pnictides at high pressure

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**Abstract.** In the present paper we have pointed out the weaknesses of the approach by Aynyas *et al* [1] to study the structural phase transition and elastic properties of thorium pnictides. The calculated values of phase transition pressure and other elastic properties using the realistic and actual approach are also given and compared with the experimental and previous theoretical work.

**Keywords.** Thorium pnictides; B1–B2 phase transition; elastic constants.

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In a paper entitled ‘Structural phase transition and elastic properties of thorium pnictides at high pressure’, Aynyas *et al* [1] have calculated the structural and elastic properties of thorium monopnictides at high pressure by using the rigid ion potential model. Though the model used by them is too good and simple to explain these properties and gives values close to the experimental findings, the model theory and method of calculation given by them is neither the realistic nor the actual one. The matching of the results claimed by these workers with the experimental data is rather forced. The weaknesses in the approach of these workers are as follows:

The potential used by Aynyas *et al* is

$$U(r) = \frac{\sum_{ij} Z_i Z_j e^2}{r_{ij}} + \sum_{ij} b\beta_{ij} \exp\left[\frac{r_i + r_j - r_{ij}}{p_{ij}}\right] + \sum_{ij} C_{ij} r_{ij}^{-6} + \sum_{ij} D_{ij} r_{ij}^{-8} \quad (1)$$

and the expressions of cohesive energies for the B1 and B2 phases are

$$U_{B1}(r) = \frac{-1.7475e^2 Z^2}{r} + 6X_{ij}(r) + 6X_{ii}(r) + 6X_{jj}(r) \quad (2)$$

and

$$U_{B2}(r^1) = \frac{-1.7627e^2Z^2}{r^1} + 8X_{ij}(r^1) + 3X_{ii}(r^1) + 3X_{jj}(r^1), \quad (3)$$

where  $r$  and  $r^1$  are nearest-neighbour separations corresponding to NaCl and CsCl phases, respectively. They have expressed the short-range potential for both the phases as

$$X_{ij}(r) = b_{ij} \exp\left(\frac{-R_{ij}}{p_{ij}}\right) C_{ij} r_{ij}^{-6} D_{ij} r_{ij}^{-8}, \quad (4)$$

where  $R_{ij} = r_{ij} - (r_i + r_j)$  and  $b_{ij}$  and  $p_{ij}$  are the range and hardness parameters and  $C_{ij}$  and  $D_{ij}$  are van der Waals coefficients which refer to dipole-dipole and dipole-quadrupole interactions respectively.

In view of eq. (1) one cannot define the short-range potential  $X_{ij}(r)$  by eq. (4). The correct definition follows as [2]

$$X_{ij}(r) = b_{ij} \exp\left(\frac{-R_{ij}}{p_{ij}}\right) - C_{ij} r_{ij}^{-6} - D_{ij} r_{ij}^{-8}. \quad (5)$$

This may be due to typographical mistake. But there are some other serious weaknesses too which cannot be due to the typographical mistake because these mistakes are repeated in their other work [3,4].

(i) They have considered the same values of anion and cation radii in both phases whereas it is noted from [2,5] that the NaCl-type structure becomes stable only if the ratio of anion radius to the cation radius is between 0.41 to 0.73 and the CsCl-type structure becomes stable if the radius ratio is above 0.73. Therefore, the assumption that the cation and anion radii have the same value in both phases is not justified. Moreover, they have calculated the values of interionic separation at different pressure by minimizing the Gibbs free energy and by this way one cannot calculate three values, viz.,  $r_i$ ,  $r_j$  and  $r_{ij}$ . Therefore, suitable choice of potential to study the B1-B2 phase transition follows as

$$X = b \exp\left(-\frac{r}{p}\right). \quad (6)$$

(ii) To determine the model parameters  $b$  and  $p$  of this potential, Aynyas *et al* [1] have used the equilibrium condition

$$\begin{aligned} \frac{b}{r_0} \left\{ \beta_{+-} \exp\left[\frac{(r_+ + r_- - r_0)}{p}\right] + 2\beta_{++} \exp\left[\frac{(2r_+ - 2r_0)}{p}\right] \right. \\ \left. + 2\beta_{--} \exp\left[\frac{(2r_- - 2r_0)}{p}\right] \right\} = \left(\frac{2a_m}{3}\right) \frac{Z^2 e^2}{2V} + 6C_{+-} r_0^{-8} \\ + 8D_{+-} r_0^{-10} + 0.75(C_{++} + C_{--}) r_0^{-8} + 0.5(D_{++} + D_{--}) r_0^{-10}, \quad (7) \end{aligned}$$

where  $V$  is the unit cell volume,  $a_m$  is the Modelung constant and  $\beta_{ij}$  are the Pauling coefficients. It is not understandable how they are getting the values of two model parameters namely  $b$  and  $p$  from single equilibrium condition, i.e. from eq. (7). Moreover, the equilibrium condition used by these workers is wrong. The

equilibrium condition  $[dU(r)/dr]_{r=r_0} = 0$  is obtained by differentiating eq. (1) with respect to interionic separation which is not the eq. (7) used by them. This is why the equilibrium condition given by them is also not correct dimensionally. In equilibrium condition, they have considered the next-nearest neighbour separation as  $2r$  whereas for the NaCl-type structure it comes out to be  $\sqrt{2}r$  [5]. The correct equilibrium condition should be written as

$$\begin{aligned} \frac{b}{(r_0 p)} \left\{ \beta_{+-} \exp \left[ \frac{(r_+ + r_- - r_0)}{p} \right] + \sqrt{2} \beta_{++} \exp \left[ \frac{(2r_+ - \sqrt{2}r_0)}{p} \right] \right. \\ \left. + \sqrt{2} \beta_{--} \exp \left[ \frac{(2r_- - \sqrt{2}r_0)}{p} \right] \right\} = \left( \frac{2a_m}{3} \right) \frac{Z^2 e^2}{2V} + 6C_{+-} r_0^{-8} \\ + 8D_{+-} r_0^{-10} + 0.75(C_{++} + C_{--}) r_0^{-8} + 0.5(D_{++} + D_{--}) r_0^{-10}. \end{aligned} \quad (8)$$

If the van der Waals interactions whose contribution to the total potential energy is negligibly small are neglected and using the potential defined by eq. (6), one gets the following correct form of the equilibrium condition:

$$\frac{b}{(r_0 p)} \left[ \exp \left( \frac{-r_0}{p} \right) + 2\sqrt{2} \exp \left( \frac{-\sqrt{2}r_0}{p} \right) \right] = \left( \frac{2a_m}{3} \right) \frac{Z^2 e^2}{2V}. \quad (9)$$

Since two potential parameters  $b$  and  $p$  are to be determined, another condition has to be used. For this purpose the thermodynamic condition given below, is generally used.

$$B = V \left( \frac{d^2 U}{dV^2} \right)_{r=r_0}. \quad (10)$$

It appears that these workers have probably fabricated the value of at least one of the potential parameters out of two short-range parameters, i.e.  $b$  or  $p$ .

(iii) The Gibbs free energies for NaCl (B1) phase and CsCl (B2) phase considered by them are, respectively

$$G_{B1}(r) = U_{B1}(r) + 2r^3 P \quad (11)$$

and

$$G_{B2}(r^1) = U_{B2}(r^1) + \frac{8}{3}(r^1)^3 P. \quad (12)$$

This expression gives the unit cell volume of B1 phase as  $2(r)^3$  and that of B2 phase as  $(8/3)(r^1)^3$ . They have calculated that the interionic separation in B2 phase is greater than in B1 phase, i.e.  $r^1 > r$ , which seems to be correct [7] and can be explained by the mechanism of the B1 to B2 transition in which the increase in pressure causes the unfolding of the bonding between the ions. But if the multiple of  $(r^1)^3$ , i.e.  $8/3$  is greater than the multiple of  $(r)^3$ , i.e.  $2$  then the volume of the unit cell should increase at transition since  $r^1 > r$ . However, it has been noted in the high pressure X-ray diffraction studies [7–15] that for B1 to B2 transition the

**Table 1(a).** Input parameters used to calculate model parameters.

Crystal	$r_0$ (Å)	$B_0$ (GPa)	% Volume collapse at transition
ThP [17]	2.9135	125	11.9
ThAs [12]	2.9890	118	11.0
ThSb [18]	3.1590	92	9.4

**Table 1(b).** Calculated model parameters.

Crystal	$b_1$ ( $10^{-19}$ J)	$p_1$ (Å)	$b_2$ ( $10^{-19}$ J)	$p_2$ (Å)
ThP	119200.0617	0.2434	158933.4156	0.2389
ThAs	180149.6984	0.2402	240199.5979	0.2365
ThSb	129848.7810	0.2600	173131.7080	0.2535

**Table 2.** Cohesive and phase transition properties of ThP, ThAs and ThSb.

Crystal	Equilibrium separation (Å)		Cohesive energy ( $10^{-19}$ J)		Transition pressure (GPa)
	$r_{B1}$	$r_{B2}$	$G_{B1}$	$G_{B2}$	
ThP					
Present	2.9135	3.0428	-50.687	-49.267	27.8
Exp. [17]	2.9135				30.0
Ref. [1]	2.9246	3.0400	-50.836	-49.598	21.4
ThAs					
Present	2.989034	3.1227	-49.572	-48.134	26.0
Exp. [12]	2.989				25.0
Ref. [1]	2.9951	3.1100	-49.454	-48.355	16.4
ThSb					
Present	3.158999	3.2714	-46.809	-45.863	11.5
Exp. [18]	3.159				9.12
Ref. [1]	3.167	3.2900	-46.942	-45.931	12.4

unit cell volume always collapses at transition. This is possible only if the unit cell volume of the B2 phase is  $(8/3\sqrt{3})(r^1)^3$  [16] instead of  $(8/3)(r^1)^3$  [1].

In view of the facts indicated from (i) to (iii), it may be emphasized, here, that the work reported by Aynyas *et al* needs a complete revision. We have, therefore predicted the phase transition pressure and the elastic properties of thorium pnictides by using the correct and realistic approach as described above. In the present study we have taken different values of range and hardness parameters in B1 and B2 phase. For B1 phase hardness ( $p_1$ ) and range ( $b_1$ ) parameters are calculated from eqs (9) and (10). For B2 phase the value of range parameter may be given as [2,16]

**Table 3.** Elastic constants and bulk modulus (in GPa).

Crystal	$C_{11}$ (GPa)	$C_{12}$ (GPa)	$C_{44}$ (GPa)	$B_0$ (GPa)
ThP				
Present	279.656	47.466	47.891	124.86
Exp. [17]				125.00
Ref. [1]	278.770	46.450	45.380	124.00
ThAs				
Present	268.747	42.465	42.781	117.89
Exp. [12]				118.00
Ref. [1]	246.240	41.460	40.460	109.00
ThSb				
Present	207.312	34.222	34.508	91.92
Exp. [18]				92.00
Ref. [1]	208.510	33.150	32.600	91.00

$$b_2 = \frac{8}{6} \times b_1 \quad (13)$$

while the hardness parameter ( $p_2$ ) may be calculated from the minima of the Gibbs free energy whereas the interionic separation ( $r^1$ ) can be calculated with the help of volume collapse at the phase transition pressure. Here it may be noted that the value of  $\exp(-r/p)$  is smaller than  $\exp((r_i + r_j - r_{ij})/p)$  and as potential parameter  $b$  is calculated from the equilibrium condition, its value for the potential of the form of eq. (6) comes out to be very large in comparison to the value for the potential of the form  $b_{ij} \exp((r_i + r_j - r_{ij})/p)$  considered by the previous workers [1]. With the knowledge of potential parameters the phase transition pressure is calculated as the pressure at which the difference of Gibbs free energy for two phases becomes zero. To calculate the second-order elastic constants we have divided them into the contributions from Coulombic and short-range forces. The Coulombic contributions are calculated following the method given by Cowley [19] and the short-range contributions are calculated as the combination of the first- and second-order derivatives of the short-range potential [16]. Further, the bulk modulus is calculated from the relation

$$B = \frac{1}{3}(C_{11} + 2C_{12}). \quad (14)$$

In the present work we have left the ThN crystal because for determining the model parameters we require the value of % volume collapse at transition, which is not known experimentally for this crystal. The input parameters and the calculated model parameters are given in tables 1(a) and 1(b). The calculated values of phase transition pressure and elastic constants achieved in the present investigation are reported in tables 2 and 3, respectively. It is evident from the results obtained in the present study that our calculated values for phase transition pressure are in better agreement with the available experimental data as compared to those of Aynyas *et al* [1]. Although the experimental values of elastic constants are not

known, the calculated values of bulk modulus by combining these elastic constants come out to be very close to the experimental values. This supports our method of calculation especially the different values of range and hardness parameter in B1 and B2 phases unlike the previous approach used by Aynyas *et al* [1].

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