Structural Phase Transition of Ytterbium Nitride under High Pressure

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Abstract

The structural and elastic properties of ytterbium nitride (YbN) with NaCl structure have been investigated by using an improved interaction potential model (IIPM). The compound YbN found to undergo from their initial NaCl (B1) phase to body centered tetragonal (BCT) phase at high pressure. The phase transition pressures and associated volume collapses obtained from the potential model developed here show a generally better agreement with available experimental data then others available in the literature. The elastic constants are also reported. This shows that the inclusion of three-body interaction and polarizability effect makes the present model suitable for high pressure studies.

Keywords: Rare earth pnictides, three body interaction, phase transition, volume collapse.

1. Introduction

The transition metal nitrides are valuable for several technological applications. Because of their great strength and durability their long established use is as protective coatings [1].The rare- earth pnictides generally have low carrier, strongly correlated systems and they show dense Kondo behavior and heavy fermion state[2,3]. The silent feature of ytterbium nitride is that it is self-compensated semimetal. Ytterbium nitride is found to have six- fold coordinated rock salt structure (Yb: 0,0,0; N : 1/2,1/2,1/2; space group Fm-3m under ambient conditions. Because of these interesting properties, the high pressure structural behavior of binary rare-earth compounds is of current interest in condensed matter research. The YbN ion is predominantly trivalent with one 4f holes. The structural properties of YbN at normal high pressure have been computed by employing full potential augmented plane wave+local orbital (FP-APW+lo) method within the GGA using the WIEN2K code by Singh et al [4].

Several pressure-induced valence and structural phase transition have been found experimentally in the REN [5–11]. These compounds possess partially filled f-electron orbital, which are highly delocalized under pressure. In this regard many theoretical [12] as well as experimental [13] researches have been carried out to understand the role of f-electrons particularly under pressure.

We have applied the improved interaction potential model (IIPM) to the present compound to study the high pressure phase transition and volume collapse. The need of inclusion of three-body interaction forces was emphasized by many workers for the betterment of results [14–16]. This IIPM model consists of long-range Coulomb energy, three body interactions corresponding to the nearest neighbour separation, effect of electronic polarizability, and energy due to the overlap repulsion represented by Hafemiester and Flygare (HF) [17] type potential and extended up to the second-neighbour ions. We refer to the work of Kumar et al. [18] who properly incorporated polarizability effect to reveal the cohesion in several alkali halides, which are generally ignored in the first principle calculation. The importance of inclusion of short range(SR) interaction and electronic polarizability has been established in our work.

2. Method of Calculation

It is well known that the application of pressure on crystals results a change in its volume that leads to an increased charge transfer (or three-body interaction effects) due to the deformation of the overlapping electron shells of the adjacent ions. The three body interaction arises during lattice vibrations when electron shells of neighboring ions overlap. This overlapping leads to the transfer of charge which interacts with other charges and many body interaction (MBI) takes place, the dominant part of which is the three body interaction. This interaction becomes more important due to the decrease in inter ionic spacing of the lattice crystal when pressure gets increased and when anions experience sufficient overlap. Besides, both an enhancement in overlap energy and the transferred charge due to the overlap in electron shells modify the ionic charge, which in its turns modifies the Coulomb energy. The expression for the modified Coulomb energy due to three body interaction

(TBI) is

$\Phi_m(r_0) = \Phi^c + \Phi^T$ (1)

$\Phi_m(r_0) = [-\alpha_M Z^2 e^2/ r]\ [1+(2n/Z)\ f(r_0)]$ (2)

Here α_M is the Madelung constant (for NaCl and for CsCl structure solids), r_0 is the equilibrium nearest neighbor (nn) ion separation, n is the number of nearest neighbor (nn), and f(r) is the TBI parameter which is dependent on the nearest neighbor distance (r) as

$f(r) = f_0 \exp(-r/\rho)$ (3)

These effects have been incorporated in the Gibbs free energy (G=U+PV-TS) as a function of pressure (P). Here, U is the internal energy, which at T= 0 K is equivalent to the lattice energy and S is the vibrational entropy at absolute temperature T. Since theoretical calculations are done at T= 0 K, the Gibbs's free energy is equivalent to enthalpy. At T= 0 K and pressure P, the Gibbs free energies for rock salt (B1, real) and body centered tetragonal (BCT) structures are given by

$G_{B1}(r) = U_{B1}(r) + PV_{B1}$ (4)

$G_{BCT}(r') = U_{BCT}(r') + PV_{BCT}$ (5)

with V_{B1} and V_{BCT} as the unit cell volumes for B1 and BCT phases, respectively. The first terms in the energies Eq. (4) and (5) are lattice energies for B1 and BCT structures and they are expressed as:

$U_{B1}(r) = [-(\alpha_m z^2 e^2)/r] - [(12\alpha_m z\, e^2\, f(r))/r] + (e^2\alpha_e)/ r^4 + 6b\beta_{ij} \exp[(r_i + r_j - r)/\rho] + 6b\, \beta_{ii}\exp[(2r_i - 1.41r)/\rho +$
$6b\beta_{jj}\exp[2r_j - 1.41r)/\rho]$ (6)

$U_{BCT}(r') = [-(\alpha'_m z^2\, e^2/r')] - [(16\alpha'_m z e^2\, f(r'))/r'] + (e^2\alpha_e)/ r^4 + 8b\beta_{ij}\exp[(r_i + r_j - r')/\rho] + 2b\beta_{ii} \exp[(2r_i - r')/\rho] +$
$b\beta_{ii}\exp[(2r_i - r'')/\rho] + 2b\, \beta_{jj} \exp[(2r_j - r')/\rho] + b\beta_{jj}\exp[(2r_j - r'')/\rho]$ (7)

Here, ze is the ionic charge, r_i (r_j) is the ionic radii of i(j) ions, ρ is the range parameter, b is the hardness parameter, f(r) is the three body interaction parameter, r is nearest neighbor (nn) separation for NaCl phase and r′ is the nearest neighbour distances corresponding to lattice parameters a and c in tetragonal structure and β_{ij} is the Pauling coefficients defined as

$$\beta_{ij} = 1 + \frac{z_i}{n_i} + \frac{z_j}{n_j}$$

where, z_i (z_j) and n_i (n_j) denote the valence and number of electrons in the outermost orbit of cations (anions). These lattice energies consist of long-range Coulomb energy (first term), three body interactions (second term), the electronic polarizability (third term) and the short range overlap repulsive interaction (fourth term).

To calculate these parameters, we have employed the following equilibrium conditions.

$[dU / dr]_{r = r_0} = 0$ and $[d^2 U / dr^2] = 9k\, r_0 B_T$ (8)

3. Result and discussion

Using the measured values of the equilibrium lattice constant (r_0) and bulk modulus (B_T) with K=2 for B1 phase, the model parameters thus calculated are given in Table 1 and are used to compute the results presented and discussed below. For simplicity, we have taken account of only a single set [ρ, b, f(r)] in B1–phase and the same set is used in BCT phase. The reason for this is that during the phase transition from B1→BCT the atomic distribution takes a different arrangement and they get arranged in BCT structure after phase transition. Inter-ionic separation changes are calculated by the minimization technique. The parameter f(r) is inter-ionic separation (r) dependent and it is therefore changed accordingly. We have followed the technique of minimization of $U_{B1}(r)$ and $U_{BCT}(r')$ at different pressures in order to obtain their inter ionic separations r and r′ corresponding to B_1 and BCT phases.

TABLE I
INPUT PARAMETERS AND MODEL PARAMETERS

Compounds	Input Parameters		Model Parameters		
	r_0 (Å)	B_T (GPa)	b(10^{-12} ergs)	ρ(Å)	f(r)
YbN	2.39	190[a]	14.691	0.318	0.0793

a. Ref. [3]

First, we have evaluated the corresponding Gibbs free energies $G_{B1}(r)$ and $G_{BCT}(r')$ and their respective differences $\Delta G = (G_{BCT}(r') - G_{B1}(r))$. The phase transition pressure (Pt) is the pressure at which ΔG approaches zero. At this pressure both the phases coexist. ΔG is an important factor in deciding the relative stability of phases. After phase transition the system becomes stable in BCT phase. We have plotted ΔG against pressure (P), as shown in Fig. 1. We have also computed the associated relative volume changes Vp/Vo which are shown in Table 2. and plotted them against the pressure as depicted in Fig. 2. It is clear from Fig. 2 that phase transition B1→ BCT occurs at about 82GPa for YbN, and the calculated volume collapse using IIPM model is 4.3% for YbN. These are close to theoretical values.

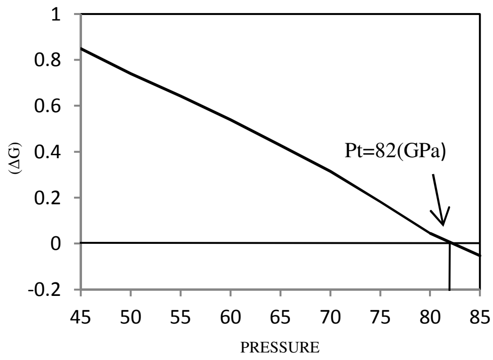

Fig.1 Variation of ΔG with Pressure

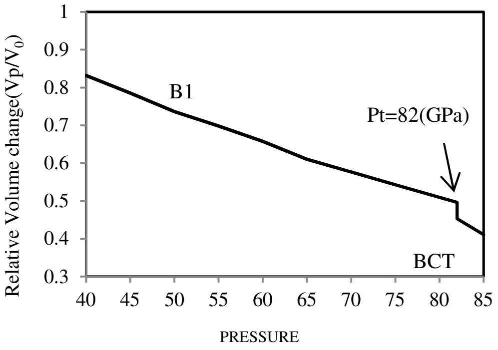

Fig.2 Variation of Volume change V_p/V_0 with Pressure

TABLE II
CALCULATED TRANSITION PRESSURES AND VOLUME COLLAPSES

Compounds	**Transition**	**Phase Transition Pressure (GPa)**	**Relative Volume change %**
YbN	B1— BCT	82 present 79.56other[a]	4.3 present

a.[19]

4. Conclusion

In summary, we have applied to extend improved interaction potential model (IIPM) to investigate the structural and elastic properties ytterbium mononitride. The results are summarized as follows:

I. The ytterbium mononitride crystallize in NaCl type (B1) structure at ambient conditions and under pressure; they transform into body centred tetragonal type (BCT) structure.
II. High pressure study of YbN compound is carried out theoretically. The pressure induced structural phase transition from B1 to BCT is predicted and compared with the experimental and other available theoretical results.
III. During the phase transition from B1 to BCT, the volume discontinuity in pressure volume phase diagram identifies the occurrence of first order phase transition.

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References

Oyama S.T.; Blackie Academic & Professional: London (1996) 107-120.

Li D. X., Oyamada A., Hashi K., Haga Y., Matsumura T., Shida H., Suzuki T., Kasuya T., Dönni A., Hulliger F. J. Mag. Mag. Mate., (1995), 140-144, 1169.

Larson P. and Lambrecht W. R.,Phys. Rev. B, (2007), 75, 045114-045128.

Blaha P., Schwarz K., Madsen G.. K. H., Kvasnicka D. and Luitz J. WIEN2k code, (2011), ISBN 3-9501031-1-2.

Jayaraman A., Lowe W. and Longinotti L. D. Phys. Rev. Lett. 36 366 (1976).

Werner A., Hochcheimer H. D., Meng R. L. and Butcher E. Phys. Lett. 97A 207 (1983).

Leger J. M., Ravot D. and Rossat-Mignod J.; J. Phys. C : Solid State Phys. 17 4935 (1984).

Leger J. M., Oki K., Rossat-Mignod J. and Vogt O. J. Phys. 46 889 (1985).

Vedel I., Redon A. M., Rossat-Mignod J., Vogt O. and Leger J. M.; J. Phys. C20 3439 (1987).

Leger J. M., Vedel I., Redon A. M., Rossat-Mignod J.; J. Mago Magn. Mater. 63 49 (1987).

Mori N., Okayama Y., Takahashi H., Haga Y. and Suzuki T. Physica B186 444 (1993).

De M. and De S. K.; J. Phys. Chem. Solids 60 337 (1999).

Leger J. M. Physica B190 84 (1993)

Sims C. E., Barrera G. D., and Allan N. L., Physical Review B, vol. 57, no. 18, pp. 11164–11172, 1998.

Rao B. S. and Sanyal S. P., Physica Status Solidi B, vol. 165, no. 2, pp. 369–375, 1991.

Froyen S. and Cohen M. L., Journal of Physics C, vol. 19, no. 15, pp. 2623–2632, 1986.

Hafemeister W. and Flygare W. H., J. Chem. Phys. 43, (1965) 795.

Kumar M., Kaur A. J. and Shankar J.; Journal of Chemical Physics 84, (1986) 5735-5741.

Singh S.K., Rana P., Nayak V. and Verma U. P.; AIP Conference Proceedings, (2013) 1536, 1083-1084.