Pressure induced phase transition in CeN with NaCl –type structure

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Abstract. We have expressed the Gibbs free energy for CeN compound as a function of pressure and charge transfer through improved interaction potential model (IIPM). The lattice energy in it has been represented by an IIPM which include Coulomb interaction, three body interaction, polarizability effect and overlap repulsive interaction. The phase transition pressure and relative compression reveal that this compound shows a B1-B2 phase transition and this approach are found to be the experimental data in future. The phase transition pressures and volume collapses obtained from this model show a generally good agreement with available results.

1. Introduction
Rare earth nitrides attract much attention due to the intricate electronic and magnetic properties related to the f-electrons. However all rare earth nitrides in rock-salt structure remain almost totally unexplored [1]. These compounds are less studied than chalcogenides and pnictides at the theoretical and experimental level. This is because rare earth nitrides are more difficult to prepare as they are less stable [2] due to the sensitivity to water vapour. The electronic configuration of rare earth nitrides shows that 5d orbital are singly filled and 4f orbitals are progressively filled up with electrons. Among Ce –based compounds CeN exhibit mixed valence behaviour. The 4f electron makes the rare earth and their compounds attractive for applications [3], such as protective materials in reactor, fire resistive materials and spintronics devices.

It seems from above literatures that the present compound is less studied; So that it motivated us to study the structural, stability and phase transitional phenomena at high pressure for CeN using improved interaction potential model (IIPM). The need of inclusion of three body interaction forces was emphasized by many workers for the betterment of results [4, 5].

2. Improved interaction potential model
It is well known that pressure causes an increase in the overlap of adjacent ions in a crystal. Consequently, charge transfer [4] takes place between the overlapping electron shells. These transferred charges interact with all other charges of the lattice via Coulomḃs law and gives rise to many body interactions, of which the most significant part is three body interaction (TBI).The increased effects of TBI, thus obtained, lead to an obvious necessity of their inclusion in the high

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pressure study of materials. A phase transition occurs when the solid becomes unstable under a given set of thermodynamic conditions .A phase of the solid is the most stable when its Gibbs free energy G(=U+PV-TS) is minimum. Here U, the internal energy at T= 0K, corresponds to the cohesive energy due to mutual interaction of the ions; S is the vibrational entropy at absolute temperature T, and V is the unit Cell volume at pressure P. At T= 0 K the Gibbs free energies for rock salt (B1) and CsCl (B2) phases can be expressed as [5]

Table 1. Input data and model parameters.

Input Parameter		Model Parameters	
r_i	1.01 A^0	b (10^{-12}erg.)	0.2318
r_j	1.71 A^0	ρ (Å)	0.216
r_0	2.506 A^0	f(r)	-0.0146
B_T	121[a]		

[a] [9].

$$G_{B1}(r^{'}) = U_{B1}(r^{'}) + PV_{B1}(r^{'}) \tag{1}$$

$$G_{B2}(r^{'}) = U_{B2}(r^{'}) + PV_{B2}(r^{'}) \tag{2}$$

$$U_{B1}(r) = \frac{-\alpha_M Z^2 e^2}{r} - \frac{12\alpha_M Ze^2 f(r)}{r} - \frac{e^2(\alpha_1 + \alpha_2)}{2r^4} + 6b\beta_{ij}\exp[(r_i + r_j - r)/\rho] + 6b\beta_{ii}\exp[(2r_i - 1.414r)/\rho] \tag{3}$$
$$+ 6b\beta_{jj}\exp[(2r_j - 1.414r)/\rho]$$

$$U_{B2}(r) = \frac{-\alpha'_M Z^2 e^2}{r^{'}} - \frac{16 \alpha'_M Ze^2 f(r)}{r^{'}} - \frac{e^2(\alpha_1 + \alpha_2)}{2r^{'4}} + 8b\beta_{ij}\exp[(r_i + r_j - r^{'})/\rho] + 3b\beta_{ii}\exp[(2r_i - 1.154r^{'})/\rho] \tag{4}$$
$$+ 3b\beta_{jj}\exp[(2r_j - 1.154r^{'})/\rho]$$

With $U_{B1}(r)$ and $U_{B2}(r)$ as the lattice energies for NaCl and CsCl structures, α_M and α'_M as Madelung constants for NaCl and CsCl structure respectively. e as charge of electron and r and r' as inter-ionic separation for NaCl (CsCl). β_{ij} is Pauling coefficients defined as $\beta_{ij}=1+(Z_i/n_i) + (Z_j/n_j)$ with $Z_i(Z_j)$ and $n_i(n_j)$ as the valence and the number of electrons of the i(j)th ion, b is hardness parameter while ρ is range parameter.

These lattice energies consists of long range Coulomb attraction (first term), long range three body or charge transfer interactions (second term), polarizability interaction (third term), and short range overlap repulsive potential (fourth term) extended up to second neighbouring ions is given by Hyfemeister and Flygare (HF) [6]. We are taking the effect of polarization to improve our results in the line of M. Kumar et al. [7] in diatomic molecules of alkali halides. We are taking this effect first time in CeN compound.

3. Computational method and results
The input data and model parameters are given in table 1. We have computed the phase transition pressure and associated volume collapses of CeN with IIPM which includes polarizability along with TBI. The results on phase transition and volume collapse are given in table 2. The lattice energies U

$_{B1}$(r) and U $_{B2}$(r) contain only three model parameters (b, ρ, f(r)) hardness, range and three body parameter, which have been calculated by using input data given in table 1 and have been computed. from the knowledge of the lattice parameter, bulk modulus and equilibrium conditions as described earlier [5] using the self consistent method.

$$[dU(r)/dr]_{r=r0} = 0 \qquad\qquad (5)$$

and

$$B_T = \frac{e^2}{12r^4}[-4.66Z(Z+12f(r))+(A_1+A_2)-2(B_1+B_2)+27.9612Zrf'(r)] \qquad (6)$$

As the stable phase is always associated with minimum of energy, we have followed the technique of minimization of Gibbs free energies of G $_{B1}$(r) (real) and G $_{B2}$ (r') (hypothetical) phases given by equation (1) and equation (2) at different pressures in order to obtain the inter-ionic separations r and r' for B1 and B2 phases associated with minimum energies. ΔG is very important factor in deciding phase transition pressure. We have plotted ΔG against pressure to obtain the phase transition pressure (P_t) at which ΔG approaches zero. Here B1 and B2 are real and hypothetical phases before phase transition and B1 becomes hypothetical phase after phase transition while B2 becomes real. The phase transition pressures so obtained are presented in table 2 and they are compared with the other's value. We have calculated the relative volumes (V (P) / V (0) and plotted them against pressures (P) to obtain the equation of state for B1 and B2 phases. There is a sudden collapse in relative volume indicating the occurrence of first order phase transition.

4. Discussion

The present compound is stable in NaCl structure at normal condition and high pressure it transforms to body centre CsCl structure. We have followed the technique of minimization of Gibbs free energies of NaCl and CsCl phases at ambient conditions corresponding to equilibrium inter-ionic separation r (r') using the IIPM model parameters listed in table 1.We have plotted the values of Gibbs free energy differences ΔG against the pressure (P) as shown in figure 1 for CeN. The phase transition pressure (P_t) is the pressure at which ΔG approaches zero. At P_t CeN undergoes a (B1-B2) transition associated with a sudden collapse in volume showing a first order phase transition. The values of P_t computed by us are in good agreement with the others results [8]. ΔG becomes negative beyond P_t predicting that at high pressure B2 phase is now thermodynamically and mechanically stable as compared to parent B1 phase.

In addition, the pressure volume behaviour of the present compound has also been studied. At the phase transition pressure there is a sudden collapse in volume has been occurred. The computed value of volume collapse for CeN has been given in table 2. The compression curve has been plotted in figure 2 for CeN. The NaCl and CsCl phases have been shown in this figure 2. It is clear that our calculated phase transition pressure is 87.6 GPa with volume collapses − $\Delta V/V_0$ of 11.44 from our IIPM model. Our computed values of P_t and volume collapse are in good agreement with the others results [8] and due to lack of experimental data we could not compare our result.
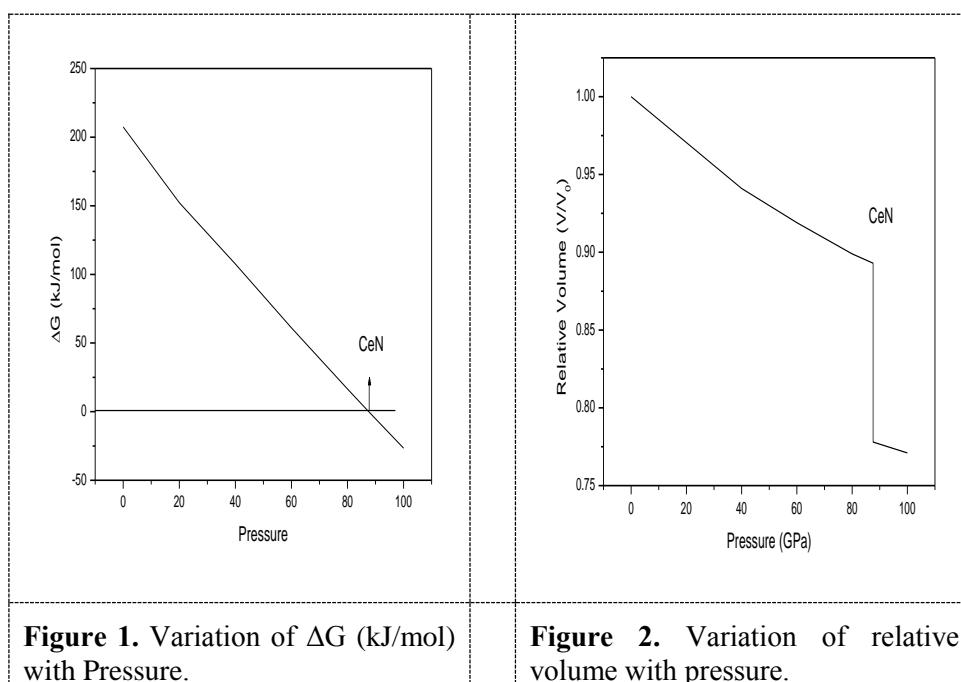
Table 2. Phase transition pressure (GPa) and volume collapse.

CeN	Phase Transition Pressure	Volume Collapse (%)
Present	87.6	11.44
Expt.	-	-
Other's	88 [7]	5.78

In conclusion, we have applied improved interaction potential model (IIPM) to investigate the structural phase transition of CeN. The results are summarized as follows.

(1) The present compound crystallizes in six-fold coordinated NaCl-type structure (B1) at normal condition and under pressure, they transform to the eight-fold-coordinated CsCl-type structure (B2).
(2) During the NaCl to CsCl phase transition, the volume discontinuity in pressure volume phase diagram identifies the occurrence of first-order phase transition.
(3) The present calculated phase transition pressure and volume collapses are in general in good agreement with the available data.

Finally, we can conclude that an improved interaction potential model (IIPM) has yielded more realistic predictions of the structural phase transition of CeN from NaCl structure to CsCl structure. The experimental result of transition pressure for CeN is not available. So our results may be used as guide to experiments for working range of pressure.

Figure 1. Variation of ΔG (kJ/mol) with Pressure.

Figure 2. Variation of relative volume with pressure.

5. References

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