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Structural Analysis and Elastic Behaviour 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 though improved interaction potential model (IIPM). The lattice energy in it has been represented by an IIPM consisting of the long range coulomb interaction, three body interaction, polarizability effect and overlap repulsive interaction effective up to the second neighbour ions. Using this approach high pressure phase transition phenomena in CeN have been explored. The phase transition pressure, volume collapse and elastic properties for CeN predicted from this approach are found to be the experimental data in future. This shows that the inclusion of three body interaction effects and polarizability effects makes the present model suitable for high pressure studies. Moreover, the elastic properties of CeN are also investigated.

Keywords: Rare earth compounds, Semiconductor, Phase transition, High pressure, Elastic properties

1. Introduction

Rare earth compounds attract much attention due to the intricate electronic properties related to the f-electrons. However rare earth nitrides in rock-salt structure remain almost totally unexplored [1]. These compounds are less studied and at the theoretical and experimental level. This is because rare earth nitrides (REN) are more difficult to prepare as they are less stable [2] due to the sensitivity to water vapour. The electronic configuration of rare earth nitride 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 REs and their compounds attractive for applications [3], such as protective materials in reactor and fire resistive materials

The lack of theoretical and experimental of REN has motivated us to study the structural, elastic stability and phase transitional phenomena at high pressure for CeN using improved interaction potential model (IIPM). In the present paper, the results of the calculation on structural, elastic and phase transition pressure have been reported.

2. Improved interaction potential model

Hydrostatic pressure on materials causes a decrease in their volume, and consequently leads to a deformation of the overlapping electron shell (of a charge transfer). These transferred (or exchanged) charges appearing in the overlap region of adjacent ions interact with all other charges (or ions) of the lattice via Coulomb's law, and give rise to many body interactions [4]. Whose most significant contributions are the three body interactions (TBI).The effects of these TBI are incorporated in the Gibbs free energy (G=U+PV) at T=0K through the lattice energy, U. Here, V is the unit cell volume at pressure P. Thus, the Gibbs free energy for NaCl (B1) and CsCl (B2) structures' can be written as:

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

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

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

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

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. Here, the first term is the long range Coulomb attraction, second term is the long range three body or charge transfer interactions, third term is the polarizability interaction, and the fourth term is the Short range overlap repulsive potential extended up to second neighbouring ions is given by Hyfemeister and Flygare (HF) [5]. We are taking the effect of polarization to improve our results. This effect was applied by M. Kumar et al. [6] 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 [7, 8] using the self consistent method.

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

and

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

As the stable phase is always associated with minimum of energy, we have followed the technique of minimization of Gibbs free energies of real and hypothetical phases. We have minimized $G_{B1}(r)$ and $G_{B2}(r')$ given by Eqs.(1) and Eqs.(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

4.1 Phase transition Properties

As, stated above we have minimized the lattice energies in both the real and the hypothetical 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 figs. 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 experimental value [9] and better than 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.

We have also computed the relative volume changes V/V_0 corresponding to the values of r and r' at different pressures and plotted them against the pressure in inset Fig. 2 for CeN. It is clear from Table 2 and Fig 2 that our calculated phase transition pressure is 68 GPa with volume collapses $-\Delta V/V_0$ of 12.62 from our IIPM model. Our computed values of P_t and volume collapse are in good agreement with the others results [8].

4.2 Elastic properties

Elastic constants provide useful information about the bonding characteristic between adjacent atomic planes and anisotropic character of the bonding and structural stability. We have calculated the second-order elastic constants (C_{11}, C_{12}, C_{44}), bulk modulus (B), Shear modulus (G), Poisson's ratio (σ), Anisotropy factor (A). The expressions of second order elastic constants (SOECs) are taken from [7]. The experimental values of elastic constants (SOECs) for REN are not available at present, but calculated values if bulk moduli agree reasonably well with the measured ones. Our calculated values of elastic constants are close to the first principles calculations [10] and reasonably well with the others results [8, 11]. The mechanical stability conditions in cubic crystals are known as $C_{11}>0$, $C_{11}>C_{12}$, $C_{44}>0$ and $C_{11}+2C_{12}>0$.The calculated elastic constants as shown in Table 2 indicate that CeN is mechanically stable. For cubic crystal, the bulk modulus is calculated in terms of the elastic constants using the following relation:

$$B=C_{11}+2C_{12}/3$$

This theoretical calculated value of bulk modulus compare good agreement with the experimental bulk modulus 153 GPa reported earlier by Jakobsen et al. [2] and well with 158GPa reported by J. Staun et al [9]. It is known that even the cubic crystal, which is isotropic structure, has anisotropy because of a fourth rank tensor property of elasticity. The elastic anisotropy factor (A) of a cubic crystal is defined as

$$A=2C_{44}/(C_{11}-C_{12})$$

We have calculated anisotropy parameter of CeN. For an isotropic crystal the value of A is 1. For any values smaller or larger than 1, indicated the presence of anisotropy. It is clear from Table 2. that CeN is anisotropic crystal. As the Poisson's ratio is an important property to know the hardness of compounds and it is also associated with the volume change during uniaxial deformation. The expression of σ as:

$$\sigma = C_{12}/(C_{11}+C_{12})$$

If $\sigma=0.5$, no volume change occurs during elastic deformation, which indicates that the material is incompressible. The low σ value means that a large volume change is associated with its deformation. It is clear from Table 2. that the value of σ is in comparable range with others values [11, 8].

5. Conclusion

Finally we can conclude that the improved interaction potential model (IIPM) has yielded more realistic predictions of the structural, elastic and phase transition of CeN from NaCl structure to CsCl structure. This model has been found to be successful in giving the unified description of the lattice dynamic, static, elastic, optic, dielectric and photo-elastic properties of ionic and semiconducting crystals. In this model the three body interactions (TBI) or charge transfer effects (CTE) owe their origin to the quantum mechanical foundation and also to the phenomenological approach in terms of the transfer or exchange of charge between the overlapping electron shells of the adjacent ionic solids.

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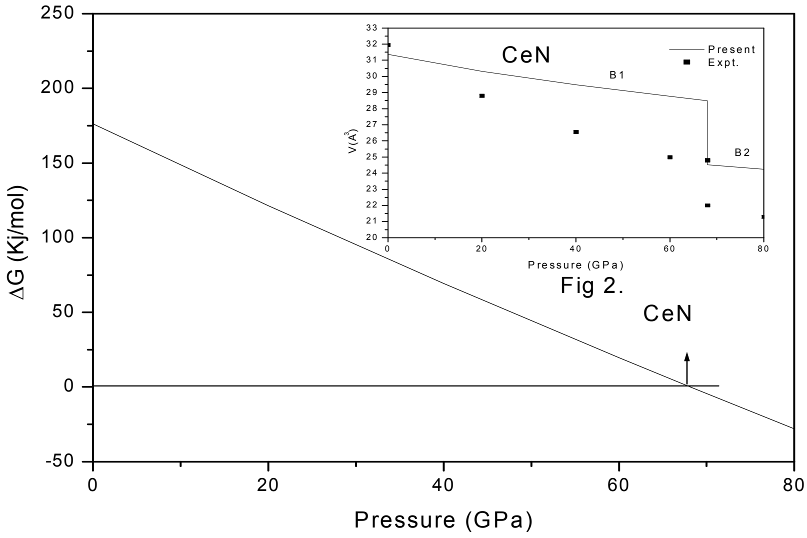

Figure 1. Variation of Gibbs free energy difference ΔG (Kj/mol) with pressure and inset figure shows the variation of volume change with pressure

Table1. Input data and model parameters

Input parameters		model parameters		
r_0 (Å)	B_T (GPa)	b (10^{-12}erg.)	ρ (Å)	f(r)
2.5035	153 [2]	0.9120	0.222	-0.01389

Table 2. Calculated Phase transition pressure P_t (GPa), volume collapse (V/V_0), elastic constants (C_{ij}) GPa ; elastic anisotropy factor A; Poisson's ratio (σ) for CeN and other theoretical values.

Solid	Present		Others	Interionic Theory	First Principle	Experiment
		LDA	GGA			
P_t	68	62	68	88	-	65-70[9]
V/V_0	12.62	5	10.8	5.8	-	10.9[9]
C_{11}	203.38	328.8[11]	310.2 [11]	299[8]	238[10]	-
C_{12}	127.64	70[11]	83.2[11]	60.8[8]	62[10]	-
C_{44}	63.34	60.8[11]	72.6[11]	63.8[8]	71[10]	-
B	152.88	159.0[9]	158.1[9]	140.2[8]	121[10]	153[2]
A	1.67	-	-	-	0.809[10]	-
σ	0.38	0.291[11]	0.264[11]	0.168[8]	0.208[10]	-

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