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Study of the Phase Transition Phenomenon in SrTe under Pressure

Shilpa Kapoor[1], Purvee Bhardwaj, Namrata Yaduwanshi, Pooja Pawar, Abdul Shukur and Sadhna Singh

High pressure Research Lab, Department Of Physics, Barkatullah University, Bhopal, MP

Abstract

The phase transition pressure and volume collapse of SrTe have been studied. A three body interaction potential (TBIP) model is developed to study the high pressure phase transition of present compound having NaCl (B_1) structure at room temperature. This model includes the long range Columbic, three body interaction forces, short range overlap forces operative up to next nearest neighbors and zero point energy effects. It is found that the inclusion of zero point energy effects has improved the results.

Keywords: Phase transition, volume collapse, three body interaction and zero point energy.

1. Introduction

The alkaline earth chalcogenides (AX: A=Mg, Ca, Sr, Ba; X=O, S, Se, Te) form a very important closed shell ionic system and crystallize in NaCl (B_1) structure at room temperature. The majority of these compounds undergo a structural phase transition from the B_1 structure is face centered cubic structure having 6 atoms of opposite type transforms to B_2 structure having coordination number 8 at a high pressure. Hence, in B_1 to B_2 Phase transition the coordination number changes from 6 to 8 [1].

The pressure volume relationships and structural transition of CaTe and SrTe at high pressure had been studied by Zimmer et al. [2] by using X-ray diffraction method which shows that SrTe transforms from B_1 to B_2 structure at 12 GPa. The structural phase transition and elastic constants of strontium chalcogenides are also reported by Khenata et al. [3].

The importance of three body interaction has been emphasized by many workers [4-5]. It has been found that three body interaction potential (TBIP) model is suitable for the successful prediction of phase transition and high pressure elastic behavior of ionic II-VI and II-V semiconductors [6], divalent metal oxides [7], and alkali halides [8]. In the present article, an effort has been made to develop an improved potential model, which has three-body interaction potential (TBIP) and zero point energy effects. Due to this, our result shows a good agreement with the available experimental data. The inclusion of zero point energy effects seems essential as it is the lowest possible energy a compound may possess and is the ground state energy of the compound. It is well known that at T=0K the energy of a compound cannot be zero but ½ (hν). This term, though not very significant, as far as Gibbs free energy is concerned, yet cannot be ignored.

2. Methodolgy

The application of pressure causes a change in volume of the crystal, which leads to an increased charge transfer (three body interaction effects) [9] due to deformation of the overlapping electron shells of the adjacent ions. This interaction becomes more important to consider due to the decrease in inter-ionic spacing of the lattice crystal when pressure gets increased and when ions experience sufficient overlap. Besides, enhance in overlap energy, the transferred charge due to the overlap in electron shells, modifies the ionic charge which in turn modifies the Coulomb energy by a factor

$$\left[1+\left(\frac{2n}{z}\right)\mathrm{f}(\mathrm{r})\right]$$

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 which depends on the nearest neighbor distance (r) [9] as

$$f(r) = f_0 e^{-r/\rho} \tag{1}$$

Where f_0 is a constant and ρ is the range parameter. In order to obtain the stability for a crystal structure, the effect of TBI has been incorporated in the Gibbs free energy (G=U+PV-TS). Here U is the internal energy at T=0K is equivalent to lattice energy, S is the vibrational energy at absolute temperature T, pressure P and volume V. The Gibbs free energy for rock salt (B_1, real) and CsCl (B_2, hyPothetical) structure at 0K can be stated by:

$$G_{B_1}(r) = U_{B_1}(r) + PV_{B_1} \tag{2}$$

$$G_{B_2}(r') = U_{B_2}(r') + PV_{B_2} \tag{3}$$

The first terms in the energies in Eqns. (2) and (3) are lattice energies for B_1 and B_2 structures. The expressions of lattice energies in Eqns. (2) and (3) are as follows:

$$U_{B_1} = \frac{-\alpha_m e^2 z^2}{r} - \frac{(12\alpha_m e^2 zf(r))}{r} + 6b\beta_{ij}\exp(\frac{r_i + r_j - r}{\rho}) + 6b\beta_{ii}\exp(\frac{2r_i - 1.414r}{\rho}) + 6b\beta_{jj}\exp(\frac{2rj - 1.414r}{\rho}) + (0.5)h\left\langle w^2\right\rangle_{B_1}^{1/2} \tag{4}$$

$$U_{B_2} = \frac{-\alpha'_m e^2 z^2}{r'} - \frac{(16\alpha'_m e^2 zf(r'))}{r'} + 8b\beta_{ij}\exp(\frac{r_i + r_j - r'}{\rho}) + 3b\beta_{ii}\exp(\frac{2r_i - 1.154r'}{\rho}) + 3b\beta_{jj}\exp(\frac{2r_j - 1.154r'}{\rho}) + (0.5)h\left\langle w^2\right\rangle_{B_2}^{1/2} \tag{5}$$

β_{ij} is the Pauling coefficient, $r_i(r_j)$ is the ionic radii of i(j) ions, $\rho(b)$ are range (hardness) parameters and $\left\langle w^2\right\rangle^{1/2}$ is the mean square frequency related to Debye temperature θ_D as

$$\left\langle w^2\right\rangle^{1/2} = k(\theta_D)/h \tag{6}$$

Here Θ_D can be expressed by well known Blackman's formula described in [10].

$$\theta_D = \frac{h}{k}\sqrt{\frac{5rB_T}{\mu}} \tag{7}$$

Where B_T and μ are respectively the bulk modulus and reduced mass of the compounds.The first term in equations (4) and (5) are long-range Coulomb energy, second terms are three body interaction forces for B_1 and B_2 phases, third terms are the short range overlap repulsion represented by Born – Mayer potential for (i, j) ions, fourth and fifth terms are overlap repulsive term extended up to next nearest neighbor ions within Hafemeister and Flygare approach [11] and the last terms are zero point energy effects [10].

With V_{B_1}(=2.00 r^3) and V_{B_2}(=1.54 r'^3) as the unit cell volumes for B_1 and B_2 phases, respectively.. The Gibbs free energy is equivalent to enthalpy at 0K. The condition of the relative stability of the two phases may be expressed as

$\Delta G = G_{B_2} - G_{B_1}$,

where G_{B_1} and G_{B_2}

are the Gibbs free energies for rock salt (B_1, real) and CsCl (B_2, hyPothetical) structure. The phase transition pressure P_t is the pressure at which ΔG→0, shows a sudden collapse in volume showing that the phase transition is of first order.

To calculate the value of Gibb's free energies, one has to determine the value of three model parameters (b, ρ, f(r)) namely hardness ,range and three body force parameter. Their values have been determined by solving the equilibrium conditions using the measured values of the equilibrium inter-ionic separation (r).

$$\frac{dU}{dr} = 0 \text{ and } \frac{d^2U}{dr^2} = 9kB_T r$$

Here, B_T is isothermal bulk modulus and k=2 for B_1 Phase.

3. Results and Discussion

The relative stability of the two phases were obtained by minimizing the lattice energies in both real and hypothetical phases at different pressures corresponding to equilibrium inter-ionic separation r(r') using the mode lparameters as listed in table I. The cohesive energy, phase transition pressure and volume collapse are listed in table II.

The calculated value of phase transition pressure (P_t= 11.7 GPa) is in reasonable agreement with experimental value (P_t= 12 GPa). The variation of ΔG with pressure for SrTe is shown in fig. 1.

The values of relative volume change (V(p)/V(0)) associated with various compressions have been obtained and plotted against pressure in fig. 2 for SrTe . The calculated value of volume collapse is in good agreement with the experimental and other theoretical values.

4. Conclusion

Finally, we can conclude that by including the zero point energy effects in the three body interaction potential (TBIP) model has yielded more realistic predictions of the structural phase transition of SrTe from NaCl structure to CsCl structure.

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Table 1

Input data and model parameters

Compound	Input parameters		Model parameters		
SrTe	r	B_T (GPa)	b($\times10^{-12}$ergs)	ρ(Å)	f(r)
	3.33	40[a]	8.103	0.481	-.00799

[a]Ref. [12]

Table 2

Calculated transition pressure and volume collapse

Compound	Transition	Transition Pressure (GPa)	Volume collapse (%
SrTe	B_1-B_2	11.95 (present)	10.7 (present)
		12 (exp)[a]	11.1 (exp)[a]
		13.24 (other)[b]	8.92 (other)[b]

[a]Ref. [12] , [b]Ref. [13]

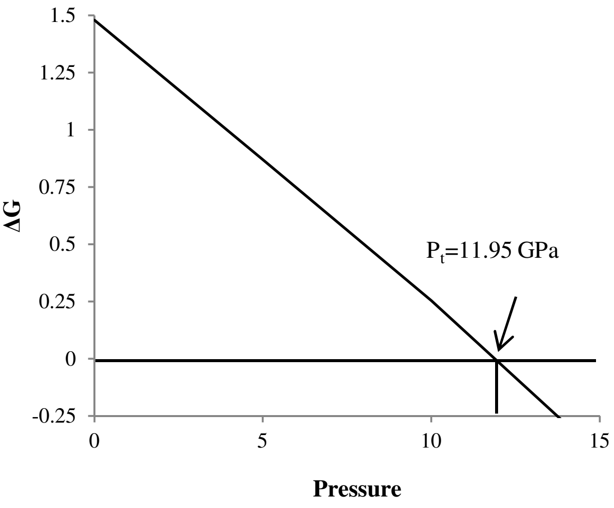

Fig. 1 Variation of Gibb's free energy with pressure.

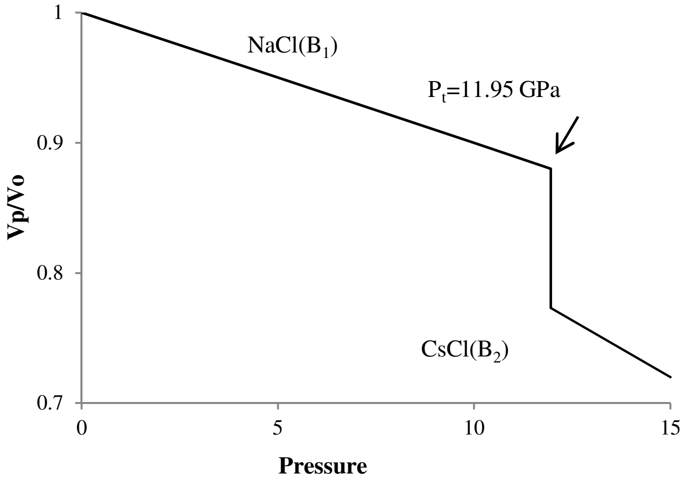

Fig. 2 Variation of volume change Vp/V_0 with pressure**.**

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