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THE STUDY OFTHE EFFECT OFTEMPERATURE IN THE PHASETRANSITION PHENOMENA A NEW APPROACH

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ABSTRACT

A new effort has been made to include the-effects of temperature in high pressure phase transition studies with Three Body Potential (TBP) model and presented in this paper. Earlier studies of the phase transitions with TBP model have been carried by assuming the equilibrium at 0° K instead of room temperature. How this theory can be formulated to study the solid - solid phase transition in the condensed materials is discussed in this article.

Key words : Phase transition, Three Body Potential (TBP) and Condensed materials.

INTRODUCTION

A number of pressure induced phase transitions B1 -> B2, B3 -> B1, etc. have been studied successfully by using three body potential model[14].This model is a realistic model as it takes appropriate account of the effects of long and short-range forces. The transfer (or exchange) of charge between the neighbouring ions occurs during the lattice vibrations. This charge transfer phenomena leads to the occurence of three body interactions,[5] which are found to be responsible forthe Cauchy violation and therefore it is considered as a realistic formulation of a model. The attractive Uc(r) Coulomb part and repulsive UFt(r) contributions due to the overlap of electron shells have also been included. The corresponding long range potential Is due to the Coulomb and three body interactions an short range potential is due to overlap repulsive and van der waals (vdw) interactions. Hence the total potential energy between ions (Ik) and (I'k') is given by : $U(r) = -Uc(r) - UT(r) - Uv(r) + U_R(r)$... (1)

Here, the first term corresponds to Coulomb energy and the second term is energy due to three body interactions (TBI)[5]. The third and fourth terms are, respectively, the contributions from the vdw dipole - dipole (d - d) and dipole - quadrupole (d - q) interactions and the Hafemeister and Flygare[6] (HF) type of short range overlap repulsive potential.To increase its versatility and make it appropriate for unified applications, the number of model parameters have been greatly reduced by expressing the three body potential function by an appropriate microscopic function given by Cochran.[7]

$f(r) = fo \exp(-r/p)$ .....(2)

Phase transition studies

The phase transitions can be easily predicted in relatively simple ionic crystals. Among such transitions, the pressure induced phase transition to occur, generally, from a structure of high symmetry (and lower order) to one of the lower symmetry (and higher order). The applications involving an increase in co-ordination (number of neighbour) and negative volume change. It is well known that the stability of a particular lattice is achieved at the minimum value for the Gibbs free energy

$G = U + PV - TS$ .....(3)

Using the TBP model, the following Gibbs free energy for real and hypothetical (hyp) structures at 0°K are written as

$G(real) = U(real) + PV(real) - TS(real)$ ..... (4)

$G(hyp) = U(hyp) + PV(hyp) - TS(hyp)$ ..... (5)

With U, P, V and S as the internal energy

(= potential energy in equilibrium), pressure, unit cell volume of the materials and entropy, respectively. These expressions are used to obtain the pressure induced phase transitions by obtaining G[= G(hyp)-G(real)] and plotting the same against the pressure.The pressure at which $\triangle$G approaches zero will be the transition pressure. In fact, the condition for a transition is that the difference in free energy between two phases satisfies the condition.

$\triangle G = \triangle H - T\triangle S = 0$ ..... (6)

Here, $\triangle$H is the change in enthalpies of two phases and H = U + PV. Here, U is the internal energy given by Eqn.(1) Now, the entropy difference can be calculated from

$S_2 - S_1 = \int [(C_2)/T]\, dT$ ..... (7)

Here, 1 and 2 stand for the first and second phases. and C_2 are the specific heats of two phases at constant pressure and their values can be calculated from the relations of Gruneisen parameter (y):

$C_i = \alpha V_i (B_T)_i / \gamma_i$; $\gamma_i = \partial \ln \Theta_D / \partial \ln V_i$ ..... (8)

Here, Θ_D is the Debye temperature, Vi is volume (i = 1,2) and $(B_T)_i$ [= (1/3) $(C_{11} + 2C_{12})$,] is the isothermal bulk modulus and Cij; $[C_{11}, C_{12})_j$ are the second order elastic constants for the phases i (= 1, 2), whose expressions are given in our earlier papers[1-4].

The entropy difference ($\triangle$S) can also be calculated from the measured values of C_1 and C_2 for all temperatures between 0 and T wherever they are available, and these results can be compared with the theoretically predicted results. To calculate the relative volume change [- $\triangle$ V(P)/V(0)] and to obtain the compression curve, relative volumes [V(P)/ V(O)] can be plotted against the pressure. Also, to understand the effect of anharmonicity on elastic constants, we have used the Hilderbrand equation of state.

$P = - dU/dV + \gamma B_T$ ..... (9)

Here, the last term is the so-called thermal phonon pressure. The formulations of the temperature derivatives of the second order elastic constants (SOEC's) can be derived using Eqn. (1) and (9). For the present investigations, the values of the parameters can be obtained from SOEC's and the second order elastic constants (Cij) Bulk modulus (B_T).

This approach of evaluating the phase transition pressures at realistic temperatures can be applied to NaCl, CsCl and ZnS compounds[8-12] along with the volume collapses associated with phase transition pressures and phase diagrams in them.The results obtained from the proposed new and realistic approach will be quite useful for the scientists working in the field and they will be reported subsequently for various materials.

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