ANALYSIS OF STRUCTURAL PHASE TRANSITION AND THERMOPHYSICAL PROPERTIES OF PTN

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Abstract

We have investigated the structural phase transition and thermophysical properties of PtN by using interaction potential model (IPM). The IPM consists of various interaction viz Coulomb interaction, three-body interaction (TBI) and overlap repulsive short range interaction. Our theoretical investigation predicts the structural phase transition of PtN from B3 to B1 structure. We found B3 to B1 phase transition at 11 GPa. At the same transition pressure (11 GPa) the volume drop confirms the first order phase transition. In addition we have also computed the thermo physical properties i.e. force constant, Reststrahlen frequency, Debye temperature and compressibility. These thermophysical properties are new and calculated in first time. The results are in general agreement with available theoretical results due to unavailability of experimental data.

Keyword: Phase transition, Thermophysical properties Transition metal nitride.

Introduction

The transition metal nitrides (TMNs) have received much attention because of technological importance. Due to their high hardness and high melting point, they exhibit interesting thermal, optoelectronic, superconducting or magnetic and semiconducting properties [1]. Among the transition metal (TM) nitrides PtN crystallizes in zinc-blende (ZB) structure at ambient pressure and at high pressure it transforms to the rock-salt (RS) structure. Peng et al. [2] have studied the phase transition and thermodynamic properties at high pressure and temperature by using ab-intio calculations.

The experimental studies for the phase transition and thermophysical properties of PtN compound are not reported and theoretical studies are also very less. To understand nature of interatomic forces in present compound we developed an interaction potential model (IPM). This IPM model possesses various interatomic interaction energies to explain the interatomic forces. So we have applied IPM to study phase transition pressure and thermophysical properties. The essential features of the present theory and method of computation for high pressure behaviour are presented in section 2. The results and discussions are presented in section 3. Section 4 represents the conclusions.

Computation Method

The application of pressure on the crystal causes the decrease in their volume, which in turn leads to an increased charge transfer (or exchange) between the overlapping electron shells of the adjacent ions. This overlapping leads to the transfer of charge which when interacts with other distant charges gives rise to many body interactions (MBI), the dominant part of MBI is three-body interactions [3]. These charge transfer effects have been incorporated in the Gibbs free energy (G=U+PV-TS). Here, U is the internal energy which at T=0K is equivalent to the lattice energy, S is the vibrational entropy at absolute temperature T. At T=0K and pressure P, the Gibbs free energy for the zinc-blend (B3, real) and NaCl (B1, hypothetical) structures are given by

$$G_{B3}(r) = U_{B3}(r) + PV_{B3}$$

(1)

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

(2)

The primary parts in (1) and (2) are lattice energies (for B3 and B1 phase) and secondary terms in both equation represent the pressure-volume term for both (B3 and B1) phases. Symbol V_{B3} (=3.08 r^3) and V_{B1} (= 2.00 r'^3) are the volumes for given phases. The present IPM describes the various interactions, these interactions are incorporated in lattice energy as

$$U_{B3}(r) = \frac{-\alpha_M e^2 Z^2}{r_{ij}} - \frac{4\alpha_M e^2 Zf(r)}{r_{ij}} + 4b\beta_{ij}\exp(r_i + r_j - r_{ij}/\rho)$$
$$+ 6b\beta_{ii}\exp(2r_i - 1.63r_{ij}/\rho) + 6b\beta_{jj}\exp(2r_j - 1.63r_{ij}/\rho)$$

(3)

$$U_{B1}(r) = \frac{-\alpha'_M e^2 Z^2}{r_{ij}'} - \frac{6\alpha'_M e^2 Zf'(r)}{r_{ij}'} + 6b\beta_{ij}\exp(r_i + r_j - r'_{ij}/\rho)$$
$$+ 6b\beta_{ii}\exp(2r_i - 1.414r'_{ij}/\rho) + 6b\beta_{jj}\exp(2r_j - 1.414r'_{ij}/\rho)$$

(4)

Here the entire symbols have their usual meanings [4]. α_m (α'_m) is Madelung constant for B3 (B1) phase. β_{ij} (i,j = 1,2) are the 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 ions. Ze is the ionic charge and f(r) is the three-body force parameter. r_i (r_j) are the ionic radii of ions i (j). These lattice energies consist of long range Coulomb interaction (first term), three-body interactions (second term) and short range overlap repulsive interaction (third, forth, and fifth terms) extended up to the second neighbour ions.

Result and Discussions

Structural phase transition

The present IPM specifies the three model parameters range, hardness and three-body force parameter (ρ, b and f(r)). We estimate these model parameters by using equilibrium condition, first and second differentials of cohesive energy U.

$$B_1 + B_2 = -1.261Z[Z + 8f(r)]$$
(5)

$$\left[\frac{dU}{dr}\right]_{r=r_0} = 0 \qquad (6)$$

$$\frac{d^2U}{dr} = 9kr_0B \qquad (7)$$

As we know the stable phase possesses the minimum free energy. So we have minimized Gibbs free energies to obtain the stability of both phases and the structural phase transition given by equation (1) and (2). As the pressure increases continuous change in free energy is occurred. The pressure at which Gibbs free energies of both structure are equal ($G_{B3}= G_{B1}$) is pronounced as phase transition pressure (Pt). This pressure shows the coexistence of both the phases. Fig. 1 shows that the B3 phase is more stable at P=0 GPaas it show minimum energy. But as pressure increases beyond Pt, the Gibbs free energy for B1 structure becomes more negative, which shows the stability of B1 phase. In Fig. 1, pressure 11 GPa shows the transition from B3 to B1 structure. After this, B1 phase becomes stable.

Table 1. Structural phase transition, volume collapse and thermophysical properties

Phase Transition Pressure (GPa)	Volume collapse (%)	f(10^4 dyn/cm^2)	ν_R (10^{12} Hz)	θ_D (K)	Compressibility (GPa)	References
11	16.77	81.86	40.42	581.80	1059	Present
18.2 9.85 11 .0	- - -	- - -	- - -	- 288.45 -	- - -	Other [2] Other [5] Other [6]

The other theoretical values of phase transition pressure are reported in Table 1. It is observed from Table 1 that our results of phase transition pressure signifies the good agreement with available other results [5, 6].
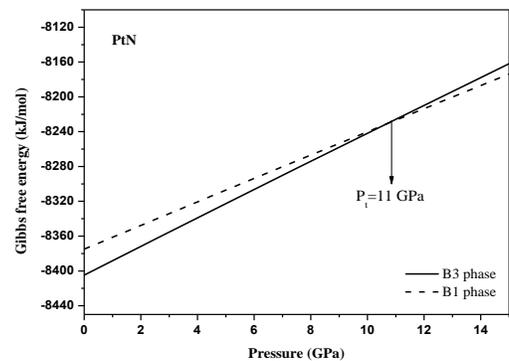

Fig. 1 Change in Gibb's free energy with pressure.

At phase transition pressure, the atoms take new positions forming a new structure B1 leading to discontinuity in volume. The discontinuity in volume at the transition pressure is obtained from the phase diagram. The values of relative volume associated with various compressions have been computed by using the interaction potential model.

The pressure dependent radii r and r' for both the structures (B3 and B1) have been used to compute the relative volume changes and are plotted against the pressure (P) in Fig. 2. The magnitudes of the discontinuity in volume collapse at the transition pressure have been obtained from the phase diagram and the values are listed in Table 1. In Fig. 2 solid lines show the real (ZB) phase and dotted lines show the hypothetical (Rock-salt) phase. The numerical values of discontinuity as relative volume change i.e. volume collapse $[-\Delta V(p_t)/V(0)]$ at the transition pressure is 16.77% for present compound. Due to unavailability of the experimental and theoretical data, the volume collapse could not be compared.
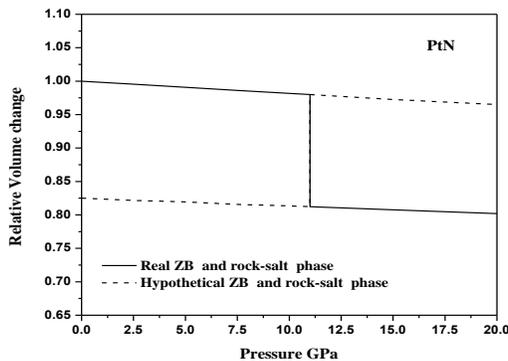

Fig. 2. Variation of relative volume with pressure

Thermophysical properties

Moreover to extend the study of PtN compound the thermophysical properties have also been calculated for the first time. The properties such as Force constants (f), Reststrahlen frequency (υ_R), Debye temperature (Θ_D) and compressibility (β) are the thermo physical properties. The expressions of Force constants (f), Reststrahlen frequency (υ_R), and Debye temperature (Θ_D) and compressibility (β) as defined in our earlier work [4]:

$$f = \frac{1}{3}\left[U_{SR}^{''}(r) + \frac{2}{r}U_{SR}^{'}(r) \right]$$

(8)

$$\upsilon_R = \frac{\left[\dfrac{f}{\mu} \right]^{1/2}}{2\pi}$$

(9)

$$\theta_D = \frac{\hbar \upsilon_R}{K}$$

(10)

$$\frac{1}{\beta} = \frac{r^2}{9v}U''(r)$$

(11)

Here U_{SR}" and U_{SR}' are the double and single derivative of short range cohesive energy, μ is the reduced mass of the compound, ℏ is the plank constant and K is Boltzmann constant.

The Debye temperature is an important thermophysical property because it is correlated with many physical properties such as elastic constants, specific heat and melting temperature. It provides the information about structure stability, structure defect availability and its density. According to Debye theory, the Debye temperature (Θ_D) is temperature at which crystal vibrate in its maximum allowed frequency and gives the explicit information about the lattice vibrations. On the same line, we can know the ability of materials, soil or rock (in terms of compressibility) to reduce in volume on the application of pressure and it is also used in earth science to quantify their ability. The estimated values of Debye temperature (Θ_D) and other thermophysical properties have been tabulated in Table 1 with other theoretical results. Also, we have plotted the pressure variation of Debye temperature in Fig. 3. It is found that the Debye temperature θ_D increases with applied pressure. There are no results available for thermophysical properties (except Debye temperature) for PtN, thus we cannot compare our results.
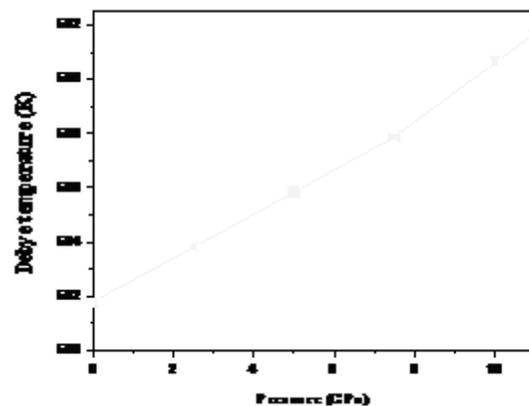

Fig. 3. Variation of Debye temperature with pressure

Conclusion

We have employed interaction potential model (IPM) to investigate the structural phase transition and thermo physical properties of PtN. The conclusions are as follows

(1) We have found that the PtN crystallize in fourfold coordinated ZB- type structure (B3) at zero pressure and under elevated pressure it transforms to the sixfold coordinated NaCl-type structure (B1).

(2) The calculated pressure at which PtN undergoes a structural phase transition from B3 to B1 phase agrees well with available theoretical result.

(3) At the phase transition pressure, the volume discontinuity in pressure volume phase diagram identifies the occurrence of first order phase transition.

(4) The calculated results of thermophysical properties (except θ_D) for present compound are new in B3 structure.

(5) Our study shows that the Debye temperature increases with pressures.

Finally we conclude that our theoretical results, in particular on the phase transition, volume collapse and thermophysical properties of Platinum nitride are reliable reference to further experimental and theoretical investigations.

Acknowledgement

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