Structural Phase Transition and Elastic Behavior of WN

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Abstract: Structural and elastic properties of WN has been investigated using theoreticalmodel calculations. The long range Coulomb,van der Waals (vdW) interaction and the short range repulsive interaction up to second-neighbor ions within the Hafemeister and Flygare approach with modified ionic charge are properly incorporated in effective interionic potential (EIOP) model.We first deduced vdW coefficients with the help of Slater-Kirkwood variational method. A structural phase transition from ambient ZnS (*B*3)-type structure to NaCl (*B*1)-type was identified in pressure volume curve in WN compound. The estimated value of transition pressure is 2GPa in WN compound. Further, the variation of second order elastic constants (C_{11}, C_{12} and C_{44}) were followed the systematic decreasing trends with pressure.

INTRODUCTION

The 5*d* transition metal nitrides have attracted interest for there physical and chemical properties, for examples, intense hardness, high melting point, chemical inertness and catalytic behavior [1-7].They be a member of a promising group of engineering materials with a broad range of industrial applications [1] Amy*etal.*[2] studied the structural and electronic properties of tungsten carbide for NaCl and WC phases. Suetin*etal.*[3–5] reported the structural stability, electronic structure and elastic properties of tungsten carbides and nitrides by first principles calculations. Isaev*etal.*[6] studied the phonon related properties of carbide and nitrides in the NaCl phase.Grossmanet al. [7] studiedthe electronic and structural properties for transition metal carbides and nitrides in detail. Furthermore, Chiu*etal.*[10] analyzed the stability of tungsten nitride. It is instructive to mention that the experimental preparation of WN, however, is tough because the incorporation of nitrogen into tungsten lattice is thermodynamically unfavorable at atmospheric pressure. Till date, most materials in the WN system are in the form of thin films formed by non-equilibrium processes and are normally poorly crystallized, which some times limits their use in diverse technological applications[11]. In this paper, the structural, elastic and their pressure dependence properties of WN are studied systematically by effective interionic interaction potential method.

THEORY AND METHOD OF COMPUTATION

The understanding of thermodynamical properties for mononitrides compounds requires the formulation of an effective interionic potential. The idea we have in mind is as follows: the change in force constants is small, the short range interactions are effective up to the second-neighbour ions, and the atoms are held together with harmonic elastic forces without any internal strains within the crystal. The effective interionic potential is expressed as

$$U(r) = \sum_{ij} \frac{Z_m e^2}{r_{ij}} + \sum_{ij} b\beta_{ij} \exp\left(\frac{r_i + r_j - r_{ij}}{\rho}\right) + \sum_{ij} c_{ij} r_{ij}^{-6} + \sum_{ij} d_{ij} r_{ij}^{-8}. \tag{1}$$

Here, long-range Coulomb is represented by first term,second term correspond to [12] form of short-rangerepulsive energies and van der Waals multipole are represented by third and fourth terms respectively. The

symbols: c_{ij} and d_{ij} are the van der Waals coefficient and β_{ij} being the pauling coefficients, respectively. $Z_m e$ is the modified

Table 1. van der Waals coefficients of WN compound.(c_{ij} in units of 10^{-60} erg cm^6 and d_{ij} in unit of 10^{-76} erg cm^8). C and D are the overall van der Waals coefficients.

Compound	c_{ii}	c_{ij}	c_{jj}	C	d_{ii}	d_{ij}	d_{jj}	D
WN	1969	268.9	42.009	1938	2331	251.975	23.673	1326

Table 2. Model parameters, calculated transition pressures and volume collapse for WN compound.

Compo- und	Input parameter				Model parameters			Calculated transition pressure P_t (GPa) and volume collapses ΔV (%)	
	r_i	r_i	a(A°)	B_T(GPa)	Z_m^2	$b(10^{-12}$erg)	ρ (10^{-1} Å)	P_t (GPa)	ΔV (%)
WN	1.23	0.65	4.73	260	4	12.8	2.87	2	15.3

Table 3. Calculated values of density of mass ρ (x10^{30} in kg/m^3), longitudinal (S_L), transverse (S_T) and average (S_M) sound velocities in m/sec and Debye temperature (θ_D) in K for WN in $B3$ phase.

Compound	P	S_L	S_T	S_M	θ_D
WN	2.87	6.08	3.465	3.959	60.5

ionic charge and parametrically includes the effect of Coulomb screening effects, b and ρ are short-range parameters. Thus, the effective interionic potential contains only three free parameters (Z_m, b and ρ) which can be determined from the crystal properties[13].

We know that a specific phase is stable only when its free energy is minimum for the specified thermodynamic conditions. As we vary the temperature or pressure or any other variable acting on the systems, the free energy changes continuously. A phase transition is said to occur when the changes in structural details of the phase are caused by such variations of free energy. The mono nitride transform from their initial $B3$ to $B1$ structure under pressure. The stability of a particular structure is decided by the minima of Gibbs's free energy, $G = U + PV - TS$, where U is internal energy, which at 0 K corresponds to the cohesive energy, S is the vibrational entropy at absolute temperature T, pressure P and volume V. The Gibb's free energies: $G = U + PV - TS$, where U is internal energy, which at 0 K corresponds to the cohesive energy, S is the vibrational entropy at absolute temperature T, pressure P and volume V.

$$G_{B3}(r) = U_{B3}(r) + 3.08Pr^3 \tag{2}$$
$$G_{B1}(r') = U_{B1}(r') + 2Pr'^3 \tag{3}$$

forZnS ($B3$) phase and for NaCl ($B1$) phase they become equal at the phase-transition pressure P and at $T = 0$ K. Here the abbreviations U_{B3} and U_{B1} represent cohesive energies for $B3$ and $B1$ phases, respectively.

Further, the study of the second-order elastic constants (SOEC) (C_{11}, C_{12} and C_{44}) at 0 K is need attention for understanding the nature of the interatomic forces in them. Since these elastic constants are functions of the first- and second-order derivatives of the short-range potentials, their calculations will provide a further check on the accuracy of short-range forces in WN compound. Following [10] and subjecting the dynamical matrix to the long-wavelength limit, we find the expressions for the SOEC for $B1$ phase as:

$$C_{11} = \frac{e^2}{4r_0^4}\left[-5.112Z_m^2 + A_1 + \frac{(A_2 + B_2)}{2}\right], \tag{4}$$

$$C_{12} = \frac{e^2}{4r_0^4}\left[0.226\,Z_m^2 - B_1 + \frac{(A_2 - 5B_2)}{4}\right], \tag{5}$$

$$C_{44} = \frac{e^2}{4r_0^4}\left[2.556\,Z_m^2 + B_1 + \frac{(A_2 + 3B_2)}{4}\right], \tag{6}$$

where (A_1, B_1) and (A_2, B_2) are the short-range parameters for the nearest and the next nearest neighbors, respectively. These parameters are defined as

$$A_1 = \frac{4\, r_0^3}{e^2}\left[\frac{d^2}{dr^2}V_{ij}(r)\right]_{r=r_0}, \tag{7}$$

$$A_2 = \frac{4(r_0\sqrt{2})^3}{e^2}\left[\frac{d^2}{dr^2}V_{ii}(r)+\frac{d^2}{dr^2}V_{jj}(r)\right]_{r=r_0\sqrt{2}}, \tag{8}$$

$$B_1 = \frac{4\, r_0^2}{e^2}\left[\frac{d}{dr}V_{ij}(r)\right]_{r=r_0}, \tag{9}$$

$$B_2 = \frac{4(r_0\sqrt{2})^2}{e^2}\left[\frac{d}{dr}V_{ii}(r)+\frac{d}{dr}V_{jj}(r)\right]_{r=r_0\sqrt{2}}, \tag{10}$$

where $V_{ij}(r)$ and $V_{ii}(r)$ $[V_{jj}(r)]$ are the overlap potentials between the nearest and the next nearest neighbors, respectively. Here, $r_0\sqrt{2}$ denotes the next nearest neighbor distance in $B1$ phase.
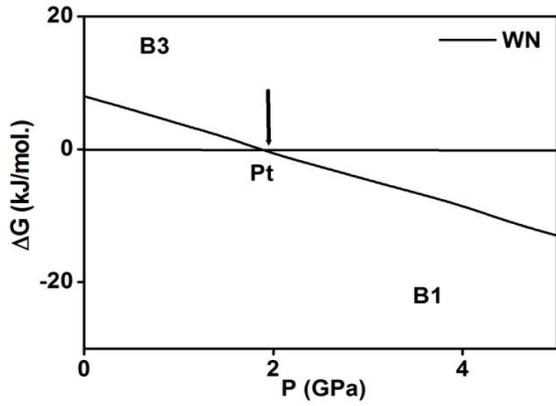

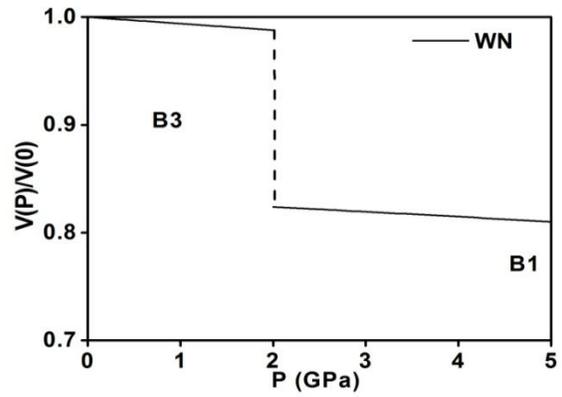Figure 1. Variation of Gibbs free energy difference (ΔG) with pressure (P)

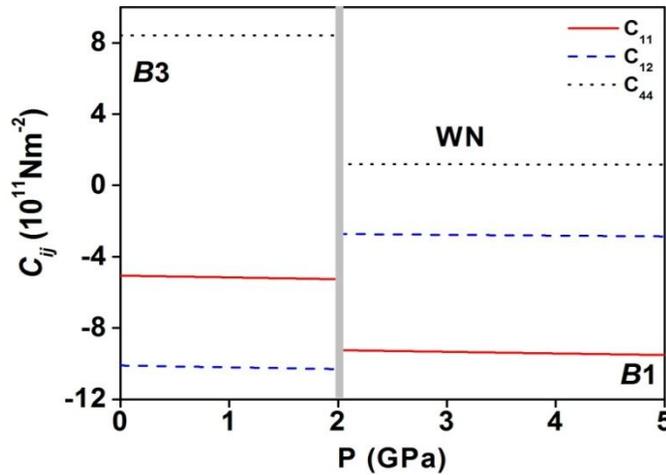Figure 2. Variation of $V(P)/V(0)$ as a function of pressure for WN.

Figure 3. Variation of second order elastic constants (SOEC) with pressure (P).

RESULT AND DISCUSSION

As mentioned in the earlier, the developed effective interionic potential model have three freeparameters, namely, modified ionic charge, range and hardness parameters (Z_m, ρ and b). Toestimate the free parameters, we first deduce the vdW coefficients from the Slater-Kirkwoodvariational method [17] and are listed in table 1. We consider that the WN compound to be partiallyionic. It is instructive to mentioned that we have deduced the values free parameters modified ioniccharge (Z_m), range (ρ) and hardness (b) from the utilization of equilibrium distance and the bulkmodulus following the equlibrium conditions [18]and tabulated in table 2.In an attempt to reveal the structural phase transition of the test materials, we minimise theGibbs's free energies $G_{B3}(r)$ and $G_{B1}(r')$ for the equilibrium interatomic spacing (r) and (r'). Then theGibbs's free energy difference ΔG [= $G_{B1}(r')$ - $G_{B3}(r)$] have been plotted as functions of pressure (P)in Fig. 1 by using the developed interionic potential as discussed above. Let us summarize the results of the plots.The pressure corresponding to ΔG approaching to zero is the phase transition pressure (Pt)[indicated by arrows in figure]. At zero pressure, the $B3$ crystal phase is thermodynamically andmechanically stable, while the $B1$ is not. As pressure increases, beyond the phase transition pressure(Pt), the $B1$ system becomes mechanically and thermodynamically stable (its ΔG function value isnegative than that of $B3$ crystal). Eventually, and at a pressure higher than the theoreticalthermodynamic transition pressure, the $B3$ crystal becomes thermodynamically unstable while the$B1$ phase remains stable up to the greatest pressure studied (≈ 5 GPa). In WN compound acrystallographic transition from $B3$ to $B1$ occurs. These results may be successfully compared withthose available reported data [16] and are tabulated in Table 2.

The estimated value of pressure dependent radiusfor both structures, the curve of volume collapse with pressure to depict the phase diagram isillustrated in Fig. 2. It is noticed from the plot that our approach has predicted correctly the relativestability of competitive crystal structures, as the values of ΔG are positive. The magnitude of thediscontinuity in volume at the transition pressure is obtained from the phase diagram and its value istabulated in Table 2.Further, the elastic properties define the properties of material that undergoes stress, deforms and thenrecovers and returns to its original shape after stress ceases. These properties play an important partin providing valuable information about the binding characteristic between adjacent atomic planes,anisotropic character of binding and structural stability. Hence, to study the stability of WNcompound in ZnS ($B3$) and NaCl ($B1$) structures, we have calculated the elastic constants at normaland under hydrostatic pressure by using developed effective interionic potential. Fig. 3 shows thevariation of second-order elastic constants (SOEC) with pressure in $B3$ and $B1$ phase for WNcompound. We note that C_{11}, C_{12} and C_{44}decreasesnearly linearly with pressure. At phase transitionpressure WN has shown a discontinuity in SOEC, which is in accordance with the first-order character of the phase transition. We have also estimated the density of mass ρ (x10^{30} in kg/m^3), longitudinal (S_L), transverse (S_T) and average (S_M) sound velocities in m/sec and Debye temperature (θ_D) in K for WN in $B3$ phase and tabulated in table 3.

CONCLUSIONS

In the present study, we have investigated the structural, elastic properties and their pressure dependence of WN using developed model potential. The structural phase transformation at which WNcompound undergoes the structural transition from $B3$ to $B1$ is predicted at 2GPa, which isconsistent with reported data. The variations of elastic constants with pressure follow a systematictrend in both the phases.

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