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# Analysis of structural properties of refractory compounds at high temperature and pressure using a potential model

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ABSTRACT

In this paper we focused on the structural and elastic properties of four transition metal mononitrides (TMNs) (M=Ti, Nb, Hf and Zr) by using realistic three body interaction potential (RTBIP) model, including the role of temperature. These TMN compounds have been found to undergo NaCl (B1) to CsCl (B2) phase transition, at a pressure quite high as compared to other binary systems. We successfully obtained the phase transition pressures and volume changes at different temperatures. In addition, elastic constants of TMNs at different temperatures are discussed. The present theoretical results have been compared with the available experimental data and predictions of LDA theory.

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## 1. Introduction

The compounds of transition metals show a variety of applications ranging from protective hard coatings (generally TMNs, of the IIIB–VIB group [1,2]) to optoelectronic devices (mostly IIIA and VA groups [3]) to potential hydrogen storage materials such as $Li_3N$ [4]. TMNs are generally materials of high hardness with high young's modulus. Particularly TiN among the super hard compounds which is often used in surface coatings and cutting tools.

Hard superconducting materials are of considerable interest for specific electronic applications. The transition-metal compounds (e.g. NbN, NbC, TiN, HfN) having the sodium chloride (B1) structure are known as refractory compounds. They also show extreme and exclusive physical properties of hardness, brittleness, high melting point, and some of them show a relatively high superconducting transition temperature [5–7]. Due to these properties, they have technological applications in various fields, and also are interesting from the point of view of fundamental studies. Hence they have attracted attention of many physicists for theoretical [8–13] as well as experimental [14–18].

Papaconstantopoulos et al. [8] studied high pressure phase transition and bulk properties of V and VI TMNs using first principle calculations. The transition metal nitrides (as also carbides and oxides) usually contain vacancies. The effect of metalloid (N, C or O) vacancies on the bonding properties of TiN and VN have been investigated by Zhukov et al. [9]. The electronic, cohesive, and thermodynamic properties have been reported for 3d and 4d transition metal monocarbides and mononitrides with rock salt structure [10–12]. The electronic and magnetic properties of the mononitrides in the rock salt and zinc sulfide structures formed with 3d transition metals have been studied by Shimizu et al. [13].

Chen et. al. [14,15] studied high-pressure phonon spectra of transition-metal nitrides HfN, ZrN, and NbN by Raman-scattering measurements. Using Raman scattering and X-ray diffraction they reported a quantitative study of pressure effects on the superconducting transition temperature $T_C$ and the electronic stiffness of NbN, and they found that superconducting temperature $T_C$ increases initially with pressure and then saturates up to 42 GPa. Using angle-dispersive synchrotron powder X-ray diffractometry with a diamond anvil cell, the equation of states, elastic properties and hardness of TMN (TM=Zr, Nb, Hf) [16] are investigated by them. Oya et al. [17] found that NbN crystallizes in cubic structure and also have hexagonal structure. The electronic structure of hex-NbN and NaCl-NbN are measured by X-ray photoemission spectroscopy and ellipsometric measurements [18].

On the other hand lot of study is available for B1–B2 transition and elastic properties in selected transition metal nitrides by phenomenological models. They are mainly based on two body potential models [19]. The thermo-physical properties of transition metal carbides and nitrides with NaCl structure were calculated using the Debye–Gruneisen model combined with ab initio calculations [20]. The elastic constants and electronic structure of transition metal nitrides and carbides are calculated by using ab initio density

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functional perturbation theory [21]. The electronic structure and bonding mechanism of NbN and NbC are studied by means of the accurate first-principles total energy calculations using the full potential linearized augmented plane wave method (FP-LAPW) [22]. Out of these, most of the theoretical studies have been done by taking temperature as zero, but the Gibbs free energy ($G = H - TS$, where H-enthalpy, T-temperature and S-entropy) is a function of temperature, and experiments are also carried out at room temperature (300 K) and not at zero temperature. Most of the works on B1–B2 transition based on phenomenological models were based on the assumption $T = 0$ K ignoring the role of temperature.

So to fill this gap in the present work we are incorporating temperature effects in three body potential model and this has made our model RTBIP more realistic. Earlier theoretical studies of phase transition with TBIP model have been carried by assuming equilibrium at 0 K instead of room temperature (300 K). In addition to the effect of temperature our model includes the effect of three body interactions, importance of which is already established [23–26]. The need of inclusion of TBI forces was emphasized by many workers for betterment of results [27–29]. These studies were based on two body potentials and they remarked that the results could be improved by including non-rigidity in potential model. We have already employed our TBIP approach to study high pressure behavior in some B3–B1 and B1–B2 transitions [30–32]. This model is also able to explain the Cauchy violation ($C_{12} \neq C_{44}$) in second order elastic constants.

The purpose of present work is to study the structural, elastic and thermo-physical properties at higher temperatures of TMNs theoretically. We have studied the phase transition pressures and volume changes of TMNs at different higher temperatures and the second order elastic constants are also calculated. The outline of this paper is as follows: potential model and method of computation is given in Section 2 and the results are discussed in Section 3 and concluded in Section 4.

## 2. Potential model and method of computation

It is well known that pressure causes a compression in the crystal, and consequently it alters the charge distribution of the electron shells. As a result of this, a deformation of the overlapping electron shells of the adjacent ions takes place which leads to an increased charge-transfer (or three-body interaction (TBI)) [33]. 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 anions experience sufficient overlap. Besides, enhance in overlap energy the transferred charge due to the overlap in electron shells, modifies the ionic charge which modifies the coulomb energy by $\{1 + (2n/z)\}$, 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 and is dependent on the nearest neighbor distance ($r$) [31].

$$f(r) = f_0 \exp\left(\frac{-r}{\rho}\right) \tag{1}$$

In order to obtain the stability condition for a crystal structure, we minimize Gibbs free energy by using minimization technique. The effect of TBI is introduced in the expression of Gibbs free energy, ($G = U + PV - TS$). Here $U$ is the internal energy, which at $T = 0$ K is equivalent to the lattice energy, $S$ is the vibrational entropy at absolute temperature $T$. Since the theoretical calculations are done at $T = 0$ K, the Gibbs free energy is equivalent to enthalpy (H). This is not a realistic approach because experiments are carried out at room temperature and not at $T = 0$ K. This fact causes discrepancy in comparability of theoretical results with experimental data. To obtain better comparability with experimental results we have taken account of the room temperature in pressure induced theoretical calculations. The Gibbs free energies for rock salt (B1, real) and CsCl (B2, hypothetical) structures at room temperature $T = 300$ K is given by

$$G_{B1}(r) = U_{B1}(r) + PV_{B1} - TS_1 \tag{2}$$

$$G_{B2}(r) = U_{B2}(r) + PV_{B2} - TS_2 \tag{3}$$

With $V_{B1}$ ($= 2.00r^3$) and $V_{B2}$ ($= 1.54r'^3$) as the unit cell volumes, $S_1$ and $S_2$ as the entropies for B1 and B2 phases, respectively. In fact, the condition for a transition is that the difference in free energies between two phases approaches to zero (i.e. $\Delta G \rightarrow 0$).

$$\Delta G = \Delta H - T\Delta S \tag{4}$$

The first terms in energies (2) and (3) are lattice energies for B1 and B2 structures and they are expressed as

$$U_{B1} = \frac{-(\alpha_M z^2 e^2)}{r} - \frac{12\alpha_M z e^2}{r} f(r) + 6b\beta_{ij}.\exp\left(\frac{r_i + r_j - r}{\rho}\right) + 6b\beta_{ii}.\exp\left(\frac{2r_i - 1.41r}{\rho}\right) + 6b\beta_{jj}.\exp\left(\frac{2r_j - 1.41r}{\rho}\right) \tag{5}$$

$$U_{B2} = -\frac{\alpha_M' z^2 e^2}{r'} - \frac{16\alpha_M' z e^2}{r'} f(r') + 8b\beta_{ij}.\exp\left(\frac{r_i + r_j - r'}{\rho}\right) + 3b\beta_{ii}\exp\left(\frac{2r_i - 1.154r'}{\rho}\right) + 3b\beta_{jj}\exp\left(\frac{2r_j - 1.154r'}{\rho}\right) \tag{6}$$

Here $\beta_{ij}$ is the Pauling coefficient, $r_i$ ($r_j$) is the ionic radii of $i(j)$ ions, $S_1$ and $S_2$ are the entropies, $\rho(b)$ are the range (hardness) parameters.

The first terms in Eqs. (5) and (6) consist of long-range Coulomb energy, second terms are three-body interactions corresponding to the nearest neighbor separation $r$ ($r'$) for B1 (B2) phases, remaining terms are the energies due to the overlap repulsion represented by Born–Mayer potential for ($i,j$) ions, and extended up to the second neighboring ions by using Hafemeister and Flygare (HF) type potential. Now the entropy difference in the last term of Eqs. (2) and (3) can be calculated from the relation used by Shanker et al. [33–35] and Gaur et al. [24].

$$S_1 - S_2 = \int_1^2 \left(\frac{C_1 - C_2}{T}\right) \tag{7}$$

Here, 1 and 2 stand for the B1 and B2 phases, $C_1$ and $C_2$ are the specific heats of two phases at constant pressure and their values can be calculated from the knowledge of Gruneisen parameter ($\gamma$) and linear isothermal temperature coefficient ($\beta$) as

$$C_i = \frac{\{\beta V_i(B)\}_i}{\gamma_i} \tag{8}$$

where B is bulk modulus.

Here, Gruneisen parameter ($\gamma$) can be calculated by well-known formula as follows [36]:

$$\gamma = \frac{r_0}{6}\left[\frac{U'''(r_0)}{U''(r_0)}\right] = \frac{-r_0}{6\rho} \tag{9}$$

### 2.1. Structural properties

At ambient conditions, the B1 structure is most stable in these compounds and at high pressure they transform to body centered B2 structure. As the stable phase is always associated with minimum free energy of the crystal, we have followed the technique of minimization of Gibbs free energies of real and hypothetical phases. $\Delta G$ is an important factor in finding phase transition pressure ($P_t$). The phase transition occurs when $\Delta G$ approaches zero ($\Delta G \rightarrow 0$). The Gibbs free energy differences ($\Delta G$) are plotted against pressure to obtain phase transition pressure ($P_t$). B1 is the real phase and B2 is

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