

Structural Phase Transition and Elastic Properties of Molybdenum Nitride

Shubhangi Soni^{1,a)}, R. Kinge², K. K. Choudhary³, and Netram Kaurav^{1,a)}

¹*Department of Physics, Government Holkar Science College, Indore 452001, India.*

²*Department of Physics, Smt. G. G. Khadse College, Muktainagar, Dist. Jalgaon, Maharashtra 425306, India.*

³*Army Cadet College, Indian Military Academy, Dehradun, (UK) India-248007*

^{a)}Corresponding author: shubhangisoni08@gmail.com, netramkaurav@yahoo.co.uk

Abstract: In the present paper, structural and elastic properties of transition metal nitride (MoN) were investigated through effective inter-ionic potential method. The used potential consists of the long-range Coulomb and van der Waals (vdW) interactions and the short-range repulsive interaction of up to second-neighbor ions within the Hafemeister and Flygare approach. First, we have employed the Slater-Kirkwood variational method to estimate the vdW coefficients. The estimated value of the phase transition pressure (Pt) is 7 GPa for B3(ZnS) type structure to B1(NaCl) type structure, which is consistent with the available experimental data. We have also predicted the elastic properties MoN compound.

INTRODUCTION

High Pressure study along with ambient pressure can help to study the mechanical properties of compounds so when we use high pressure the verity of changes in the physical properties of the compounds have been observed. One of the most interesting changes is the conversion of crystal structure of the material since the volume get change with change in pressure. Although, other physical properties such as bulk modulus, lattice parameter, stiffness Debye temperature are also get changed. Most of the nitrides have stability at ambient pressure. The *d*-block elements nitrides (Transition metal nitrides; TMN) can be used in many applications, such as, coatings to protect mechanical tools, corrosion resistant, optical coatings, electrical contacts, diffusion barriers and superconductors; as well as catalysts, electrode materials for batteries and fuel-cells [1]. These compounds can also be used as materials for magnetic storage devices. In the present study, we have taken metal nitride for our calculations because of their various technological and fundamental applications as stated above. For such applications, understanding of behavior at ambient to high pressure is essential for metal nitrides. Most of the TMN exhibited a cubic NaCl structure (B1), in which two interpenetrated metal and nitrogen fcc sub lattices, so that each N(metal) atom is octahedral coordinated to 6 nearest neighbor metal (N) atoms.

Among transition metal nitrides, molybdenum nitrides have been much less studied, although their mechanical properties as well as their electrical and catalytic properties make them very attractive for many applications. In fact, Mo nitride exhibit hardness values ranging from 28 to 34 GPa, whereas those for Ti or Cr nitrides range between 18 and 24 GPa [2, 3]. Because of their strong covalent bonding, the calculated values of the bulk modulus of the stoichiometric MoN are also superconducting and the predicted value of the transition temperature for the metastable MoN phase of NaCl-B1-type cubic structure is the highest of all refractory carbides and nitrides. Much data about the properties of transition metal carbides and to a lesser extent those of transition metal nitrides has been gathered in some books and reviews [4, 5]. Since they have been much less studied, molybdenum nitrides are relatively underrepresented in such works. The present work concentrated to fill that gap by providing relatively recent data about the structure and the formation of molybdenum nitride crystal phases on the application of high pressure.

THEORY AND METHOD OF COMPUTATION

The effective inter ionic interaction potential is expressed as

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

Here, first term correspond to long-range Coulomb, second term correspond to [9] form of short range repulsive 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 is the modified ionic charge and parametrically includes the effect of Coulomb screening effect, 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 crystal properties[9].

We know that a particular structure is stable only when its free energy is minimum for the specified thermodynamic conditions. When we altered 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 compound transform from their initial B3 to B1 structure under pressure. Since the stability of a particular structure is decided by the minima of Gibbs's free energy,

$$G = U + PV - TS \quad (2)$$

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 .

$$G_{B3}(r) = U_{B3}(r) + 3.08Pr^3 \quad (3)$$

$$G_{B1}(r') = U_{B1}(r') + 2P r'^3 \quad (4)$$

for zinc blende ($B3$) 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.

The study of the second-order elastic constants (SOEC) (C_{11} , C_{12} and C_{44}) and their pressure derivatives 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 these materials. Following [10] and subjecting the dynamical matrix to the long-wavelength limit, we find the expressions for the SOEC for $B1$ phase as:

$$C_{11} = \frac{e^2}{4r_0^4} \left[-5.112Z_m^2 + A_1 + \frac{(A_2 + B_2)}{2} \right], \quad (5)$$

$$C_{12} = \frac{e^2}{4r_0^4} \left[0.226 Z_m^2 - B_1 + \frac{(A_2 - 5B_2)}{4} \right], \quad (6)$$

$$C_{44} = \frac{e^2}{4r_0^4} \left[2.556 Z_m^2 + B_1 + \frac{(A_2 + 3B_2)}{4} \right], \quad (7)$$

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

$$A_1 = \frac{4r_0^3}{e^2} \left[\frac{d^2}{dr^2} V_{ij}(r) \right]_{r=r_0}, \quad (8)$$

$$A_2 = \frac{4(r_0\sqrt{2})^3}{e^2} \left[\frac{d^2}{dr^2} V_{ii}(r) + \frac{d^2}{dr^2} V_{jj}(r) \right]_{r=r_0\sqrt{2}}, \quad (9)$$

$$B_1 = \frac{4r_0^2}{e^2} \left[\frac{d}{dr} V_{ij}(r) \right]_{r=r_0}, \quad (10)$$

$$B_2 = \frac{4(r_0\sqrt{2})^2}{e^2} \left[\frac{d}{dr} V_{ii}(r) + \frac{d}{dr} V_{jj}(r) \right]_{r=r_0\sqrt{2}}, \quad (11)$$

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.

TABLE 1: van der Waals coefficients of MoN compound. (c_{ij} in units of 10^{-60} erg cm⁶ and d_{ij} in unit of 10^{-76} erg cm⁸). 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
MoN	2417	294.203	42.009	2218	3063	292.549	23.673	1584

TABLE 2: Model parameters, calculated transition pressures and volume collapse for MoN compound.

Compound	Model parameters			Calculated P_t and V_t	
	Z_m^2	$b(10^{-12}$ erg)	$\rho(10^{-1}$ Å)	P_t (GPa) (Exp.)	V_t (%)
MoN	2.89	2.536	2.86	7, (6 [10])	12.5

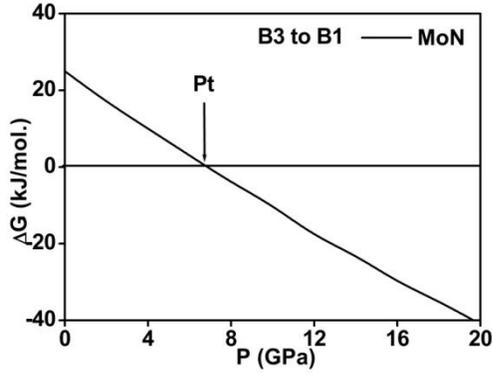


Figure 1. Variation of Gibbs free energy difference (ΔG) with pressure (P)

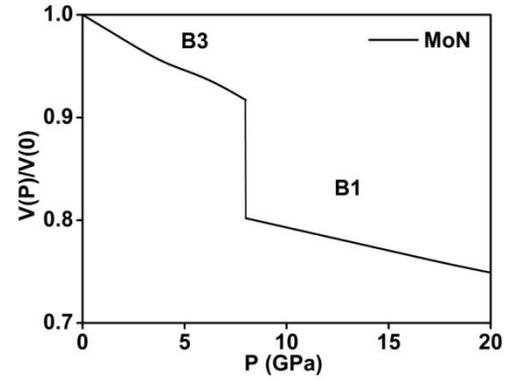


Figure 2. Variation of $V(P)/V(0)$ as a function of pressure for MoN.

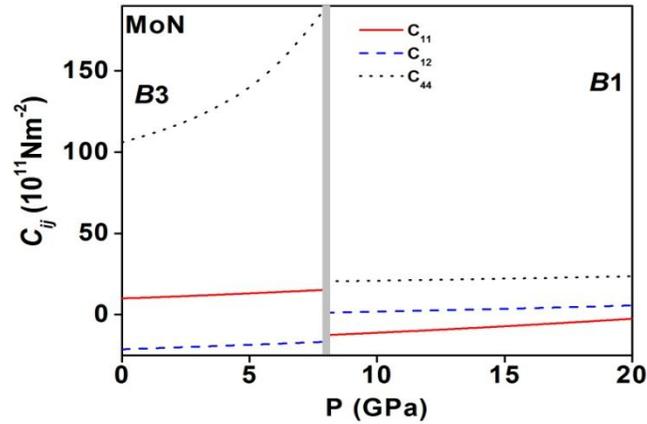


Figure 3. Variation of second order elastic constants (SOEC) with pressure (P).

RESULT AND DISCUSSION

Owing to their very good catalytic properties, molybdenum nitride is compared with noble metals; this is due to the presence of nitrogen atoms in interstitial sites of the host metal which modifies the density of states at the Fermi level. The unique combination of physical and chemical characteristics which is the result of the wide range of stoichiometry of molybdenum nitrides makes them very interesting and promising for various applications. Ambient and high pressure crystal structures have been investigated theoretically by applying pressure. Here, the effective interionic potential is constructed in a hierarchical and easy generalizable manner, wherein, we have undertaken such structural and elastic properties in an ordered way. For such purposes we have taken three free parameters, namely, modified ionic charge, range and hardness parameters (Z_m , ρ and b). To estimate all them, we first determine the vdW coefficients from the Slater–Kirkwood variational method [11] and are listed in Table 1. Although it is worth to remark that we have determine the values of material parameters such as modified ionic charge (Z_m), range (ρ) and hardness (b) from the knowledge of equilibrium distance and the bulk modulus [12]. The deduced values of the model parameters for MoN compound are given in Table 2.

Our obtained values of material parameters (MoN) allow us to predict phase transition pressure and associated volume collapse. The obtained transition pressure of MoN from ZnS ($B3$) to NaCl ($B1$) is 7 GPa as indicated in Fig. 1. On the other hand, associated volume collapse or volume discontinuity in pressure volume phase diagram identifies the structural phase transition from ZnS ($B3$) to NaCl ($B1$) type structure. Gibbs free energy is determined for both the phases and stable structure has been found at minimum Gibbs energy. From the Fig. 2 it is noticed that the volume discontinuity at phase transition pressures shows the compression of the lattice due to which the ZnS structure becomes unstable at high pressure and transforms to NaCl type structure. We have also presented the calculated values of various physical parameters in Table 2. In order to study the high-pressure dependence of elastic behavior of MoN compound we have presented the variation of second order elastic constants (C_{11} , C_{12} and C_{44}) with pressure in Fig. 3 and they are consistent with known theoretical works on other metal nitrides [12]. We comment that the EIoIP approach yields qualitative understanding with proper parameterization of the materials parameter at atomic level.

CONCLUSION

In the present study, we have investigated the structural phase transition and elastic properties of MoN by using modified interionic potential. The estimated structural and elastic properties of MoN are quite consistent with the reported data. Our results indicates that the present model is quite successful in developing the structural and elastic behavior in terms of Coulomb screening effect through the modified ionic charge parameter for these compounds.

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