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Research paper

Phase transition and ductile behavior of $Ir_xOs_{1-x}N$ alloys from theoretical point of view

Madhu Sarwan *, Sadhna Singh

High Pressure Lab, Department of Physics, Barkatullah University, Bhopal 462026, India

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ABSTRACT

Present paper reports theoretical investigation of less explored nitrides of Iridium and Osmium using semi-empirical model with charge transfer effect (CTE). This work indicates the presence of structural phase transition in these nitrides from zinc-blend (B3) to rock-salt (B1) structure on application of pressure on them. Transitions occurred at 71 GPa and 86 GPa, with sudden drops in volume of 9.54% and 8.35% in IrN and OsN. The effect of pressure on elastic properties for B3-IrN and B3-OsN is investigated for the first time. On the basis of mechanical properties, it is observed that both compounds are ductile in nature. The present study is extended to investigate transition metal alloy $Ir_xOs_{1-x}N$ via Vegard's law. To widen the applicability of our model and to explore this alloy we report structural, elastic, mechanical and thermophysical properties. The effect of pressure on Debye temperature with different concentration (x = 0, 0.25, 0.5, 0.75, 1) have also been analyzed. The results are in general in good agreement with available theoretical results.

1. Introduction

Physical properties of many materials have been studied at macro and micro level by putting them under high pressure. These properties can be tuned without changing the chemical composition on the application of pressure. It brings changes in crystal structure, elastic and mechanical properties of materials owing to composition in it. Many experimental and theoretical workers have analyzed the behavior of materials under high pressure [1–5].

The nitrides are considered worth interest because of their technological and fundamental importance [6,7]. Numerous theoretical studies are available which deal with structural, physical and optoelectronic properties of nitrides [1,3,8–11]. Among nitrides, III-V nitrides stand apart as they are mostly used in optoelectronic devices. The group of nitrides also consist transition metal nitrides (TMN) known for superconducting and semiconducting properties. Apart from these they are known for their hardness which makes them suitable candidate to alternate super hard materials like diamond and c-BN. They are preferred over diamond due to being cost-effective and relatively easy to synthesize in quantities required by industries. Thus, efforts have been devoted by researchers to find alternate super hard materials in these nitrides.

TMNs possess properties of high melting point, superconductivity, as well as electronic and optical characteristics [12]. 3d and 4d TMNs show dominating performance and large applications in protective and hard coating. 5d TMNs can be synthesized under extreme conditions [12]. IrN and OsN are members of these 5d metal nitrogen compounds, which are less explored nitrides [12–14]. They crystallize in zinc-blende (ZB) structure with space group F-43m (216) under ambient conditions and undergo a phase transition to rock-salt (RS) structure with space group Fm-3m (225) under pressure. The elastic and electronic properties of IrN and OsN nitrides have been studied using first-principles calculations in both structures ZB (B3) and RS (B1) structures [12] while structural phase transitions of IrN from B3 to B8, B1, Bh, and B2 phase have been studied by FPLMTO [13]. The elastic constants, bulk moduli, shear moduli, shear wave velocity and Debye temperature of B4 IrN are found to increase with pressure [14]. Wang et al. [15] studied the TcN, ReN, OsN and IrN with different structures by using first-principle calculations. They concluded that, TcN and ReN are stable in NbO-type structure and IrN, OsN are stable in Pmn21-type structure.

On the other hand the alloys of transition metal compounds are studied extensively [16–18]. These alloys of transition metal compounds have superior applications as compared to binary compounds. Holleck et al. [17] proved that intermediate composition of transition metal nitrides and carbides are harder than corresponding binary compounds. Chihi et al. [18] have investigated the

* Corresponding author.
E-mail addresses: madhusarwan@gmail.com (M. Sarwan), drsadhna100@gmail.com (S. Singh).

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structural, elastic and mechanical properties of $Ti_{1-x}Zr_xN$ at high pressure in B1 phase. Recently Ir-Os alloy has been studied experimentally [19]. It is revealed through the compressibility curve that there are possible changes in electronic properties at pressure 20 GPa in $Ir_{0.80}Os_{0.20}$.

With this scenario, there is no experimental work available on IrN and OsN. There is no study available for the alloy $Ir_xOs_{1-x}N$ as well. Also the works on structural, elastic and electronic properties by first principle calculations on IrN and OsN are very less demonstrated. Some of these properties are investigated at P = 0 GPa and no study on high pressure is available. As the work with phenomenological model is not available and the nature of interatomic forces are not well understood. To get the knowledge regarding the interatomic forces and to know the structural, elastic and mechanical properties of these compounds and alloy at high pressure, an effort has been made to generate an interaction potential model (IPM). This IPM consist of coulomb interaction, three-body interaction (TBI), van der Waals (vdW) interaction, short range overlap repulsive interaction and zero point energy effect.

The most important feature of TBI is the explanation of Cauchy violation which makes it different from other phenomenogical models. Also IPM has included vdW interaction which is overlooked in first principle calculations. To further improve our model, zero point energy has been included. This is the lowest possible energy which may be possessed by any material. The energy of the compound can be written as $\varepsilon = (h\upsilon)/[e^{(h\upsilon)/kt}-1] + (h\upsilon/2)$, here υ, h, t, k are the frequency, Planck constants, temperature and the Boltzmann constant of the compound. Though this energy is very small contribution to Gibbs free energy, but its inclusion makes our model more realistic.

We present the phase transition pressure, elastic, mechanical and thermo physical properties of IrN, OsN and $Ir_xOs_{1-x}N$ at high pressure and explored the high pressure dependence of these properties. This is the first time when the elastic, mechanical and thermophysical properties of both nitrides and their alloy are analyzed at high pressure comprising the zero point energy effect with TBI. The essential features of the present theory and method of computation for high pressure behavior are presented in Section 2. The results and discussions are presented in Section 3. Section 4 presents the conclusions.

2. Potential model and computation method

The pressure causes variation in volume of materials and consequently it increases charge transfer due to overlapping of electron shells of adjacent ions [3]. During this overlapping, transferred charge interacts with other charges causing many-body interaction (MBI). The main part of the MBI is a three-body interaction (TBI) [20]. This interaction becomes more important with the application of pressure as it decreases interionic spacing of ions and they experience sufficient overlap on increasing pressure. This TBI has been included in Gibbs free energy (G = U+PV-TS), which is a combination of lattice energy U, pressure P, volume V, temperature T and entropy S at absolute temperature T. The Gibbs free energy for both the structure B3 and B1 are given by

$$G_X(r) = U_X(r) + PV_X \tag{1}$$

$$G_Y(r') = U_Y(r') + PV_Y \tag{2}$$

The primary parts in (1) and (2) are lattice energies (X = B3 and Y = B1) and secondary terms in both equations represent the pressure–volume term for both (B3 and B1) phases. Symbol V_X (=3.08 r_{ij}^3) and V_Y (= 2.00 r_{ij}'3) are the volumes for given phases. The present IPM describes the various interactions, these interactions are incorporated in lattice energies expressed as [3,4]

$$U_X(r) = \frac{-\alpha_M e^2 Z^2}{r_{ij}} - \frac{4\alpha_M e^2 Z f(r)}{r_{ij}} - \left[\frac{C}{r_{ij}^6} + \frac{D}{r_{ij}^8}\right] + 4b\beta_{ij}\exp(r_i + r_j - r_{ij}/\rho) + 6b\beta_{ii}\exp(2r_i - 1.63r_{ij}/\rho) + 6b\beta_{jj}\exp(2r_j - 1.63r_{ij}/\rho) + 0.5h\left(\langle\omega^2\rangle\right)^{1/2} \tag{3}$$

$$U_Y(r) = \frac{-\alpha'_M e^2 Z^2}{r'_{ij}} - \frac{6\alpha'_M e^2 Z f'_m(r)}{r'_{ij}} - \left[\frac{C}{r'^6_{ij}} + \frac{D}{r'^8_{ij}}\right] + 6b\beta_{ij}\exp(r_i + r_j - r'_{ij}/\rho) + 6b\beta_{ii}\exp(2r_i - 1.414r'_{ij}/\rho) + 6b\beta_{jj}\exp(2r_j - 1.414r'_{ij}/\rho) + 0.5h\left(\langle\omega^2\rangle\right)^{1/2} \tag{4}$$

Here the symbols have their usual meanings [3]. b(ρ) is hardness (range) parameter, f(r) is the three-body force parameter, e is the electronic charge, α_M (α'_M) is Madelung constant for B3 (B1) phase, r_i (r_j) are the ionic radii of ions i (j). Symbol β_{ij} (i, j = 1, 2) are the Pauling coefficients which are described 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. C (C′) and D (D′) are overall van der Waal coefficients for B3 (B1) structure. The first part in lattice energies is due to Coulomb interaction, the second term is due to three-body interactions corresponding to the nearest neighbor separation (r_{ij}) and (r'_{ij}), Third part is van der Waal interactions, rest terms are energy due to the overlap repulsion extended up to the second neighbor ions and the last term is due to the zero point energy. Where $\langle\omega\rangle^{1/2}$ is the mean square frequency related to the Debye temperature θ_D as

$$\left\langle\omega^2\right\rangle^{1/2} = k\theta_D/h \tag{5}$$

Here Θ_D is the Debye temperature and its value is determined by well known Blackman's formula [21].

$$\theta_D = \left(\frac{h}{k}\right)\sqrt{(5r_0B)/\mu} \tag{6}$$

where B and μ are the bulk modulus and reduced mass of the compounds.

Vegard's law is employed to pure compounds and parameters of intermediate concentrations of mixed compounds have been computed using it. According to this law [22], the mixed crystals, are considered as a collection of average ions whose masses, force constants, and effective charges are considered to scale linearly with concentration (x). Though the violation of this law is observed experimentally and theoretically in semiconductors alloy [23–25] and the violation may be correlated by considering bowing parameter. Generally Vegard's law is given by

$$a(A_xB_{1-x}C) = xa_{AC} + (1-x)a_{BC} \tag{7}$$

Here "a" is the lattice parameter for pure and mixed compound, AC is IrN, BC is OsN and x represents concentrations. The values of model parameters (b, ρ, f(r)) for end point members will be same and the values of these for mixed crystal ($Ir_xOs_{1-x}N$) are estimated with the Vegard's law for different concentrations (x = 0, 0.25, 0.5, 0.75, 1). We assume that these model parameters vary linearly with x.

$$b(A_xB_{1-x}C) = xb_{AC} + (1-x)b_{BC} \tag{8}$$

$$\rho(A_xB_{1-x}C) = x\rho_{AC} + (1-x)\rho_{BC} \tag{9}$$

$$f(r)(A_xB_{1-x}C) = xf(r)_{AC} + (1-x)f(r)_{BC} \tag{10}$$

Materials undergo deformation on the application of stress and they regain their original dimensions after removal of stress. We get important information regarding a relationship between the mechanical and dynamical behavior of materials from elastic constants. They also offer information on the elasticity, stability and