

Structural study of Novel (superhard) material: NiO

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Abstract. We have investigated the pressure-induced phase transition of NiO and other structural properties using three-body potential approach. NiO undergoes phase transition from B1 (rocksalt) to B2 (CsCl) structure associated with a sudden collapse in volume showing first-order phase transition. A theoretical study of high pressure phase transition and elastic behaviour in transition metal compounds using a three-body potential caused by the electron shell deformation of the overlapping ion was carried out. The phase transition pressure and other properties predicted by our model is closer to the phase transition pressure predicted by Eto *et al.*

Keywords. Phase transition; volume collapse; transition metal compounds.

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1. Introduction

The investigation of the behaviour of transition metal compounds under high pressure is very important from two viewpoints, namely the interests in an antiferromagnetic Mott-type insulator in solid state physics and their roles in the interior of the Earth. NiO has many applications in various fields: (1) For introducing electrical ceramics such as thermistors and varistors, e.g. ferrites, pigments for ceramic, glass and glazes, (2) NiO can be reacted with acid to form salt and other compounds, e.g. nickel sulfamate for electroplating and nickel molybdate for hydrodesulfurisation catalysts, (3) gold-doped NiO film can be used as transparent electrodes, and in optoelectronic devices. It is also used in automobile fan shrouds, avionics, artificial joints, armored vehicles, artificial limbs, and architectural hardware.

NiO is an antiferromagnetic Mott-type insulator with a Neel temperature (T_N) of 523 K. Above (T_N), NiO has a cubic rock salt (B1) structure. Below (T_N) the magnetic moments are aligned ferromagnetically on the (111) plane along one of the [112] directions of the cubic cell, and the moments between the adjacent planes are coupled antiferromagnetically with each other. Recently, the total

energies of the distorted B1 and B2 structures of NiO were calculated within the density functional formalism by the local spin-density approximation (LSDA) using an optimized pseudopotential method. In the present study, we measured the phase transition pressure, and compared it with other experimental and theoretical results. LSDA calculation results predicted a transition pressure of 318 GPa for the distorted B1-to-B2 transition in NiO [1]. Our results are also in good agreement with this.

The high-pressure studies on various materials are significantly important both from basic and applied point of view. The transition metal monoxides play an important role in solid-state technology as they have many-fold scientific, industrial and technological applications [2–5]. The transition metal compounds MX (M denotes a transition metal element and X denotes one of the non-metal elements C, N or O) have recently attracted much attention because of their high hardness, high melting point, wear and corrosion resistance [2,4,6]. They have the largest cohesive energy and replacement of carbon by nitrogen or titanium by vanadium decreases the cohesive energy [7].

The three-body interactions have been considered to arise from the charge transfer effects during the overlapping of electron shells of the adjacent ions [8]. These effects have been incorporated in the Gibbs free energy ($G = U + PV - TS$) as a function of pressure (P) and three-body interaction (TBI). Phase transition pressure has been computed as the pressure where Gibbs free energy difference becomes zero. The plot of ΔG against pressure gives the phase transition pressure (P_t) at the pressure at which ΔG becomes zero (figure 1).

An important feature of the present theoretical work is that using minimum number of parameters, we have calculated many properties to unveil the behaviour of matter under high pressure. These properties include the behaviour of matter under high pressure, second-order elastic constants, volume collapses, etc.

2. Theory and method

Application of pressure on a crystal leads to an increased charge transfer (or three-body interaction effect), due to the deformation of the overlapping electron shells of the adjacent ions. The stability of a particular lattice structure is achieved at the minimum value of the Gibbs free energy ($G = U + PV - TS$). Here U is the internal energy which at 0 K is equivalent to lattice energy and S is the vibrational entropy at absolute temperature T . Three-body interactions are of great importance at high pressure when the interionic separation decreases considerably and coordination number increases [3,8,9]. The Gibbs free energy, at $T = 0$ K and pressure (P), for the real (B1) and hypothetical (B2) phases is given by

$$G_{B1}(r) = U_{B1}(r) + PV_{B1}(= 2.0 r^3), \quad (1)$$

$$G_{B2}(r) = U_{B2}(r) + PV_{B2}(= 1.54 r^3), \quad (2)$$

where the first terms in the above equations represent the lattice energies for the B1 and B2 structures expressed as

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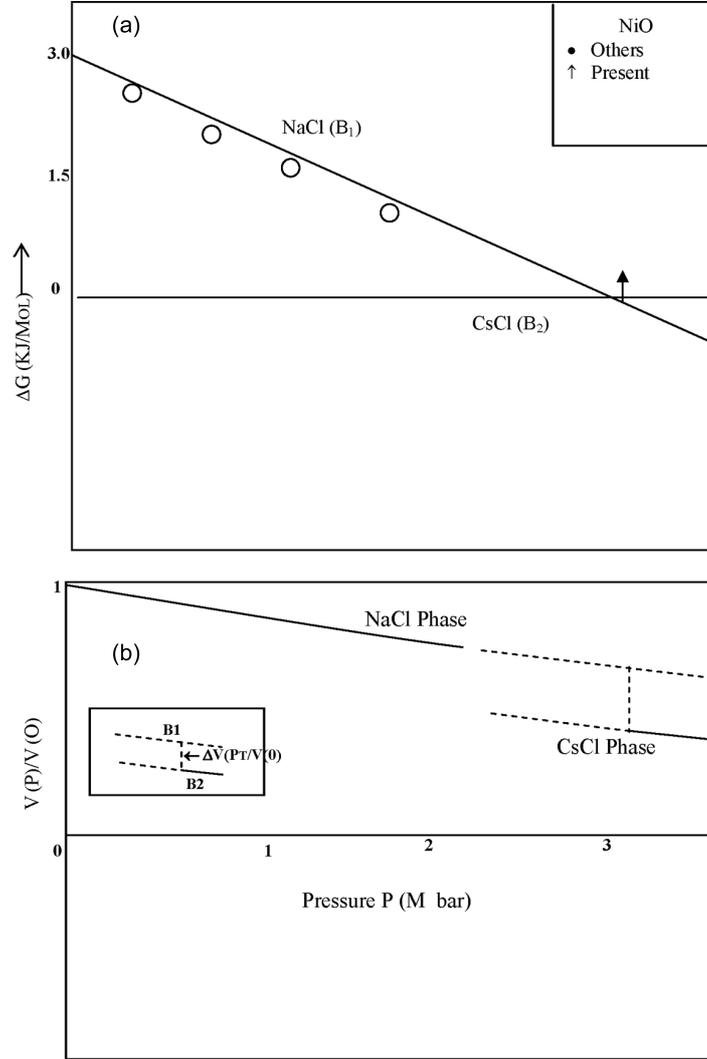


Figure 1. Variation of Gibbs free energy differences ΔG against pressure P and variation of relative volume $V(P)/V(O)$ with pressure P for NiO.

$$U_{B1}(r) = -\alpha_M Z e^2 ((Z + 12f(r))/r) + 6b\beta_{+-} \exp((r_+ + r_- - r)/\rho) + 6b\beta_{++} \exp((2r_+ - \sqrt{2}r)/\rho) + 6b\beta_{--} \exp((2r_- - 1.41r)/\rho) \quad (3)$$

$$U_{B2}(r') = -\alpha'_M Z e^2 ((Z + 16f(r'))/r') + 8b\beta_{+-} \exp((r_+ + r_- - r')/\rho) + 3b\beta_{++} \exp((2r_+ - \sqrt{2}r')/\rho) + 3b\beta_{--} \exp((2r_- - 1.154r')/\rho). \quad (4)$$

Here, the first two terms are the long-range Coulomb and TBI energies [8]. The remaining terms correspond to the overlap repulsion represented by Hafemeister

Table 1. Input data and model parameters of NiO.

Crystal	Input data		Model parameter		
	r (Å)	B_T (Mbar)	b (10^{-21} J)	ρ (Å)	$f(r)$
NiO	1.477	1.47	10.833	0.50	0.04280

Reference [6] and *CRC Handbook of Physics and Chemistry* edited by R C West (CRC, Boca Raton, Fla, 1981)

Table 2. Phase transition pressure, volume collapse, bulk modulus, second-order elastic constants, shear modulus and stiffness constant.

	NiO	Ref.
P_t (Mbar)	3.00	Present
	3.18	Others
$\Delta V(P_t)/V_0$	10%	Present
B_T (Mbar)	1.69	Present
	1.47	Exp.
C_{11} (Mbar)	12.518	Present
	11.981	Others ^a (LDA)
	12.503	Others ^a (GGA)
C_{12} (Mbar)	17.39	Present
	16.92	Others ^a (LDA)
	16.12	Others ^a (GGA)
C_{44} (Mbar)	1.7124	Present
	1.80	Others ^a (LDA)
	1.82	Others ^a (GGA)
C_L	16.66	Present
C_S	-2.44	Present

^aT Eto *et al* [1]

and Flygare (HF) potential and extended up to the first (+ -) and second (+ + and - -) neighbour ions, $\alpha_M(\alpha'_M)$ is the Madelung constant for B1 (B2) phase, $\beta_{ij}(ij = +-)$ are the Pauling coefficients, Ze is the ionic charge with e as the electronic charge, $b(\rho)$ are the hardness (range) parameters, $r_+(r_-)$ the ionic radii of +(-) ions taken from [3] and $r(r')$ is the nearest neighbour separation of B1 (B2) phase which may be conveniently expressed as $f(r) = f_0 \exp(-r/\rho)$ [9], with f_0 as a constant.

3. Results and discussion

We have evaluated the values of $GB1(r)$ and $GB2(r')$ at different pressures and the corresponding Gibbs free energy difference $\Delta G(= GB1(r) - GB2(r'))$.

These values of P_t for NiO are reported in table 2 and compared with other theoretical results (table 2). We have also calculated second-order elastic constants (SOECs) C_{11} , C_{12} , C_{44} and their combination $C_L = (C_{11} + C_{12} + 2C_{44})/2$ and $C_S = (C_{11} + 2C_{12})/3$. The formulations for second-order elastic constants have been taken from Singh and Gupta [10]. From the overall study we may conclude that the present three-body potential approach is fairly adequate for the prediction of high pressure B1–B2 phase transition, associated volume collapses, bulk modulus and second-order elastic constants. Also the stability criterion in NiO has been checked.

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