

Theoretical Analysis of the Structural Phases of MnO Under High Pressure

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Abstract: In the present paper, we have evaluated the phase transformation and elastic properties of MnO at high pressure by formulating effective interionic interaction potential. The elastic constants, including 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, are derived. Assuming that both the ions are polarizable, we employed the Slater-Kirkwood variational method to estimate the vdW coefficients. From the present study, we predict a structural phase transition from NaCl structure (*B1*) to CsCl structure (*B2*). The estimated value of the phase transition pressure (*P_t*) and the magnitude of the discontinuity in volume at the transition pressure are consistent as compared to the other theoretical data. The variations of elastic constants with pressure follow a systematic trend identical to that observed in others compounds of NaCl type structure family.

INTRODUCTION

Transition metal monoxide (MnO) has continuously raised the interest of theoreticians and experimentalists over the past decades. As strongly correlated materials they show a number of interesting structural and electronic properties. Due to strong electronic correlations, their properties cannot be calculated from first principles within classical approximations (such as LDA, local density approximation or GGA, generalised gradient approximation) of density functional theory, one of the newest instruments of theoretical solid-state physics. A number of recent experimental and theoretical studies are focused on ultrahigh pressure transformations in these oxides [1–4]. In this regard, previous studies have argued intensively for the existence of several pressure-induced phase transitions in MnO. Ohnishi predicted that a pressure-induced high-spin–low spin transition in MnO should occur at 70–130 GPa based on the crystal field theory [5]. Moreover, recent first-principles computations have predicted a magnetic collapse at 149 GPa [6] and stabilization of the metallic *B8* structure [7] of MnO at very high pressure. However, Static compression data at room temperature suggested no phase transition up to 60 GPa [8]. On the other hand, recent shock experiment [9] showed a phase transition of MnO with a volume decrease of 8 % around 90 GPa and suggested a *B1*-*B2* transition. A recent study using high pressure in situ X-ray diffraction study of MnO to 137 GPa and comparison with shock compression experiment [10].

In relation to the lattice models, for getting discussion on the mechanical properties of several solids and alloys, charge transfer approach [11], following Hafemeister and Flygare [12] type overlap repulsion extended up to second neighbor ions besides short-range interactions. We refer to the pioneering work of Tosi [13], who properly incorporated van der Waals interaction along with dipole-dipole (*d-d*) and dipole-quadrupole (*d-q*) interactions to reveal the cohesion in several ionic solids. Motivated from above studies [5 - 10] for the successful description of the high pressure phase transition of binary semiconducting compound, an effective interionic interaction potential (EIoIP), was employed that are able to explain structural phase transition pressure and second order elastic constants, including ambient-pressure phenomena.

THEORY AND METHOD OF COMPUTATION

The understanding of thermodynamical properties for MnO compound needs the formulation of an effective interionic potential. The effective interionic potential between pair of ions (i and j^{th}) 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, long-range Coulomb is represented by first term, second term correspond to Hafemeister and Flygare form of short-range repulsive energies [12] and van der Waals multipole are represented by third and fourth terms, respectively. The Pauling coefficients β_{ij} are defined as: $\beta_{ij} = [1 + (z_i/n_i)/(z_j/n_j)]$ with z_i (z_j) and n_i (n_j) as the valency and number of outermost electrons in the anions (cations), respectively. The symbols: c_{ij} and d_{ij} are representing the dipole-dipole ($d-d$) and dipole-quadrupole ($d-q$) van der Waals coefficients. $Z_m e$ is the modified ionic charge and parametrically includes the effect of Coulomb screening effects. b (hardness) and ρ (range) 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 [14].

An isolated phase is stable only when its free energy is minimum for the specified thermodynamic conditions. As the temperature or pressure or any other variable acting on the systems is altered, the free energy changes smoothly and 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 test materials transform from their initial $B1$ to $B2$ structure under pressure. The structural stability of a particular structure is decided by the minima of Gibbs free energy. Since these theoretical calculations are performed at $T = 0$ K, Gibbs free energy became equal to the enthalpy, $H = U + PV$. For a given pressure, a stable structure is one for which thermodynamic potential (G or H) has its lowest value.

We have estimated the Gibbs free energy for both the $B1$ and $B2$ phases. The Gibbs free energies $G_{B1}(r) = U_{B1}(r) + 2Pr^3$ for NaCl ($B1$) [real] phase and $G_{B2}(r') = U_{B2}(r') + [8/3\sqrt{3}]Pr'^3$ for CsCl ($B2$) [hypothetical] phase become equal at the phase-transition pressure P and at zero temperature *i. e.*, $\Delta G (= G_{B1} - G_{B2})$. Here, U_{B2} and U_{B1} represent cohesive energies for $B1$ and $B2$ phases, and are

$$U_{B1}(r) = -1.7475 \frac{e^2 Z_m^2}{r} + 6V_{ij}(r) + 6V_{ii}(r) + 6V_{jj}(r), \quad (2)$$

and

$$U_{B2}(r') = -1.7627 \frac{e^2 Z_m^2}{r'} + 8V_{ij}(r') + 3V_{ii}(r') + 3V_{jj}(r'). \quad (3)$$

Here r and r' are nearest-neighbor (nm) separations corresponding to NaCl and CsCl phases, respectively. The short-range potentials (V_{ij}) (in equations 2 and 3) for both the phases between the ions follow

$$V_{ij}(r) = b \beta_{ij} \exp\left(\frac{r_i + r_j - r_{ij}}{\rho}\right) - c_{ij} r_{ij}^{-6} - d_{ij} r_{ij}^{-8}; \quad i, j = 1, 2. \quad (4)$$

b and ρ being the short-range parameters. The effective interionic interaction potential can then have three material parameters: modified ionic charge (Z_m), range (b) and hardness parameters (ρ), which can be determined from the known crystal properties.

The study of the second-order elastic constants (SOEC) (C_{11} , C_{12} and C_{44}) and their pressure derivatives at 0 K is quite important 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 [14, 15] and subjecting the dynamical matrix to the long-wavelength limit, we find the expressions for the SOEC for $B1$ phase as:

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

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

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

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. We shall now compute numerically the high pressure phase transition and elastic properties for $B1$ phase in the next section.

Table 1: The values of van der Waals coefficients c_{ij} ($i, j = 1, 2$) [in units of 10^{-60} erg cm⁶], d_{ij} ($i, j = 1, 2$) [in units of 10^{-76} erg cm⁸] and overall van der Waals coefficients (C, D) for MnO compound

	vdW coefficients							
	c_{11}	c_{12}	c_{22}	C	d_{11}	d_{12}	d_{22}	D
MnO	520.8	98.43	23.94	1141	679.3	99.10	11.18	885

Table 2: Crystal data and model parameters for MnO

	Material Parameters			Model Parameters			
	r_i (Å)	r_j (Å)	a (Å)	B_T (GPa)	Z_m^2	ρ (10^{-1} Å)	b (10^{12} erg)
MnO	1.5	1.3	4.446 [10]	160 [10]	2.82	3.11	3.55

Table 3: Calculated (reported) transition pressure and volume collapse in MnO compound

Compound	Transition pressure P_t (GPa)	Volume collapses (%)
MnO	134 (137 ^a , 70-130 ^b , 90 ^c)	16

^aRef. [10], ^bRef. [5], ^cRef. [9],

RESULT AND DISCUSSION

The effective interionic potential is constructed in a hierarchical and easy generalizable manner. We have undertaken such structural and elastic properties in an ordered way. For such purposes we have then three free parameters, namely, modified ionic charge, range and hardness parameters (Z_m , ρ and b). To estimate the free parameters, we first deduce the vdW coefficients from the Slater-Kirkwood variational method [16] and are listed in table 1. We consider that the MnO compound to be partially ionic.

It is perhaps worth to remark that we have deduced the values free parameters modified ionic charge (Z_m), range (ρ) and hardness (b) from the knowledge of equilibrium distance and the bulk modulus following the equilibrium conditions [14,15]. The input data along with their relevant references and the model parameters for MnO compounds are given in table 2.

In an attempt to reveal the structural phase transition of the test materials, we minimise the Gibbs's free energies $G_{B1}(r)$ and $G_{B2}(r')$ for the equilibrium interatomic spacing (r) and (r'). The Gibbs's free energy difference $\Delta G [= G_{B2}(r) - G_{B1}(r)]$ have been plotted as functions of pressure (P) in Fig. 1 by using the interionic potential discussed above. Let us summarize the results of the plots. The pressure corresponding to ΔG approaching to zero is the phase transition pressure (P_t) [indicated by arrows in figure]. At zero pressure, the $B1$ crystal phase is thermodynamically and mechanically stable, while the $B2$ is not. As pressure increases, beyond the phase transition pressure (P_t), the $B2$ system becomes mechanically and thermodynamically stable (its ΔG function value is negative than that of $B1$ crystal). Eventually, and at a pressure higher than the theoretical thermodynamic transition pressure, the $B1$ crystal becomes thermodynamically unstable while the $B2$ phase remains stable up to the greatest pressure studied (≈ 150 GPa). In MnO compound a crystallographic transition from $B1$ to $B2$ occurs. These results may be successfully compared with those available reported data [5,9,10] and are tabulated in Table 3.

Let us now estimate the values of relative volumes associated with various compressions following Murnaghan equation of state [17]

$$\frac{V}{V_0} = \left(1 + \frac{B'}{B_0} P\right)^{-1/B'} \quad (12)$$

V_0 being the cell volume at ambient conditions. The estimated value of pressure dependent radius for both structures, the curve of volume collapse with pressure to depict the phase diagram is illustrated in Fig. 2. It is noticed from the plot that our approach has predicted correctly the relative stability of competitive crystal structures, as the values of ΔG are positive. The magnitude of the discontinuity in volume at the transition pressure is obtained from the phase diagram and its value is tabulated in Table 3.

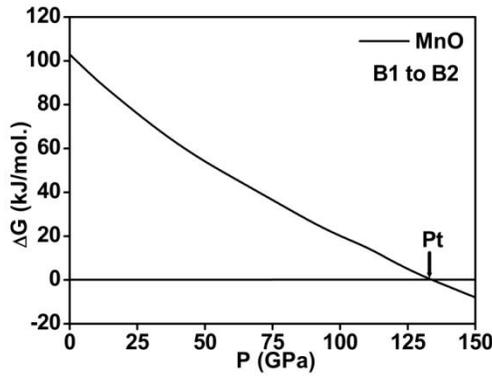


Figure 1. Variation of Gibbs free energy difference (ΔG) with pressure (P)

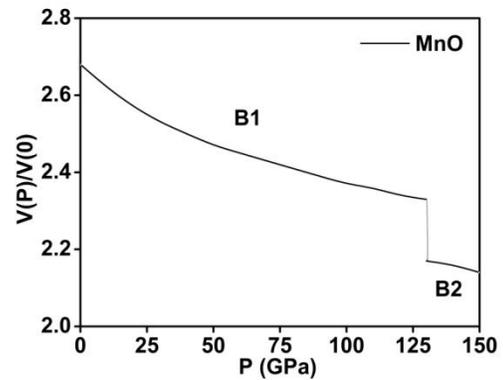


Figure 2. Variation of $V(P)/V(0)$ as a function of pressure for MnO compound.

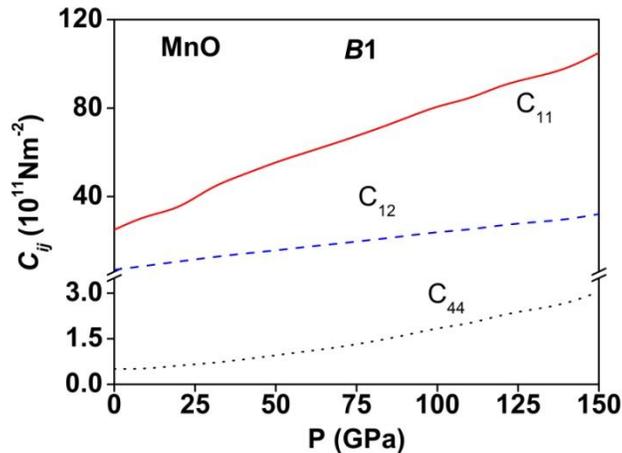


Figure 3. Variation of second order elastic constants (SOEC) with pressure (P).

In order to study the high-pressure elastic behaviour of these compounds, we have computed the second-order elastic constants (SOEC) and their variation with pressure as shown in Fig. 3. We note that C_{44} has very marginal pressure dependence and does not tend to zero at the phase transition pressure, which is in accordance with the first order character of the transition. On the contrary, the values of C_{11} and C_{12} increase linearly with pressure rapidly. The variations of elastic constants with pressure follow a systematic trend identical to that observed in others compounds of NaCl type structure family [15].

CONCLUSIONS

An effective interionic interaction potential is formulated in analyzing the structural as well as elastic properties in MnO compound. The obtained values of free parameters allow us to predict phase transition pressure and associated volume collapse. The main result of the paper is the vast volume discontinuity in pressure volume phase diagram identifies the structural phase transition from NaCl to CsCl structure. From our calculated results it can be emphasized that the present approach reproduced the structural properties at high pressure consistently, in terms of the screening of the effective Coulomb potential through modified ionic charge (Z_m^2). The variations of elastic constants with pressure follow a systematic trend identical to that observed in others compounds of NaCl type structure family.

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