

Structural and Elastic Properties of MgX (X=Se, Te) Semi Conducting Compounds under High Pressure

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Abstract

In the present paper, we have investigated the high-pressure structural phase transition of magnesium chalcogenides using the three-body potential (TBP) model. Phase transition pressures are associated with a sudden collapse in volume. The phase transition pressures and associated volume collapses obtained from TBP are in reasonably good agreement with experimental data. In addition, the elastic constants and their combinations with pressure are also reported. It is found that TBP has promise to predict phase transition pressure, elastic constants, and their pressure derivatives for other chalcogenides as well.

Key Words: Alkaline earth chalcogenides, phase transitions, high-pressure.

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1. Introduction

High pressure experimental research on structural phase transformations have been approaching a stage of systematic study and understanding of a series of materials with analogous physical and/or chemical properties. The study of pressure induced phase transformations and relative behavior of materials based on their calculations or measurements have become quite interesting in recent years. An example is found in III-V semi conducting compounds, where the structural optical and electrical properties at high pressure have been extensively studied. The alkaline earth chalcogenides AX ($A = \{\text{Be, Mg, Ca, Sr, Ba}\}$; $X = \{\text{O, S, Se, Te}\}$) form a very important closed shell ionic system crystallizing in NaCl-type structure at room conditions, exceptions being BeO and MgTe (which crystallize in wurtzite structure) and the Beryllium chalcogenides (which crystallize in the zinc-belede structure) [1, 2].

With the application of pressure, the NaCl-type (B1) structure of the alkaline-earth chalcogenides undergoes structural phase transition to CsCl-type (B2) structure with eight-fold coordination. These compounds are technologically important materials having many applications ranging from catalysis to microelectronics. They have also applications in the area of luminescent devices [3]. Among these compounds, the magnesium chalcogenides (MgX, $X = \text{O, S, Se, Te}$) are and MgTe are wide band gap semiconductors and are of technological and scientific interest. The first three have rock-salt structure and transform under pressure to the cesium chloride structure [4]. MgTe possesses wurtzite structure [5], but recently it has been found that the wurtzite structure undergoes a phase transformation at 1–3.5 GPa to the nickel arsenide structure and that

this structure persists after unloading and annealing [6]. The two ab-initio calculations on MgTe reported in the literature [7] also find a nickel arsenide ground state at $T = 0$. For MgSe one calculation of three structures was reported [8]. This paper presents theoretical results of phase transition of B1 to B2 phase.

The earlier theoretical studies of C. E. Sims, B. S. Rao and Froyen and Cohen, of B1-B2 transitions were based on two body potential [9,10]. Froyen and Cohen [9] successfully studied phase transition phenomena in some alkali chlorides using the pseudo potential total energy (PTE) method with minor disagreements in results. They remarked that results could be improved by including the effect of non-rigidity of ions in the model. Sims et al. found larger differences with measured values in transition pressures and activation energies. They concluded that possible reasons for disagreements include the failure of the two body potential model.

Motivated by the situation arises from these results and remarks of Sims et al., and Froyen and Cohen, for incorporating the charge transfer mechanism, we thought it pertinent to incorporate the charge transfer through three-body interaction, as it arises basically due to the deformation of electron shells. This three body potential model had been used earlier for the successful predictions of phase transitions and high-pressure elastic behavior of ionic II-VI and III-V compound semiconductors [10] and divalent metal oxides [11].

In the present paper we have studied the phase transition phenomena in AX compounds using three body potential (TBP), model. This TBP includes long range Columbic, three body interactions, Van der Waals and short range overlap repulsive interactions. The potential model and method of calculation are given in section II. The results are discussed in III.

2. Potential Model and Method of Calculations

The application of pressure on the crystals causes decrease in their volume, which in turn leads to an increased charge transfer (or three-body interaction effects) due to the existence of the deformed (or exchange) charge between the overlapping electron shells of the adjacent ions. This overlapping leads to the transferred (or exchange) of charges which when interact with the other distant charges and give rise to many body interactions (MBI). The dominant part of MBI is the three body interaction (TBI) [12]. To understand this mechanism, let us designate A, B and C as ions located at positions (lk) , $(l'k')$ and $(l''k'')$ in an ionic crystal having an ionic charge $\pm Ze$ with l and k as the cell and basis indices, as is shown in Figure 1. Also, C is the nearest neighbour (nn) of ion A and separated by a distance $r = |r(lk, l''k'')|$ and separated from ion B by distance $|r(lk, l'k')|$. The transferred charge (dq_k) between ions A and B is given by the relation

$$dq_k = \pm ze f_k r(lk, l''k'') = \pm Ze f_k(r). \quad (1)$$

The occurrence of the above transferred charge leads to a modified charge for A (or C) as

$$z_m e = z_k e + n e f_k r(lk, l''k'') \cong z_k e [1 + (2n/z) f_k r(lk, l''k'')]^{1/2}. \quad (2)$$

Here, n is the number of the nearest neighbour (nn) ions, e is the electronic charge, $f_k(r)$ is the three body potential function such that $f_k(r) = (Z_k/Z) f(r)$. The expression for the modified Columbic energy due to the three body potential (TBI) is

$$\phi_m(r) = \phi^c + \phi^T, \quad (3)$$

$$\phi_m(r) = [-\alpha_M z^2 e^2 / r] [1 + (2n/z) f(r)], \quad (4)$$

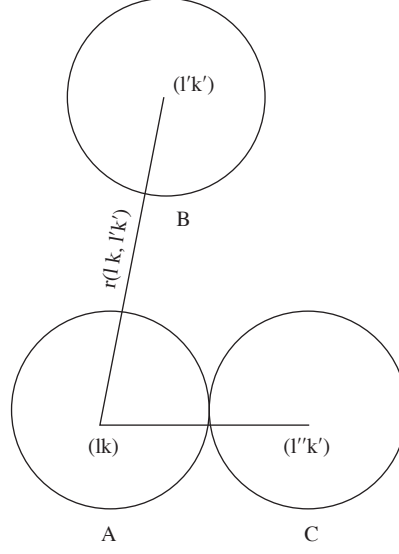


Figure 1. Schematic representation of three body interactions model showing the three ions A, B and C with positions $(lk, l'k', l''k'')$.

where, α_M is the Madelung constant and is 1.7476 (1.7629) for NaCl (CsCl) structure, r is the equilibrium nn ion separation, n is the number of nn ions, and $f(r)$ is the TBI parameter and is dependent on the nearest neighbour ion distance r as

$$f(r) = f_0 \exp(-r/\rho). \quad (5)$$

These effects have been incorporated in the Gibbs free energy ($G = U + PV - TS$) as a function of pressure and three body interactions (TBI), which are the most dominant among the many body interactions. Here, U is the internal energy of the system equivalent to the lattice energy at temperature near zero and S is the entropy. At temperature $T = 0$ K and pressure P the Gibbs free energies for rock salt (B1, real) and CsCl (B2, hypothetical) structures are given by the following relations:

$$G_{B1}(r) = U_{B1}(r) + PV_{B1}(r) \quad (6)$$

$$G_{B2}(r') = U_{B2}(r') + PV_{B2}(r'). \quad (7)$$

With $V_{B1} (= 2.00r^3)$ and $V_{B2} (= 1.54r'^3)$ as unit cell volumes for B₁ and B₂ phases, respectively. The first terms in (6) and (7) are lattice energies for B₁ and B₂ structures and they are expressed as:

$$U_{B1}(r) = \frac{-\alpha_m z^2 e^2}{r} - \frac{(12\alpha_m z e^2 f(r))}{r} - \left[\frac{C}{r^6} + \frac{D}{r^8} \right] + 6b\beta_{ij} \exp [(r_i + r_j - r)/\rho] \\ + 6b\beta_{ii} \exp [(2r_i - 1.414r)/\rho] + 6b\beta_{jj} \exp [(2r_j - 1.414r)/\rho] \quad (8)$$

$$U_{B2}(r') = \frac{-\alpha'_m z^2 e^2}{r'} - \frac{(16\alpha'_m z e^2 f(r'))}{r'} - \left[\frac{C'}{r'^6} + \frac{D'}{r'^8} \right] + 8b\beta_{ij} \exp [(r_i + r_j - r')/\rho] \\ + 3b\beta_{ii} \exp [(2r_i - 1.154r')/\rho] + 3b\beta_{jj} \exp [(2r_j - 1.154r')/\rho] \quad (9)$$

Here, α_m and α'_m are the Madelung constants for NaCl and CsCl structure, respectively; C (C') and D (D') are the overall Van der Waal coefficients of B1 (B2) phases; β_{ij} ($i, j=1,2$) are the Pauling coefficients; Ze is the ionic charge and b (ρ) are the hardness (range) parameters; r (r') are the nearest neighbor separations for NaCl (CsCl) structure; $f(r)$ is the three body force parameter with three body interaction; r_i (r_j) are the ionic radii of ions i (j). These lattice energies consists of long range Coulomb energy (first term),

three body interactions corresponding to the nearest neighbor separation r (r') (second term), vdw (Van der Waal) interaction (third term), energy due to the overlap repulsion represented by Hafemeister and Flygare (HF) type potential and extended up to the second neighbour ions (fourth, fifth and sixth terms). The modified model potential TBP described above for the NaCl and CsCl phases contains three model parameters, namely the range, hardness and modified three body force parameters (b , ρ , $f_m(r)$). The values of elastic constants are:

$$C_{11} = (e^2/4a^4)[-5.112Z(Z + 12f(r)) + A_1 + (A_2 + B_2)/2 + 9.3204za f'(r)] \quad (10)$$

$$C_{12} = (e^2/4a^4)[0.226Z(Z + 12f(r)) - B_1 + (A_2 - 5B_2)/4 + 9.3204za f'(r)] \quad (11)$$

$$C_{44} = (e^2/4a^4)[2.556Z(Z + 12f(r)) - B_1 + (A_2 + 3B_2)/4] \quad (12)$$

The expression of elastic constants, Van der Waals coefficients and pressure derivatives are used by us, which are reported elsewhere [13, 14].

The expressions for pressure derivatives of second order elastic constants (SOEC's) are as follows:

$$\frac{dk}{dp} = -(3\Omega)^{-1} \left[\begin{array}{l} 13.980Z(Z + 12f(r)) + C_1 - 3A_1 + C_2 - 3A_2 \\ -167.7648za f'(r) + 41.9420za^2 f''(r) \end{array} \right], \quad (13)$$

$$\frac{ds}{dp} = -(2\Omega)^{-1} \left[\begin{array}{l} 23.682Z(Z + 12f(r)) + C_1 + (C_2 + 6A_2 - 6B_2)/4 \\ -50.0752za f'(r) + 13.9808za^2 f''(r) \end{array} \right], \quad (14)$$

$$\frac{dC_{44}}{dp} = -(\Omega)^{-1} \left[\begin{array}{l} -11.389Z(Z + 12f(r)) + A_1 - 3B_1 + \frac{C_2 + 2A_2 - 10B_2}{4} \\ +44.6528Za f'(r) \end{array} \right], \quad (15)$$

where,

$$K = \frac{1}{3} (C_{11} + 2C_{12}), \quad S = \frac{1}{2} (C_{11} - C_{12})$$

and

$$\Omega = -2.330Z(Z + 12f(r)) + A_1 + A_2 + 21.9612za f'(r).$$

The values of A_i , B_i , and C_i have been evaluated from the knowledge of b and ρ and the vdw coefficients.

3. Results and Discussion

The Three Body potential described in the previous section for NaCl (B_1) and CsCl (B_2) structures contain three model parameters: b , ρ , $f(r)$. These parameters are calculated using the lattice energy and equilibrium condition. The input crystal data for MgX compounds are given in Table 1. Using the measured values of the equilibrium lattice constant r_0 , bulk modulus for B_1 phase and using the equilibrium conditions

Table 1. Input data and model parameters.

Input parameters	MgSe	MgTe
r_i (Å)	0.72 ^a	0.72 ^a
r_j (Å)	1.91 ^a	1.84 ^a
r (Å)	2.25 ^a	2.96 ^a
B_T (GPa)	65.4 ^b	54.5 ^b
Model parameters		
B (10^{-12} ergs)	3.489	2.923
ρ (10^{-8})	0.425	0.368
$f(r)$	-0.403	-0.291

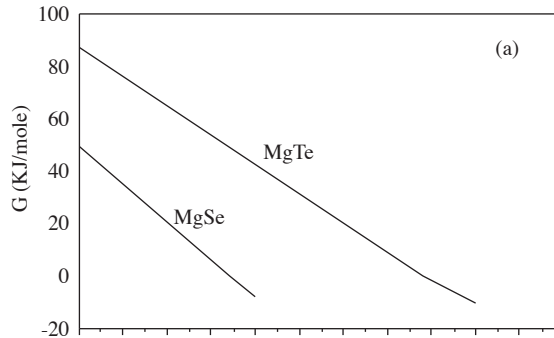
a-ref. [15] b-ref. [16].

$$du/dr = 0$$

and

$$d^2U/dr^2 = 9kr_0B_T.$$

Model parameters have been calculated and are shown in Table 1. We have followed the technique of minimization of $U_{B_1}(r)$ and $U_{B_2}(r')$ at different pressures in order to obtain inter ionic separation r and r' for B_1 and B_2 phases, respectively, associated with minimum energies. We have evaluated the corresponding $G_{B_1}(r)$ and $G_{B_2}(r')$ and their respective differences $\Delta G = G_{B_1}(r) - G_{B_2}(r')$ and have plotted against pressure P and shown in Figure 2(a) for MgSe and MgTe, respectively. MgSe and MgTe at ambient pressure crystallize in the NaCl structure and undergo a transition to the CsCl structure upon compression. The phase transition pressure P_t is the pressure at which ΔG approaches zero. Figures 2(a) and 2(b) show that our present computed phase transition from NaCl-type [B_1] to CsCl-type [B_2] structures in MgSe at 156 GPa and MgTe at 68.2 GPa, respectively. Relative volume changes $V_{(p)}/V_{(0)}$ have been plotted against pressure and depicted in Figures 2(a) and 2(b) for MgSe and MgTe, respectively. It is clear from Table 2 and Figure 2(b) that our calculated volume collapses $-\Delta V_{(p)}/V_{(0)}$ from our modified model for MgSe, and MgTe are 3.6% and 5.6%, which are close to the experimental values of MgSe and MgTe compounds 3.5% and 5.52%, respectively. The second order elastic constants (SOEC's) and pressure derivatives of these magnesium chalcogenides have been calculated by using equations (5), (6) and (7) and are given in Table 3. Our calculated values of pressure derivatives of MgSe and MgTe are in good agreement with experimental data and others are given in Table 3.


Figure 2(a). Variation of ΔG (kJ/mol) with pressure for MgSe and MgTe.

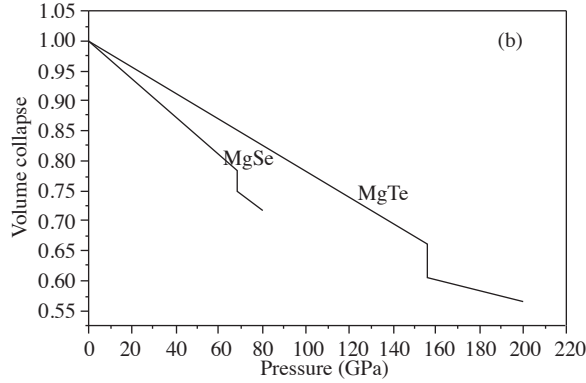


Figure 2(b). Variation of volume change V_P/V_0 with pressure for MgSe and MgTe.

Table 2. Phase transition Pressure and volume collapse of MgSe and MgTe.

Crystal		Phase transition pressure (GPa)	Volume change (%)
MgSe	Present	156	3.6
	Others	160 ^a	3.50 ^a
	Experiment	107 ± 8 ^b	-
MgTe	Present	68.2	5.6
	Others	69.6 ^a	5.52 ^a
	Experiment	> 60 ^c	-

a: ref. [18]; b: ref. [4]; c: ref. [17].

Table 3. Elastic constants and pressure derivatives of MgX.

Properties	MgSe	MgTe	Ref.
C_{11} (GPa)	204.23	185.36	Present
	-	-	Others
C_{12} (GPa)	48.56	29.88	Present
	-	-	Others
C_{44} (GPa)	54.20	31.86	Present
	-	-	Others
dK/dP	4.53	4.32	Present
	4.14 ^a	4.04 ^a	Others
dS/dP	3.48	4.69	Present
	-	-	Others
dC ₄₄ /dP	-0.26	-0.33	Present
	-	-	Others

a: ref. [16].

The pressure derivatives of second order elastic constants presented in Table 3 show that the values of dC_{44}/dP obtained from the modified TBP model are in agreement with available experimental data and others works. It is clear that during the phase transition from NaCl to CsCl, the volume discontinuity in pressure volume phase diagram identifies the same trend as the experimental approach.

Based on the above it may be concluded that the present three body potential model is adequately suitable for describing the phase transition phenomena and elastic properties of magnesium chalcogenides.

An overall assessment shows that in general, our values are close to experimental data and give a better match than other theoretical data. The success achieved in the present investigation can be ascribed to the

inclusion of the charge transfer (or three body) effect they seems to be of great importance at high pressure when the inter-ionic potential reduces considerably and the coordination number increases.

Finally, we conclude that the improved three body potential model has yielded somewhat more realistic predictions of the phase transition and high-pressure behavior of the alkaline earth and transition metal oxides compared to those achieved from the relatively more sophisticated models based on microscopic approach. The inclusion of three body interactions has improved the prediction of phase transition pressures over that obtained from the two-body potential, thus demonstrating the usefulness of the present model for estimating the actual high-pressure behavior of these magnesium chalcogenides.

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