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Theoretical High Pressure Study for Thermoelastic Properties of NaCl-B1

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ABSTRACT

The evaluation of $\frac{V}{V_o}$, Bulk modulus K, Lattice parameter a, First Grüneisen parameter γ, Second Grüneisen parameter q, and Debye temperature θ_D for NaCl-B1 under high pressure has been achieved in this work by using two equations of state (Dodson EOS and Thomsen EOS). The results obtained by the two EOSs have been compared with each other and with other theoretical and experimental data published in literature. The results obtained by using Dodson EOS show more agreement with data given in literature than the results obtained by using Thomsen EOS.

Keywords: High pressure, Thomsen EOS, Dodson EOS, NaCl-B1.

دراسة نظرية تحت الضغط العالي لخصائص المرونة الحرارية لـ NaCl طورB1

الملخص

باستخدام معادلتي الحالة (Dodson EOS and Thomsen EOS) تم استقصاء تغير (الحجم النسبي و معامل المرونة الحجمي K و ثابت الشبيكة a و معامل كرونشين الأول γ و معامل كرونشين الثاني q و درجة الحرارة ديباي θ_D) لـ NaCl طورB1 تحت الضغط العالي. قورنت النتائج المستحصلة باستخدام معادلتي الحالة مع بعضها البعض، فضلا عن المقارنة مع البيانات النظرية والتجريبية المنشورة في الأبحاث العلمية. وأظهرت المقارنة ان النتائج التي تم الحصول عليها باستخدام معادلة الحالة لـ Dodson كانت أكثر توافقا، مع البيانات المنشورة في الأبحاث العلمية، من النتائج التي تم الحصول عليها باستخدام معادلة الحالة لـ Thomsen.

الكلمات الدالة: الضغط العالي، معادلة الحالة لـ Thomsen، معادلة الحالة لـ Dodson ، NaCl-B1.

INTRODUCTION

The determination of pressure - volume - temperature (P-V-T) relation of solid materials is a problem of considerable importance in basic and applied science (Recio *et al.*, 1993). The pressure -volume- temperature relationship termed as equation of state (EOS), with the help of EOS, one can determine various properties of crystals under varying conditions of pressures and temperatures (Kumar and Kumar, 2007).

The knowledge of the properties of the simple ionic solids under the conditions of high temperatures and pressures is of fundamental concern to solid-state physics and is important for characterizing the earth's deep interior. The alkali halides are important prototypes for such studies (Chen *et al.*, 2004).

Thermoelastic and thermodynamic properties such as thermal expansivity, bulk modulus, Grüneisen parameter and Debye temperature are of central importance for understanding the behavior of solids (Sun *et al.*, 2008).

Sodium Chloride is one of the most important materials and a typical ionic solid in high-pressure research, used as a pressure gauge in laboratory measurements of compression data (Boehler and Kennedy, 1980; Liu and Bassett, 1973; Decker, 1971) and it has been calibrated extensively through various methods (Brown, 1999; Decker, 1971).

Moreover X-ray diffraction studies can be conveniently made, using devices such as the diamond anvil cell (DAC), thereby affording a useful way of measuring pressure through its effect on the lattice spacing change of simple cubic solids, volume changes at high pressures are measured and, the pressure is estimated using an equation of state. Serious efforts have been made to develop an equation of state of NaCl-B1 phase for its importance as one of the simplest ionic crystals and a commonly used pressure calibrant at pressures below 30GPa (Brown, 1999; Birch, 1986; Decker, 1971).

NaCl has a stable structure (B1) up to a pressure of about 30Gpa, and its melting temperature is about 1074K, thus we have a wide range of pressures and temperatures for studying the equation of state and thermoelastic properties of NaCl (Chauhan and Singh, 2007). NaCl was used to serve as a solid pressure transmitting medium (Birch, 1986; Klotz *et al*., 1995).

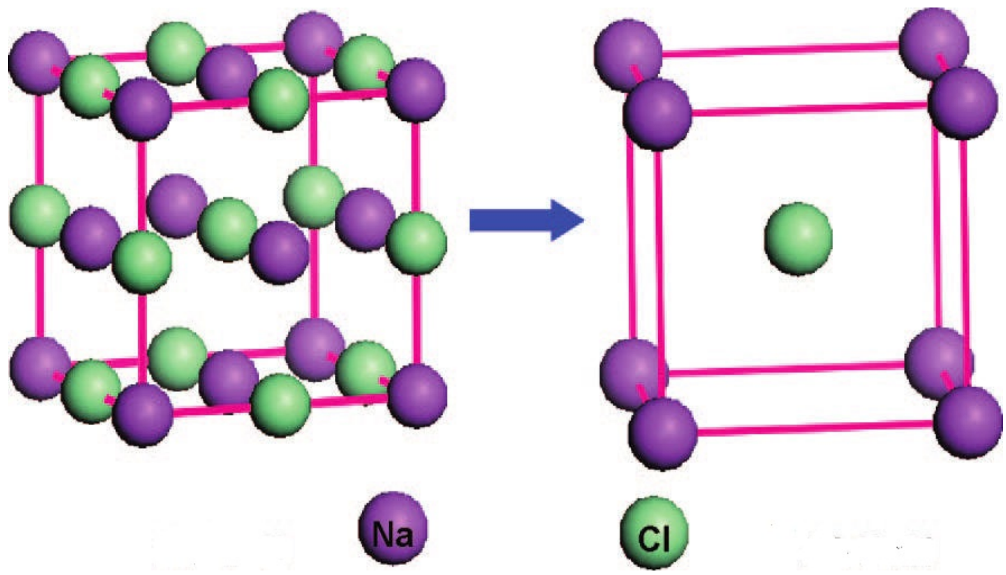
NaCl transforms from the B1 (NaCl-type) to the B2 (CsCl-type) structure at about 30GPa and 300K (Bassett *et al*., 1968; Sorensen, 1983). The behavior of NaCl at high pressures is generally described by the isothermal bulk modulus K_o and its pressure derivatives K_o' and K_o'' at atmospheric pressure, the values of these parameters show a considerable disagreement among the many authors partly because they depend on the choice of the equation used to describe the experimental data (Boehler and Kennedy, 1980).

This work proposed evaluating NaCl-B1thermoelastic properties and its phonon frequency spectrum under high pressure by using Dodson and Thomsen EOSs.

Structures of B1 and B2 of NaCl

(Fig. 1) shows the structure of B1 and B2 for NaCl. B1-phase is a useful pressure scale only at pressures less than 30 GPa, the *B*2 phase of NaCl would be more useful as a pressure standard at high pressures since it is stable over wide temperature and pressure ranges up to 3000 K and far above 100 GPa (Ueda *et al*., 2008). Values of bulk modulus at atmospheric pressure K_o and its pressure derivatives K_o' are listed in Table (1).

NaCl-



NaCl-B1
B2

Fig. 1: Structures of B1 and B2 phases of NaCl (Lu *et al.*, 2008).

Table 1: Values of Bulk modulus at atmospheric pressure K_o and its First pressure derivative K'_o for NaCl-B1.

K_o (Gpa)	K'_o (Gpa)	References
24	5.5	Chauhan and Singh, 2007
23.5	5.35	Taravillo *et al*., 1996
23.88	5.20	Birch, 1986
23.97	5.01	Boehler and Kennedy, 1980
23.8	4.0	Sorensen, 1983
24.0	5.38	Demarest and Jr., 1972

THEORETICAL DETAILS

This section presents two equations of state used with all thermoelastic parameters that are investigated under high pressure in the present work for NaCl-Bl.

- **Equations of state (EOS):**

- **Dodson EOS:**

(Dodson, 1987) suggested simple two parameter EOS given as

$$P_{Do}=\frac{27}{8}K_oK_o'^2\left[\left(\frac{V}{V_o}\right)^{-2/3}-1+4\left\{1-\frac{2}{3K_o'}\right\}\times\left\{1-\left(\frac{V}{V_o}\right)^{-1/3}-\frac{1}{6}\left(1-\frac{2}{3K_o'}\right)Ln\left(\frac{V}{V_o}\right)\right\}\right] \quad \text{....……(1)}$$

Where

P_{Do} -Pressure evaluated by using Dodson EOS, V-volume under high pressure P, V_o -volume under atmospheric pressure. The relation, although empirical, fits all metals and metal alloys tested by (Dodson, 1987), and also fits semiconductors, ionic crystals, and with a lesser degree of success, organic compounds.

- **Thomsen EOS:**

Depending on the finite strain concept, where strains are uniquely determined by hydrostatic pressure. (Thomsen, 1970), suggested an EOS for solids in the form

$$P_{Tho}=\frac{3K_o}{2}\left[\left(\frac{V}{V_o}\right)^{-1/3}-\left(\frac{V}{V_o}\right)^{1/3}\right]\left[1+\frac{3}{4}K_o'\left(1-\left(\frac{V}{V_o}\right)^{2/3}\right)\right] \quad \text{…………… (2)}$$

Where

P_{Tho} - high pressure evaluated by using Thomsen EOS.

- **Bulk Modulus**

An important aspect of the EOS is the bulk modulus defined as

$$K=-V\left(\frac{dP}{dV}\right)_T \quad \text{………………..….(3)}$$

On the derivation of equations (1 and 2) with respect to volume and substituting in to eq.(3). Equations (4 and 5) give a variation of bulk modulus with high pressure by using Dodson EOS (K_{Do}) and Thomsen EOS (K_{Tho}) as

$$K_{Do} = \frac{27}{8} K_o K_o'^2 \left[\frac{2}{3}\left(\frac{V}{V_o}\right)^{-2/3} - 4\left(1 - \frac{2}{3K_o'}\right)\left\{\frac{1}{3}\left(\frac{V}{V_o}\right)^{-1/3} - \frac{1}{6}\left(1 - \frac{2}{3K_o'}\right)\right\}\right] \quad \text{.................(4)}$$

$$K_{T\,ho} = \frac{K_o}{2}\left[\left(\frac{V}{V_o}\right)^{-1/3} + \frac{3}{4}K'\left(\frac{V}{V_o}\right)^{-1/3} + \frac{3}{2}K_o'\left(\frac{V}{V_o}\right)^{1/3} + \left(\frac{V}{V_o}\right)^{1/3} - \frac{9}{4}K_o'\left(\frac{V}{V_o}\right)\right] \quad \text{..............(5)}$$

- **Lattice Parameter**

Pressure dependence of lattice parameter of a solid is determined by (Radi *et al.,* 2007*)* depending on Murnaghan EOS (Murnaghan, 1937) as:

$$a = a_o\left(1 + K_o'\frac{P}{K_o}\right)^{\frac{-1}{3K_o'}} \quad \text{..................(6)}$$

Where

a_o and a are lattice parameters at atmospheric pressure and under high pressure P respectively.

But the term $\left(1 + K_o'\frac{P}{K_o}\right)^{\frac{-1}{K_o'}}$ in Murnaghan EOS is equivalent to $\frac{V}{V_o}$.

Hence equation (6) can be rewritten as

$$a = a_o\left(\frac{V}{V_o}\right)^{1/3} \quad \text{.......................(7)}$$

- **Grüneisen parameter**

(Boehler and Ramakrishnan, 1980) expressed pressure dependence of Grüneisen parameter by the following relation.

$$\gamma_P = \gamma_o\left(\frac{V}{V_o}\right)^{q} \quad \text{.....................(8)}$$

Where

γ_o , γ_P - Grüneisen parameter at atmospheric pressure and under high pressure respectively. q- second Gruneisen parameter. q has been considered of an equal unity or a constant value.

But (Jeanloz, 1989; Agnon and Bukowiniski, 1990), suggested that q could be changed under high pressure as:

$$q = q_o\left(\frac{V}{V_o}\right)^{n} \quad \text{............................(9)}$$

Where

q_o and q are

second Grüneisen parameters at atmospheric pressure and under high pressure respectively, with (*n*) as an equal unity or a positive number.

- **Debye temperature (θ_D)**

Debye temperature (θ_D) or Debye characteristic temperature is a characteristic of each substance appearing in Debye theory of specific heats and given by:

$$\theta_D = \frac{\hbar\omega_D}{k_B} \qquad \text{.......................... (10)}$$

Where
θ_D - is the Debye temperature at atmospheric pressure, k_B - Boltzmann constant,
ω_D - Debye frequency at an atmospheric pressure.

Where a solid is considered as an elastic continuum whose maximum vibrational frequency is such that the corresponding number of vibrational modes is equal to the total number of degrees of freedom. As vibrational frequencies depend on equilibrium position which is changed with the pressure as a result of V/V_o variation with the pressure. (Preston *et al.*, 1962) expressed Debye temperature under high pressure as

$$\theta_P = \theta_D \left(\frac{V}{V_o}\right)^{-\gamma_P} \qquad \text{..........................(11)}$$

Where
θ_P - Debye temperature under high pressure. While (Decker, 1971) expressed Debye temperature as a function of Grüneisen parameter as:

$$\theta_P = \theta_D \exp\left(\left(\gamma_o - \gamma_P\right)/q\right) \qquad \text{.......................... (12)}$$

CALCULATION AND RESULTS

- **Calculation of $\frac{V}{V_o}$ for NaCl-B1 using Dodson and Thomsen EOSs.**

On substituting values of K_o and K'_o, the first row of Table (1), in Dodson EOS, eq. (1) one time, and in Thomsen EOS, eq. (2) another time. (Fig. 2) shows the results of variation of V/V_o with high pressure obtained by using Dodson and Thomsen EOSs in comparison with the theoretical and experimental data published in the scientific literature.

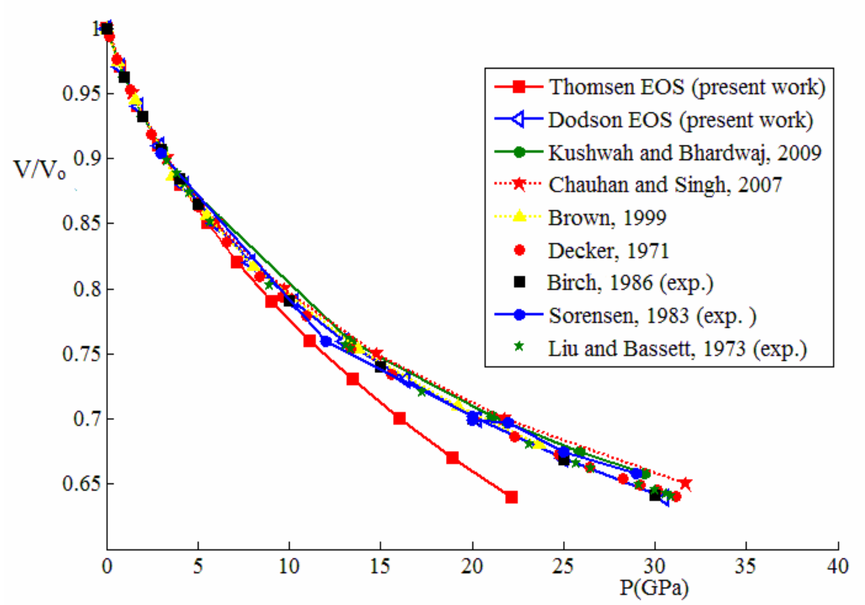


Fig. 2: Variation of V/V_o with high pressure for NaCl-B1, by using Dodson and Thomsen EOSs, in comparison with other works.

■ **Evaluation of bulk modulus *K* under high pressure for NaCl-B1, using Dodson and Thomsen EOSs.**

Substituting values of K_o and K'_o from Table (1-first row) and V/V$_o$ from (Fig. 2) in to eq. (4) and eq. (5), give values of bulk modulus, (K_{Do}) and (K_{Tho}) at different pressures corresponding to different V/V$_o$ of (Fig. 2). The Obtained results are shown in (Fig. 3), in comparison with the experimental and theoretical data of different literature.

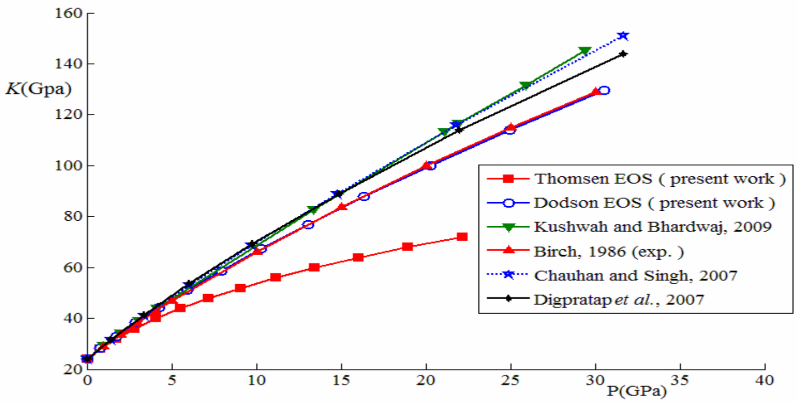


Fig. 3: Variation of bulk modulus *K*, for NaCl-B1, with high pressure, using Dodson and Thomsen EOSs, in comparison with experimental and theoretical data published in literature.

■ **Evaluation of Lattice parameter *a* for NaCl-B1 under high pressure**

On combining (a_o=5.6402) (Bassett *et al.*, 1968), with V/V$_o$ results from (Fig. 2), in equation (7). Lattice parameter *a* has been evaluated at different pressures by using Dodson EOS one time and Thomsen EOS another time. (Fig. 4) shows the variation of NaCl-B1 lattice parameter with high pressure in comparison with the experimental data.

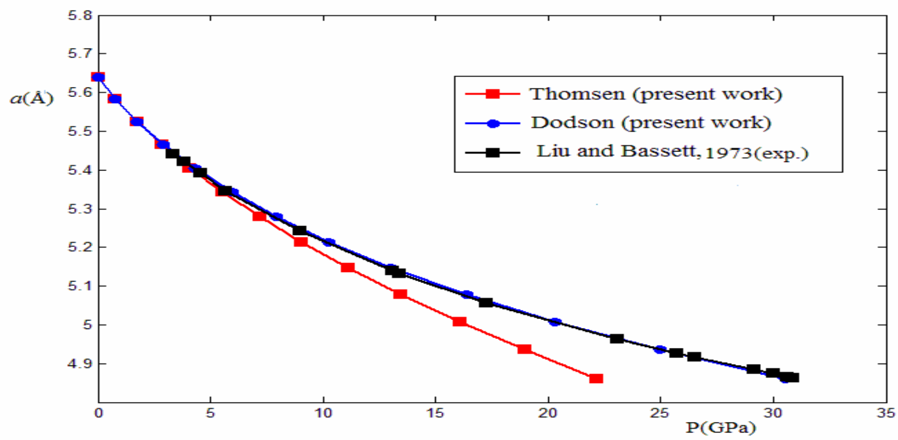


Fig. 4: Variation of NaCl-B1 lattice parameter *a* with high pressure using Dodson and Thomsen EOSs in comparison with experimental data.

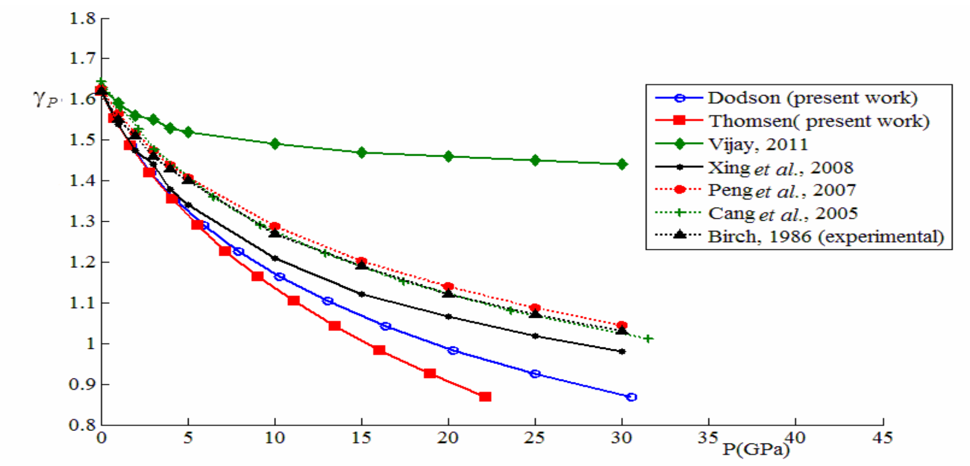
■ **Evaluation of first Grüneisen parameter γ_P for NaCl-B1 under high pressure using Dodson and Thomsen EOSs.**

On substituting the experimental value of the Grüneisen parameter γ_o from Table (2)-(Birch,1986), and the value of second Grüneisen parameter q_o from (Roberts and Ruppin, 1971), using V/V_o results shown in (Fig. 2) - (Dodson and Thomsen values) in to equation (8) (considering q as a volume independent parameter and $q = q_o = 1.4$), gives the results, for variation of first Grüneisen parameter γ_P with the pressure as shown in (Fig. 5A).

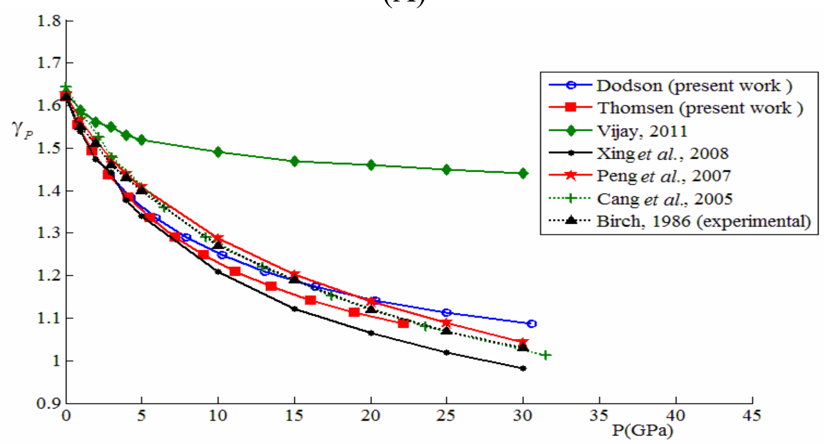
On the other hand, combining equations (8 and 9) with V/V_o values of (Fig. 2)- (Thomsen and Dodson values) and recalculate the variation of γ_P parameter of NaCl-B1 with the pressure. (Fig. 5B) shows the values of γ_P variation with high pressure by considering the volume dependence of second Grüneisen parameter q .

Table 2: Values of the first Grüneisen parameter γ_o and second Grüneisen parameter q_o for NaCl-B1

γ_o	q_o	**References**
1.62		Birch, 1986
1.61	1.4	Roberts and Ruppin, 1971
1.62	1.3	Boehler and Ramakrishnan, 1980



(A)



(B)

Fig. 5: Variation of first Grüneisen parameter of NaCl-B1 under high pressure by using Dodson and Thomsen EOSs, in comparison with data of other works.
A: *q* is volume independent parameter.
B: *q* is volume dependent parameter.

■ **Evaluation of Debye Temperature θ_P of NaCl-B1 under high pressure using Dodson and Thomsen EOSs.**

- **Case 1:** Grüneisen parameter (γ_o) is volume independent:

Using (θ_D=320) (Swenson, 1985), and value of Grüneisen parameter ($\gamma_P = \gamma_o$=1.62)- (Birch, 1986) and Substituting V/V$_o$ values from (Fig. 2) (Thomsen and Dodson), in to eq.(11) which could be rewritten as

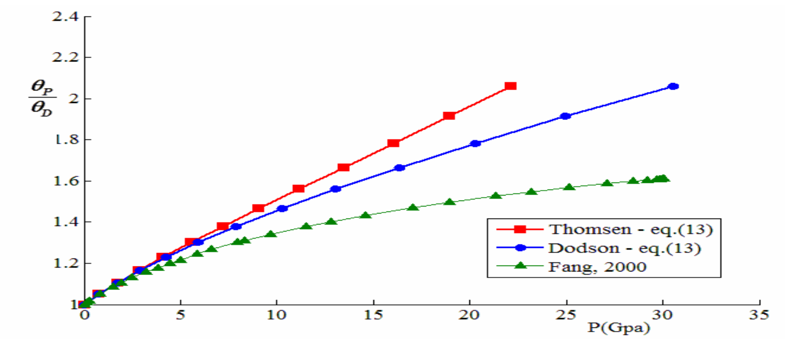
$$\theta_P = \theta_D \left(\frac{V}{V_o} \right)^{-\gamma_o} \qquad \text{..........................(13)}$$

Fig. (6A) shows the variation of $\frac{\theta_P}{\theta_D}$ with high pressure using Dodson EOS one time and Thomsen EOS another time, in comparison with the theoretical data of (Fang, 2000).

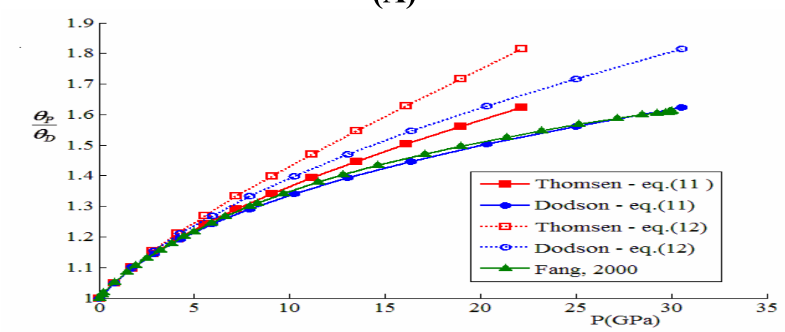
- **Case 2:** Grüneisen parameter γ_P is a volume dependent:

On considering the variation of Grüneisen parameter γ_P with high pressure according to eq.(8) and eq.(9), with q as a volume dependent parameter, combining them with equation (11), and substituting V/V$_o$ from Fig. (2) (Thomsen and Dodson values) at different pressures. (Fig. 6B) shows the variation of $\frac{\theta_P}{\theta_D}$ with high pressure on considering the pressure dependence of γ_P and q parameters.

Similarly, the calculations for (θ_P) by using equation (12) are combined with (γ_P and q – eq.8, 9) give results shown in (Fig. 6B) with a less agreement with (Fang, 2000) data.



(A)



(B)

Fig. 6: Variation of $\frac{\theta_P}{\theta_D}$ of NaCl-B1, under high pressure using Dodson and Thomsen EOSs, with in comparison with theoretical data of (Fang, 2000).
A: Grüneisen parameter γ is a volume independent.
B: Grüneisen parameter γ is a volume dependent.

DISCUSSION

1- The results of all works, including the present work, on variation of (V/V$_o$, K, a, and θ_P) are in complete agreement under high pressure up to 3GPa.While results for γ_P are in less agreement.

2- The results obtained, in the present work, using Dodson EOS show more agreement than that obtained by using Thomsen EOS with all data of other works. This may be attributed by the facts that Thomsen EOS based on finite strain, while Dodson EOS based on density functional theory which give it more generality.

3- On evaluation of variation of γ_P, for the case where second Grüneisen parameter q is volume independent, both Dodson and Thomsen EOSs give results of less agreement with the data of other works Fig.(5A). In considering volume dependent of second Grüneisen parameter q as represented in eq. (9), both Dodson and Thomsen EOSs give results which show a good agreement with the data of other works especially with the experimental data of (Birch, 1986) as shown in Fig. (5B).

Fig. (5-A, B) show that the results given by (Vijay, 2011) cannot match with the results obtained in the present work, for γ_P, or with any data of other works.

4- On considering variation of Debye temperature with high pressure, for the case where Grüneisen parameter γ is volume independent, both Dodson and Thomsen EOSs give results of less agreement with that of other works (Fig. 6A). These results, especially that obtained by using Dodson EOS, improved and show a very good agreement with the data of (Fang, 2000) in considering Grüneisen parameter γ_P to be volume dependent as represented in equation (11).

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