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An empirical equation of state to study high pressure compression behavior of solids

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ABSTRACT

The Suzuki formulation widely used in literature to study the thermal expansion of solids at constant pressure is extended to study the compression of solids at constant temperature. Two slightly different formulations are used and a modified form is proposed on an empirical basis. The Shanker formulation, which has been derived on the similar ground, is also included in the study. It is found that the earlier relations are applicable up to a finite range of pressure. The deviation occurs as the pressure range is increased. The modified relation gives results, which are in better agreement with the experimental data as compared with the earlier relations in the high pressure range for sodium halides viz. NaF, NaCl, NaBr and NaI. This demonstrates the validity of the simple relation proposed in the present paper.

KEYWORDS

High pressure;
Elasticity;
Equation of State.

INTRODUCTION

High compression occurs due to high pressures which are encountered from deep down the earth to the astrophysical objects. Due to pressure many effects happen such as pressure ionization, modification in electronic properties, phase changes and several phenomenons in applied field[1]. For this, pressure versus volume relations of condensed matter known as equation of state (EOS) is a vital input. No doubt many EOS exist in the literature, but still there is a need to judge on their suitability under strong compressions. The problem of small compression (V/V_0 d" 0.9) seems to be almost settled. Because in this range, most of the EOSs give the same answer and the Murnaghan EOS has been found to be the best[2]. Thus, for suitability an EOS should be tested under strong compression, in addition to the small compression.

In high pressure, generally the finite strain theory given by Birch is used[3]. However, Birch theory rates no more than a passing mention as discussed in detail by Staecy[4]. The attention has also been given to the theory based on atomic potential as presented by Rydberg[5]. The theory was drawn to attention by Vinet et al[6] and referred as Vinet or universal EOS. Stacey[4] has reviewed all these methods and pointed out that most of the finite strain theories are of limited interest and a new approach that makes use of thermodynamic constraints is required[4].

Following Mie-Gruneisen theory Suzuki[7,8] reported

a relation known as Suzuki formulation[8-10]. The Gruneisen theory of thermal expansion as formulated by Born and Huang[11] has been used by Shanker et al[12], which seems to be inspired from Suzuki. These authors included a higher order term for the change in the expansion of potential energy. Suzuki theory has been widely used in the literature[9,10] to study the thermal expansion of solids, which has been followed by Shanker formulation[13,14]. It has been discussed in the earlier literature[13,14] that these theories give good results under the effect of temperature at zero pressure viz. isobaric condition. But, these methods have not been extended to study the properties of solids under high pressure at room temperature viz isothermal condition. Thus, it becomes legitimate and may be useful to extend these methods to study the properties of solids under high pressure, which is the purpose of present work. However recent investigation says that a lot of work is in progress based on equation of state[15-20]. The method of analysis is given in section 2 and the obtained results are discussed in section 3.

METHOD OF ANALYSIS

The Gruneisen theory of thermal expansion as formulated by Born and Huang[11] has been used by Shanker et at[12]. These authors included higher order term for the change in volume in the expansion of potential energy and reported an expression for V/V_0 which reads as follows[12].

$$\frac{V}{V_0}-1=\frac{1-\left[1-2\left(\frac{B'_0+1}{B_0}\right)P_{Th}\right]^{1/2}}{(B'_0+1)} \quad (1)$$

Where V/V_0 is the relative change in volume, B_0 the bulk modulus, B_0' the first order pressure derivative of bulk modulus, P_{Th} the thermal pressure.

It has been argued by Kushwaha and Shanker[21] that Eq. (1) may be rewritten as follows, when pressure P is not equal to zero.

$$\frac{V}{V_0}-1=\frac{1-\left[1-2\left(\frac{B'_0+1}{B_0}\right)(P_{Th}-P)\right]^{1/2}}{(B'_0+1)} \quad (2)$$

When thermal pressure is zero (P_{Th}=0) Eq. (2) gives

$$\frac{V}{V_0}-1=\frac{1-\left[1-2\left(\frac{B'_0+1}{B_0}\right)P\right]^{1/2}}{(B'_0+1)} \quad (3)$$

Or

$$P=B_0\left[\left(1-\frac{V}{V_0}\right)+\left(\frac{B'_0+1}{2}\right)\left(1-\frac{V}{V_0}\right)^2\right] \quad (4)$$

In the literature Mie-Gruneisen Debye theory is being widely used. Using this Suzuki[9] reported what became known as the Suzuki relation for thermal expansivity. This reads as follows[9,10]:

$$\frac{V}{V_0}=\frac{\left[1+2k-\left(1-\frac{4kE_{Th}}{Q}\right)^{1/2}\right]}{2k} \quad (5)$$

Where $k=\frac{(B'_0-1)}{2}$, $Q=\frac{B_0V_0}{\gamma_0}$, γ_0 is the Gruneisen ratio and E_{Th} is the thermal energy.

Shanker[12] used $p_{Th}=\frac{\gamma_0 E_{Th}}{V_0}$ and rearranged eq. (5) as follows:

$$\frac{V}{V_0}-1=\frac{1-\left[1-2\left(\frac{B'_0-1}{B_0}\right)P_{Th}\right]^{1/2}}{(B'_0-1)} \quad (6)$$

Where P_{Th} is the thermal pressure.

Eq (2) is valid at P=0. Following the arguments of Kushwaha and Shanker[21] when P is not equal to zero, eq. (6) may be rewritten as follows[21]:

$$\frac{V}{V_0}-1=\frac{1-\left[1-2\left(\frac{B'_0-1}{B_0}\right)(P_{Th}-P)\right]^{1/2}}{(B'_0-1)} \quad (7)$$

Now, when thermal pressure is zero (P_{Th}=0), eq (7) gives the following simple relation:

$$\frac{V}{V_0}-1=\frac{1-\left[1+2\left(\frac{B'_0-1}{B_0}\right)P\right]^{1/2}}{(B'_0-1)} \quad (8)$$

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Or

$$P = B_0\left[\left(1-\frac{V}{V_0}\right)+\left(\frac{B_0'-1}{2}\right)\left(1-\frac{V}{V_0}\right)^2\right] \quad (9)$$

Here, it is very clear that eq. (9) is based on the approximation that $P_{Th} = \frac{\gamma_0 E_{Th}}{V_0}$, which simply means that $\frac{\gamma}{V}$ is a constant[10]. Moreover, this approximation is not always true and therefore in the present paper, we modify P_{Th} and Q as follows:

$$P_{Th} = \frac{\gamma E_{Th}}{V}, Q = \frac{B_0 V_0}{\gamma}. \quad (10)$$

Combining eq. (5) and (10), we get the following relation:

$$\frac{V}{V_0}-1 = \frac{1-\left[1-2\left(\frac{B'_0-1}{B_0}\right)\left(\frac{V}{V_0}\right)P_{Th}\right]^{1/2}}{\left(B'_0-1\right)} \quad (11)$$

When P is not equal to zero, eq (11) may further be rewritten as follows:

$$\frac{V}{V_0}-1 = \frac{1-\left[1-2\left(\frac{B'_0-1}{B_0}\right)\left(\frac{V}{V_0}\right)\left(P_{Th}-P\right)\right]^{1/2}}{\left(B'_0-1\right)} \quad (12)$$

Now when P_{Th}=0, eq (12) gives the following simple relation:

$$P = B_0\left(\frac{V_0}{V}\right)\left[\left(1-\frac{V}{V_0}\right)+\left(\frac{B'_0-1}{2}\right)\left(1-\frac{V}{V_0}\right)^2\right] \quad (13)$$

Eq (13) can be written on an empirical basis in the following form:

$$P = B_0\left(\frac{V_0}{V}\right)^n\left[\left(1-\frac{V}{V_0}\right)+\left(\frac{B'_0-1}{2}\right)\left(1-\frac{V}{V_0}\right)^2\right] \quad (14)$$

Where n is parameter which depends on bulk modulus and the first order pressure derivative of the bulk modulus. Moreover, it is directly proportional to the first order pressure derivative of the bulk modulus while inversely proportional to the bulk modulus and may be given by the relation:

$$n = k\left(\frac{B'_0}{B_0}\right)^{1/6} \quad (15)$$

Here- k has the value 3.25 and B_0 is in kbar.

In the present paper, we use all these equations (4), (9), (13) and (14) to study the compression behaviour of four ionic solids, viz. NaF, NaCl, NaBr and NaI.

RESULT AND DISCUSSION

We have thus presented a critical analysis of Suzuki formulation under high pressure at constant temperature, which have been widely used to study the thermal expansion of solids at constant pressure[9]. For the purpose, we used eq. (9) and eq. (13) derived on slightly different ways, and also modified eq. (13) on an empirical basis [eq. (14)]. These formulations are used to calculate the isothermal compression of four different materials viz. NaCl, NaF, NaBr and NaI. The input parameters required are given in TABLE (1)[22]. The results obtained using these equations are reported in the TABLE (2-5) along with the experimental data[23,24] for the comparison purpose. It is found that all these equations give the similar results in small compression range (low pressure). The deviation occurs as the pressure range is increased. At high pressure eq. (9) is found to deviate largely from the experimental data, which are improved by eq. (13). The Shanker formulation[12] derived on the similar basis (eq.4) is also included in the study which gives the results lying in between to that of the equation (9) and (13). Among all these relations [eqs. (4), (9), (13)], it is found that eq. (13) gives the better results but it also deviates from the experimental results. We therefore modified eq. (13) in the form of eq.(14) on an empirical basis. The results obtained from eq. (14) are in good agreement with the experimental data[23,24]. Moreover, eq. (14) involves an additional parameter n, which depends on the material considered. It is found that n is related to the bulk modulus and the first order pressure derivative of the bulk modulus and increases with increase of the first order pressure derivative of the bulk modulus while decreases with increase of the bulk modulus. It should be mentioned that the Suzuki model is based on the Taylor series expansion of potential energy. During this expan-

sion, only the second order term has been considered by neglecting the higher order term. This approximation must be introducing serious errors as discussed in detail by Wang and Reeber[25]. In the present work, we conclude that the Suzuki formulation, which was basically reported to study the thermal expansion of solids at constant pressure, needs some modification under high pressure at constant temperature. We suggest modification in the form of eq. (14) which seems to be simple and give good results for the solids considered in the present work. Due to the simplicity and applicability of eq. (14), it may be good interest to the researchers engaged in high pressure behavior of solids.

TABLE 1 : Values of input parameters used in the present work; from Ref.[22].

Solid	B_0(kbar)	B_0'	n
NaF	465	5.28	1.5
NaClNaBr	240199	5.395.46	1.71.8
NaI	151	5.59	1.9

TABLE 2 : Calculated values of pressure, P (in kbar), at different compressions along with the experimental data [23, 24], for NaF.

V/V_0	P(kbar) Eq.(4)	P(kbar) Eq.(9)	P(kbar) Eq.(13)	P(kbar) Eq.(14)	P(kbar) Exp[23,24]
1	0	0	0	0	0
0.9830	10	10	10	10	10
0.9623	20	19	20	20	20
0.9462	29	28	30	30	30
0.9319	38	36	39	40	40
0.868	87	79	91	98	94
0.832	119	106	128	140	140
0.804	147	130	161	180	180
0.782	171	149	190	215	210
0.778	175	152	196	222	224

TABLE 3 : Calculated values of pressure, P (in kbar), at different compressions along with the experimental data [23, 24], for NaCl.

V/V_0	P(kbar) Eq.(4)	P(kbar) Eq.(9)	P(kbar) Eq.(13)	P(kbar) Eq.(14)	P(kbar) Exp[23,24]
1	0	0	0	0	0
0.9627	10	9	10	10	10
0.9325	20	19	20	21	20
0.9067	29	27	30	32	30
0.8828	39	35	40	43	40
0.76	102	88	116	140	135
0.702	140	118	169	215	200
0.697	143	121	174	224	220
0.675	159	134	198	261	250
0.658	172	144	218	293	290

TABLE 4 : Calculated values of pressure, P (in kbar), at different compressions along with the experimental data [23, 24], for NaBr.

V/V_0	P(kbar) Eq.(4)	P(kbar) Eq.(9)	P(kbar) Eq.(13)	P(kbar) Eq.(14)	P(kbar) Exp[23,24]
1	0	0	0	0	0
0.9561	10	10	10	10	10
0.9206	20	19	20	22	20
0.8913	29	27	30	33	30
0.8663	38	35	40	45	40
0.746	92	79	106	134	130
0.725	102	88	116	158	160
0.663	140	117	177	248	240
0.633	160	133	210	302	290
0.616	171	142	230	339	340

TABLE 5 : Calculated values of pressure, P (in kbar), at different compressions along with the experimental data [23, 24], for NaI.

V/V_0	P(kbar) Eq.(4)	P(kbar) Eq.(9)	P(kbar) Eq.(13)	P(kbar) Eq.(14)	P(kbar) Exp[23,24]
1	0	0	0	0	0
0.9422	10	10	11	11	10
0.899	20	19	21	23	20
0.8652	29	27	31	36	30
0.8364	38	34	41	48	40
0.694	93	79	113	158	150
0.648	115	96	148	219	210
0.641	118	99	154	230	230
0.609	135	112	184	287	280
0.599	141	116	194	307	310

CONCLUSION

Thus present theory reveals that the Suzuki formulation requires some modification under high pressure and thus modified Suzuki formulation gives good results compared to the Suzuki formulation itself and valid for high pressure range for sodium halides.

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