

A Comparative Study of Pressure Dependence of Compression-Ratios of Lithium Halides

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(Received February 4, 2007)

Abstract: A theoretical model is developed to investigate the pressure dependence of the compression ratios of Lithium halides. The method is based on concept of modified Gruneisen parameter. The results obtained for Lithium halides are discussed and compared with Tait's results (calculated) and the available experimental data. It is concluded that the present model found to be in good agreement with the experimental data (available).

Key words: Compression ratios, Modified Gruneisen parameter, Halides.

1. Introduction

The pressure and temperature dependent properties of various class of solids are of fundamental interest to the geophysical and geochemical theories of earth's interior¹⁻⁸. Various forms of EOS for studying high pressure behavior of solids have been developed by numerous investigators using inter ionic potentials⁹⁻¹³ as well as phenomenological approaches. EOS¹⁴⁻¹⁶ neon has also been derived from the finite strain theory by Birch^{17,18}. A common feature of the phenomenological EOS is that they represent the relationship between pressure and volume which can be expressed analytically involving two quantities only viz B_0 , B_0^1 which are respectively the isothermal bulk modulus and its first pressure derivative, both at zero pressure.

This is not always the case for EOS derived from interionic-potentials using some specific potential function for which the short range potential energy is high e.g., if we use an exponential function for ϕ ¹⁹, then the derived EOS is a complicated expression involving potential parameters¹⁰. It is difficult to eliminate these parameters in terms of simple relationship containing B_0 & B_0^1 . In present paper we developed a method using the concept of modified Grunesien parameter for ionic crystals to obtained analytical forms of EOS containing B_0 calculated results from Tait's theory¹³ are also in better agreement with available experimental data.

2. Method Formulation and Analysis

For predicting the pressure dependence of elastic constants, we use the concept of modified Grunesien parameter g_{MT} defined as follows²⁰ :

$$(2.1) \quad g_{MT} = -V_0 \left[\frac{\partial \ln M}{\partial V} \right]_T,$$

where V_0 is the volume at atmospheric pressure and room temperature. M represents any of the elastic constants or moduli such as C_{11} , C_{12} , C_{44} or bulk modulus B . Equation (2.1) forms the basis to study the pressure dependence of M at a fixed temperature. Integration of equation (2.1) under isothermal condition yields²⁰

$$(2.2) \quad M(T, P) = M(T, 0) \exp \left\{ -g_{MT} \frac{\Delta_T V}{V_0} \right\},$$

where $\Delta_T V$ is an isothermal volume change given by

$$(2.3) \quad \Delta_T V = V(T, P) - V(T, 0).$$

If we put isothermal bulk modulus B in place of M in equation (2.2), we get

$$(2.4) \quad B(T, P) = B(T, 0) \exp \left\{ -g_{BT} \frac{\Delta_T V}{V_0} \right\}.$$

Equation (2.4) describes an isothermal variation of bulk modulus with pressure. We have from equation (2.4) at constant temperature

$$(2.5) \quad dP = - \left[\frac{B(T, 0)}{V(T, P)} \right] \exp \left\{ -g_{BT} \frac{\Delta_T V}{V_0} \right\} dV,$$

which integrates to

$$(2.6) \quad P = B(T, 0) \exp(g_{BT}) \left\{ E_1 \left[g_{BT} \frac{V(T, P)}{V_0} \right] - E_1 \left[g_{BT} \frac{V(T, 0)}{V_0} \right] \right\},$$

where $E_1(x)$ is the exponential integral given by

$$(2.7) \quad E_1(x) \approx x^{-1} \cdot e^{-x} \frac{(1 + \frac{a_1}{x} + \frac{a_2}{x^2})}{(1 + \frac{b_1}{x} + \frac{b_2}{x^2})},$$

which approximates to

$$(2.8) \quad E_1(x) \approx x^{-1} \cdot e^{-x} \left[1 + \frac{a_1 - b_1}{x} \right] \approx x^{-1} \frac{(x-1)}{x^2}$$

since $a_1 - b_1 \simeq 1$.

For Simplicity, we first consider $T = T_0$. Then, using the approximation (2.8), equation (2.6) reduces to

$$(2.9) \quad P = \left[\frac{(g_{BT} - 1)}{g_{BT}^2} \right] B_0 \left\{ \left(1 + \frac{\Delta_T V}{V_0} \right)^{-2} \left[\frac{g_{BT} (1 + \frac{\Delta_T V}{V_0}) - 1}{g_{BT} - 1} \right] \exp \left[-g_{BT} \frac{\Delta_T V}{V_0} \right] - 1 \right\},$$

where $B_0 = B(T_0, 0)$ and $\frac{\Delta_T V}{V_0} = \frac{[V(T_0, P) - V_0]}{V_0}$.

If g_{BT} is sufficiently large, this equation reduces, to

$$(2.10) \quad P = \left[\frac{(g_{BT} - 1)}{g_{BT}^2} \right] B_0 \left\{ \left(1 + \frac{\Delta_T V}{V_0} \right)^{-1} \exp \left[-g_{BT} \frac{\Delta_T V}{V_0} \right] - 1 \right\},$$

which is the modified Tait's equation discussed by Grover et al.²¹.

Again, when g_{BT} is 3 or 4, the approximations contained in equation (2.10) are not satisfactory, and equation (2.7) is needed to characterize $E_1(x)$. In order to express $\frac{\Delta_T V}{V_0}$

(which is negative) as an explicit function of P, equation (2.10) may be inverted in the following manner. Since

$$(2.11) \quad \left(1 + \frac{\Delta_T V}{V_0} \right)^{-1} \exp \left[-g_{BT} \frac{\Delta_T V}{V_0} \right] = \frac{V_0 B}{V B_0} = \frac{V_0}{B_0} \left(\frac{\partial P}{\partial V} \right)_T.$$

Equation (2.10) integrated to give

$$(2.12) \quad \frac{\Delta_T V}{V_0} = - \left[\frac{(g_{BT} - 1)}{g_{BT}^2} \right] \ln \left\{ 1 + \left[\frac{g_{BT}^2}{(g_{BT} - 1)} \right] \frac{P}{B_0} \right\}.$$

For an understanding behavior of solids under the effect of high pressure and also in some geophysical applications, we need data on the Bulk modulus B_0 as a function of pressure. In principle, the compression ratio V/V_0 can be determined from an isothermal equation of state representing the relationship between pressure and volume at a fixed temperature. Tait's¹³ has derived the equation of state relating pressure P and compression $\frac{V}{V_0}$ as follows:

$$(2.13) \quad \frac{\Delta V}{V_0} = \frac{1}{\alpha} \ln (1 + \beta P)$$

where $\alpha = (1 + B'_0)$ and $\beta = \alpha / B_0$. However, in such a procedure, we require data on bulk-modulus B_0 and its pressure derivative B'_0 at atmospheric pressure ($P = 0$ K.bar), as far as B_0 and B'_0 are concerned their experimental values based on ultrasonic measurements are available²². The calculated compressions are compared with those experimental values^{23,24,27} in Sec-3. We have used data on g_{BT} , B_0 , B'_0 in table 1.

Table-1: Values of input data^{20,25,26} on g_{BT} , B_0 and B'_0

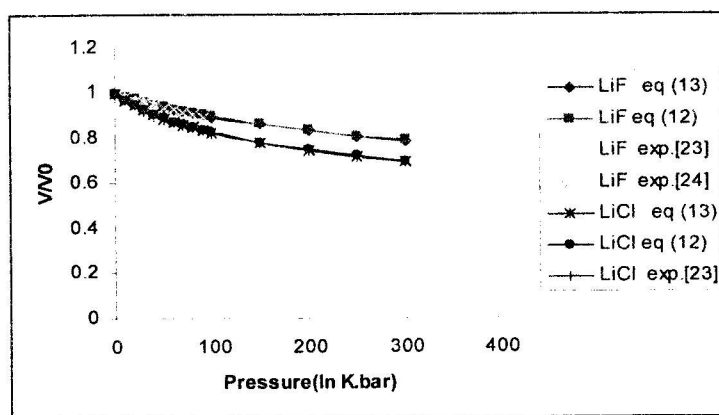
Crystal	g_{BT} [20]	B_0 (k bar) [25]	B'_0 [26]
LiF	5.30	665	5.38
LiCl	5.63	297	5.71
LiBr	5.68	235	5.75
LiI	6.17	171	6.24

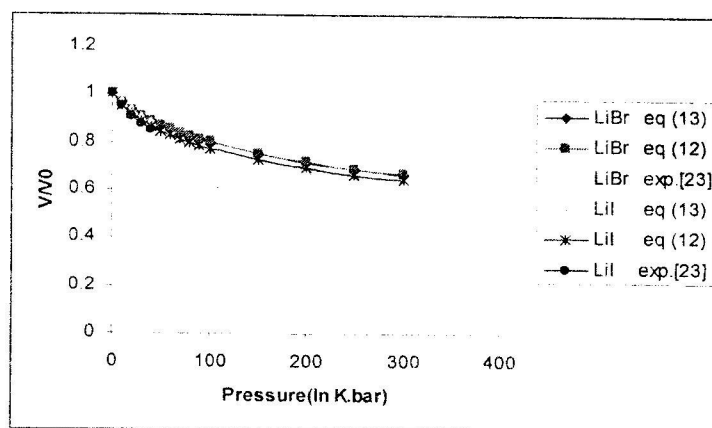
Since experimental values for B_0 , B'_0 are available for all the crystals under study, we use them to determine the compression ratio V/V_0 in equation (2.12, 2.13). The calculated values of V/V_0 are given in table 2. The values obtained from (2.13) are sufficiently close to the experimental values for all Li halides

Table-2: Experimental^{23,24,27} and calculated (2.12, 2.13) values of V/V_0 for Lithium halides.

Pressure	LiCl			LiF				
	[23]	eq(2.13)	eq(2.12)	[23]	[27]	[24]	eq(2.13)	eq(2.12)
0	1	1	1	1	1	1	1	1
5	0.9852			0.9924				
10	0.971	0.9696	0.9697	0.9852		0.9854	0.9856	0.9857
15	0.9576			0.9782	0.978			
20	0.9448	0.9444	0.9446	0.9716	0.971	0.9717	0.9725	0.9725
25	0.9327			0.9654	0.964			
30	0.9213	0.9229	0.9232	0.9594	0.958	0.9589	0.9604	0.9605
35	0.9106			0.9538	0.952			
40	0.9006	0.9041	0.9046	0.9485	0.946	0.9467	0.9491	0.9493
45	0.8912		0.8961	0.9435	0.94			0.944
50		0.8873	0.8880			0.9352	0.9386	0.9388
60		0.8723	0.8732			0.9243	0.9287	0.9291
70		0.8587	0.8597			0.914	0.9195	0.9199
80		0.8462	0.8473			0.9041	0.9107	0.9112
90		0.8346	0.8359			0.8946	0.9024	0.9030
100		0.8239	0.8254				0.8946	0.8952
150		0.7796	0.7817				0.8602	0.8614
200		0.7454	0.7481				0.8321	0.8337
250		0.7177	0.7211				0.8082	0.8102
300		0.6942	0.6978				0.7876	0.7898

Pressure	LiBr			LiI		
	[23]	eq (13)	eq (12)	[23]	eq (13)	eq (12)
0	1	1	1	1	1	1
5	0.9811			0.9728		
10	0.9632	0.9626	0.9626	0.9487	0.9515	0.9516
15	0.9463			0.9273		
20	0.9306	0.9328	0.9330	0.9083	0.9156	0.9159
25	0.9159			0.8913		
30	0.9023	0.9079	0.9084	0.876	0.8872	0.8878
35	0.8897			0.862		
40	0.8782	0.8867	0.8874	0.8492	0.8636	0.8645
45	0.8677		0.8779	0.8371		0.8542
50		0.8681	0.8690		0.8435	0.8446
60		0.8516	0.8527		0.8260	0.8272
70		0.8367	0.8381		0.8104	0.8118
80		0.8232	0.8248		0.7964	0.7980
90		0.8108	0.8126		0.7837	0.7855
100		0.7994	0.8013		0.7720	0.7740
150		0.7527	0.7554		0.7252	0.7278
200		0.7172	0.7205		0.6902	0.6934
250		0.6886	0.6924		0.6624	0.6660
300		0.6647	0.6689		0.6392	0.6431

Fig.1: Plot of compression V/V_0 v/s Pressure for LiF and LiCl

Fig.2: Plot of compression V/V_0 v/s Pressure for LiBr and LiI**Table- 3:** Percentage deviation of Lithium halides with the source (table-2) at maximum (available) pressure.

Halide	Source	Max. pressure (in K.bar)	% Deviation	
			Eq.(12)	Eq(13)
LiCl	[23]	45	0.5	0.5
LiF	[23]	45	0.05	0.05
LiF	[27]	45	0.42	0.4
LiF	[24]	90	0.94	0.87
LiI	[23]	45	2.03	2.0
LiBr	[23]	45	1.17	1.14

3. Results and Discussion

The ultrasonic measured values B_0 and B'_0 have been used in the analysis of pressure and compression (V/V_0). The experimental (available) and calculated (2.12, 2.13) values of compression curves are compared (up to 300 K.bar) in fig 1 and 2. Vaidya- Kennedy²³ reported for all used crystals up to 45 K.bar, and Yagi²⁴ has reported experimental data for LiF up to 90 K.bar, but Bridgman²⁷ reported up to 45 K.bar for the same. For the sake of comparison, we have included these experimental data^{23,24,27} in fig. (1 and 2)

For Lithium Fluoride, our calculated results eq.(2.12, 2.13) and obtained from T. Yagi²⁴ are in good agreement and deviation is 0.9 %at max pressure 90 K.bar, While Vaidya and Kennedy²³ and Bridgman²⁷ experimental value up to 45 K.bar shows good agreement with deviation about 0.049% and 0.42% respectively. No any polymorphic transitions were observed in Lithium halides for pressure interval investigated. This is in agreement with the results of Pistorius and Snyman^{28, 29, 30}. The rest Li halides are also in fair agreement with experimental compressions as given in table-3. On the basis of over all

discussion, it may be concluded that this model approach adopted by us is capable of providing a better agreement of high pressure behavior of Lithium halides.

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