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Equation of state for the prediction of compression Behaviour of Alkali Iodides

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ABSTRACT

The equation of state (EOS) of a solid (pressure–volume relation) plays an important role in condensed matter physics, which are very useful for the general understanding of the behaviour and the application of condensed matters. Its role becomes more crucial especially in case of those materials which have high range of compressibility. In the present work, pressure of three different alkali metal halides viz. NaI, KI, and RbI has been calculated at different compression ranges using four different isothermal equation of state (EOS) viz Kumar EOS, Shanker EOS, Brennan Stacey EOS, Poirier- Tarantola EOS. A critical analysis and comparative study among the calculated values of pressure to test the validity of various equations of states suggest that Shanker EOS gives good agreement with experimental result.

Key words: Equation of States, Alkali Metal Halides, Compression Behaviour and pressure-induced structural transformations.

INTRODUCTION

ALKALI-Iodide crystals have been investigated very intensively because they can be represented quite well by the simple ionic lattice model. It is known that the RbI and KI have the NaCl-type structure at room temperature and atmospheric pressure, undergo a Polymorphic transition to the CsCl-type structure 3.9 kbar. This transition is accompanied by a considerable sudden change in volume14%. An examination of the P-V dependences of rubidium Iodide shows that the change in the internal energy, which accompanies the polymorphic transition in these salts, represents a very small fraction of the lattice energy of either phase of these compounds. Sodium Iodide is one of the oldest members of optical engineering family which shows an abrupt phase chase changes at high compression region which makes it a slandered optical device in the field of detection technology. The high pressure sodium iodide arc lamp requires the use of a buffer gas to limit the transport of energy from the arc discharge to the arc tube walls via chemical reaction.

The equation of state (EOS) of a solid (pressure–volume relation) plays an important role in condensed matter physics, because the knowledge of the EOS is of central importance for the general understanding of the behaviour and the application of condensed matters [1] at extreme compressions.

In the present work, pressure of three different alkali metal iodides viz. NaI, KI and RbI has been calculated at different compression ranges using four well known equation of state (EOS) viz. Kumar EOS, Shanker EOS, Brennan Stacey EOS, Poirier- Tarantola EOS. A comparative study has also been made among the calculated values of pressure to test the validity of various equation of states.

Theory

The derivation of EOS of a thermodynamic system is based on a fundamental theorem which equates the negative of pressure to the isothermal volume derivative of a Helmholtz free energy function, F. The function F consists of two terms in the case of solids, the first of which represents the potential energy of a non vibrating lattice while the second owes its origin to the pressure of the thermal vibrations.

An Equation of state can be derived from the volume derivative of lattice potential energy [2-8] by using the relation

$$P = -\left(\frac{dW}{dV}\right)_T \qquad (1)$$

where W for an ionic crystal can be written as the sum of electrostatic energy and short range overlap repulsive energy

$$W = -\alpha_M \frac{Z^2 e^2}{V^{1/3}} + \Phi(V) \qquad (2)$$

Kumar has presented a derivative of the UTE on the basis of Chopelas - Boehler approximation [9,10] and gave an EOS known as Kumar EOS

$$P = \frac{K_0}{K_0^{'} + 1}\left[\left\{\exp\left(K_0^{'} + 1\right)\left(1 - \frac{V}{V_0}\right)\right\} - 1\right] \qquad (3)$$

Poirier and Tarantola [11] derived an equation of state using finite strain theory by considering the strain function Є= log(l_0/l) given as

$$\mathrm{P} = \mathrm{K}_0\left(\frac{\mathrm{V}_0}{\mathrm{V}}\right)\left[\ln\left(\frac{\mathrm{V}_0}{\mathrm{V}}\right) + \left\{\left(\frac{\mathrm{K}_0^{'} - 2}{2}\right)\right\}\left\{\ln\left(\frac{\mathrm{V}_0}{\mathrm{V}}\right)^2\right\}\right] \qquad (4)$$

Using the free volume formula [12] for the Grüneisen parameter γ and assuming that the Grüneisen parameter γ is proportional to volume, Brennan and Stacey[5] obtained an EOS which is given as

$$P = \frac{3K_0\left(\frac{V}{V_0}\right)^{-4/3}}{\left(3K_0^{'} - 5\right)}\left[\exp\left\{\frac{\left(3K_0^{'} - 5\right)\left(1 - \frac{V}{V_0}\right)}{3}\right\} - 1\right] \qquad (5)$$

On the basis of Born lattice theory [13] taking the volume derivative of short range force constant, Shanker obtained a equation of state known as Shanker EOS [14, 15] which are as

$$P = \frac{\left[K_0\left(\frac{V}{V_0}\right)^{-4/3}\right]}{t}\left[\left(1-\frac{1}{t}+\frac{2}{t^2}\right)\{\exp(ty)-1\}+y\left(1+y-\frac{2}{t}\right)\exp(ty)\right] \qquad (6)$$

where

$$y = 1-\frac{V}{V_0} \qquad \text{and} \qquad t = \left(K_0^{'}-\frac{8}{3}\right)$$

K_0 is isothermal bulk modulus and $K_0^{'}$ is the first derivative of isothermal bulk modulus at zero pressure.

RESULTS AND DISCUSSION

The pressure have been calculated at different compression ranges (from V/V_0=1.0 to 0.1) for different alkali metal iodides viz. NaI. KI, and RbI using four different isothermal equation of state viz. Kumar EOS, Shanker EOS, Brennan Stacey EOS, Poirier Tarantola EOS (3-6). The calculated values are displayed in table (2 -4). The input values of isothermal bulk modulus (K_0) and its first pressure derivative ($K_0^{'}$) at zero pressure are taken from the literature [16] displayed in table (1). The logarithmic values of calculated pressure obtained by using different isothermal EOS have been plotted against the logarithmic values of unit cell volume ratio (V/V_0) and shown graphically, displayed in figure (1-3). The result thus obtained shows very interesting pattern i.e. the graph plotted between logarithmic value of pressure vs logarithmic value of unit cell volume ratio (V/V_0) appears linear characteristic [fig. (1 - 3)].

Another remarkable characteristic is observed that the variation in value of pressure from compression range V/V_0 = 1.0 to 0.5 are minimum but as the compression increases the variation in the values of pressure also increases. Pressure (P) vs. unit cell volume ratio (V/V_0) relation for all the three alkali iodides are almost same with slight variation upto V/V_0 = 0.5 but as the compression increases variation in pressure gradually increases and after V/V_0 = 0.3 it increases abruptly which is crystal clear from figure (1 – 3).

When we consider about the success of equation of state derived from certain scientists, we have observed that the calculated values of pressure at different compression by using Kumar EOS and Shanker EOS gives a good agreement with experimental values whereas Brennan-Stacey and Poirier-Tarantola EOS shows an abrupt deviation. It is observed that Brennan - Stacey equation of state shows deviation in upward direction, where as Poiries – Tarantola EOS gives a linear type projection. Now the question arises, why both these equations of state show a variation of marked difference.

Brennan-Stacey EOS is based on assumption that Grüneisen parameter is proportional to volume and is obtained on account of free volume formula. The metallic crystals have a packed arrangement, Due to this reason Brennan EOS in case of bulk metallic glasses fails hopelessly.

The Poirier-Tarantola proposed an equation of state derived using Hencky logarithmic strain [3] equivalent to the Eulerian strain for small strain and better behaved for large strain. The reference strain is neither the initial nor the final configuration, but the instantaneous configuration of the body being deformed. In uniaxial deformation as the instantaneous volume (V) of the body is increased by an infinitesimally small increment dV, the ratio (dV/V) is considered as an increment of the current state of strain

$$dE=(dV/V)$$

When the solid goes from volume V_0 to V the total finite strain or normal strain also called the Hencky measure of strain.

$$E_H=(1/3)\log(V/V_0)$$

It has been observed that Hencky strain as a function of the ratio (V_0/V) and in this way what we find that is as the compression increases this potential deviates from other potential and successively it shows a pseudo linear characteristic. The conclusion is very interesting and it requires a critical and comprehensive study for further research work.

Table-1 The input values of isothermal bulk modulus (K_0) & its first pressure derivative (K_0') at ero pressure [16]

S.No.	Sample	K_0 (GPa)	K_0' (GPa)
1	NaI	14.87	5.57
2	KI	11.51	5.48
3	RbI	10.49	5.60

Table -2 Calculated values of pressure (P) in GPa as a function of V/V_0 at different compressions using different equation of state from equations (3-6) for "NaI"

V/V_0	P (GPa) Kumar EOS (3)	P (GPa) Poirer -Tarantola EOS (4)	P (GPa) Brennan- Stacey EOS (5)	P (GPa) Shanker EOS (6)
1.00	0.00	0.00	0.00	0.00
0.90	2.10	1.86	2.09	2.10
0.80	6.15	4.64	6.06	6.10
0.70	13.97	8.68	13.63	13.82
0.60	29.03	14.52	28.31	28.99
0.50	58.08	23.05	57.89	59.93
0.40	114.08	35.89	121.28	127.03
0.30	222.06	56.34	271.89	288.05
0.20	430.24	92.62	704.97	754.74
0.10	831.62	174.83	2662.47	2876.10

Table -3 Calculated values of pressure (P) in GPa as a function of V/V_0 at different compressions using different equation of state from equations (3-6) for "KI"

V/V_0	P (GPa) Kumar EOS (3)	P (GPa) Poirer -Tarantola EOS (4)	P (GPa) Brennan- Stacey EOS (5)	P (GPa) Shanker EOS (6)
1.00	0.00	0.00	0.00	0.00
0.90	1.62	1.44	1.61	1.61
0.80	4.71	3.57	4.65	4.68
0.70	10.63	6.65	10.38	10.53
0.60	21.92	11.10	21.43	21.94
0.50	43.51	17.59	43.53	45.06
0.40	84.77	27.35	90.54	94.81
0.30	163.61	42.87	201.46	213.35
0.20	314.28	70.36	518.27	554.64
0.10	602.19	132.61	1941.66	2096.59

Table -4 Calculated values of pressure (P) in GPa as a function of V/V_0 at different compressions using different equation of state from equations (3-6) for "RbI"

V/V_0	P (GPa) Kumar EOS (3)	P (GPa) Poirer -Tarantola EOS (4)	P (GPa) Brennan- Stacey EOS (5)	P (GPa) Shanker EOS (6)
1.00	0.00	0.00	0.00	0.00
0.90	1.49	1.32	1.48	1.48
0.80	4.36	3.28	4.29	4.32
0.70	9.92	6.14	9.67	9.81
0.60	20.68	10.29	20.14	20.62
0.50	41.49	16.35	41.29	42.76
0.40	81.75	25.47	86.75	90.88
0.30	159.64	40.00	195.05	206.67
0.20	310.32	65.80	507.24	543.14
0.10	601.82	124.28	1921.64	2076.14

Fig. 1-3 The logarithmic graph between calculated values of pressure (P) against V/V$_0$ for NaI (Fig. 1), KI (Fig. 2) and RbF (Fig. 3) using different isothermal equation of state from equations (3-6)

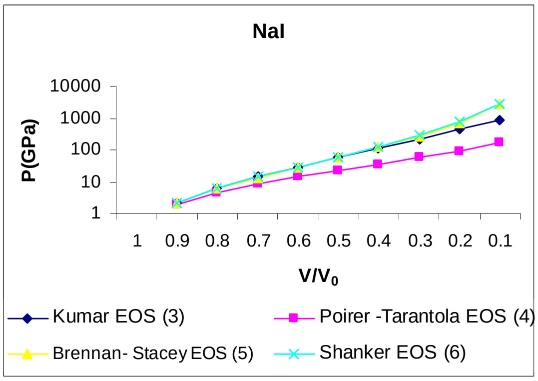

Fig. 1

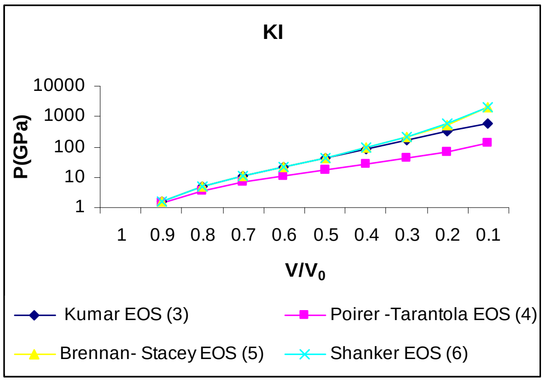

Fig. 2

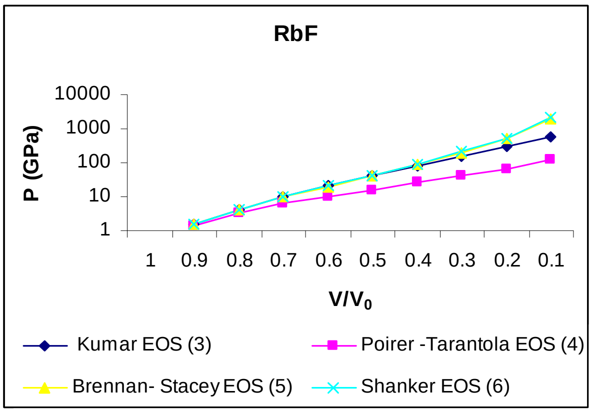

Fig. 3

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