

TALLON'S EQUATION OF STATE FOR ALKALI-HALIDES

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ABSTRACT

It is rather well known that properties of solids under the effect of high pressure and high temperature provide valuable information for understanding the thermodynamic behavior, the equation of state, and the thermoplastic properties. Experimental studies conducted so far; have not been able to attain the extreme pressure and temperature conditions that exist in the earth's lower mantle. Thus theoretical studies play an important role in advancing our knowledge of high pressure-high temperature physics of solids. Such studies involve the use of various thermodynamic relations and approximations regarding the variation of thermal expansion coefficient, bulk modulus, Anderson-Gruneisen parameter and the other related parameters with pressure and temperature. Reliable values of these quantities have been measured experimentally [1, 2] at room-temperature and atmospheric pressure. However, considerable uncertainties exist regarding their variation under high pressure (100 K bar) and high temperature ($\approx 1000-2000$ K).

INTRODUCTION

The high pressure behavior of various solids can only be well understood if we have data on the bulk modulus as a function of pressure. In principle, the isothermal bulk modulus K_T can be determined from an isothermal equation of state representing the relationship between pressure and volume at a fixed temperature. We, therefore, select a number of equations of state most widely used and frequently reported in the recent literature [6,22,77] and shall make use do them to find corresponding relevant expressions for the pressure dependence of the bulk modulus.

The recent past has witnessed a considerable and growing interest in the study of pressure dependence of thermal expansivity α of various solids both by experimental and theoretical methods [16-18]. However, uncertainty exists in the experimental results obtained so far. Thus, there is still a need of developing accurate theoretical equations to provide insight into the high pressure behavior of solids. We shall make a comprehensive analysis of various relations proposed so far for computing the value of thermal expansivity under varying pressure and study the assumptions implied in the derivation of such relations. The study of these relations can also give us information about the nature of variation of the Anderson-Gruneisen parameter with pressure.

In order to study the equation of state and thermodynamic properties at simultaneously elevated pressure and temperature, we have to introduce certain modifications in Murnaghan and Birch's equation of state. This can be achieved following the work of Plymate and Stout [16], who has incorporated a factor for thermal effect in the Murnaghan assumption for bulk modulus. The equation of state thus developed shall be used to calculate P-V-T and α (T,P).

To understand the thermo elastic behaviour of solids adequately, it is necessary to have the knowledge of temperature dependence of elastic constants. Some phenomenological models [19-22] have been developed by various workers to study this. Yamamoto et. al. [23], have measured the elastic constants, bulk modulus, and thermal expansivity for NaCl Crystal in the temperature range 298-766 K. We shall investigate the temperature and pressure dependence of compression ratio (V/V₀), Bulk modulus (K) and thermal pressure dependence of a expansivity by using Tallon's model and shall compare the results with those from Tait's equation, Fei-Saxena EOS., Kumar model and Raju et. al. models as well as with the available experimental data in order to test the suitability of models employed in the temperature Range 298-1073K respectively for 17 alkali halide crystals.

The thesis has been organized as follows. In chapter-I, we give an introduction of various aspects of the present study. Equation of state for ionic solids are reviewed and discussed in chapter II. Analysis based on interionic potentials is presented in chapter III. Fundamental thermodynamic definitions, Relations and approximations are given in chapter IV. Modified forms of equations of state are formulated in chapter V. Numerical analysis, results, and discussions are presented in chapter VI. Summary and conclusions are given in chapter VII. On the basis of the present study, it has been possible to prepare five research papers as mentioned below:

- 1) Analysis of compression ratios of sodium halides up to 300 k bar; Acta Ciencia Indica, Vol. **XXXII P**, No.3, 331 (2006).
- 2) Analysis of compression ratios of cesium chloride up to 300 k bar; Acta ciencia Indica; Vol. **XXXII P**, No. 3, 257 (2006)
- 3) Analysis of temperature dependence of thermal expansivity of geophysical minerals; *proceedings of national seminar on recent trends in advancement of mathematical and physical sciences*, (RTAMPS) *Phy.* 13 (2006)
- 4) A comparative study of pressure dependence of compression ratios of Lithium-halides presented at **9th conference of Int. Acdm. Of Phy. Sciences Feb.-2007 Agra** & accepted for publication in **PAPIAPS-Allahabad**.
- 5) Analysis of Temperature dependence of Bulk modulus Of Geophysical minerals – **presented in CONIAPS-IX- 2007 AGRA**.

EQUATION OF STATE

The equation of state which connects volume (V), pressure (P) and temperature (T) for a substance, is of central importance over the whole of condensed matter physics. Solutions to a

variety of important problems in Earth science depend on accurate predictions of molar volumes (V) of crystalline solids at a given temperature and pressure. Such predictions are essential for knowing whether a solid is relatively compressed or expanded at depth in the Earth and for meaningful calculations of the pressure and temperature dependence of thermal expansivity, bulk modulus, entropy, and other thermodynamic properties.

RESULTS AND DISCUSSION

(a) BIRCH EQUATION OF STATE FOR ALKALI HALIDE CRYSTALS:

The Birch equation of state is derived from the theory of finite strain [9] by considering the Eulerian strain of an elastic isotropic medium under isothermal hydrostatic compression. The pressure is obtained from the strain energy of Helmholtz potential ϕ per unit mass using the thermodynamic relation for an isotherm,

$$P = - \left[\frac{\partial \phi}{\partial V} \right]_T \quad (6.1)$$

Where ϕ is a function of V and T . The Eulerian strain component f as considered by Birch [9] is related to the ratio of compressed volume V to uncompressed volume V_0 as follows:

$$\frac{V}{V_0} = (1 + 2f)^{-3/2} \quad (6.2)$$

The strain energy can be represented by an infinite series consisting of a sum of powers of f with coefficients which are functions of temperature alone. In accordance with the 2nd order Birch equation of state we retain only the first three terms in the power series expansion and adopt the following form [9].

$$\phi = \frac{9}{2} K_0 V_0 f^2 \left[1 + \frac{2}{3} af + \frac{1}{2} bf^2 \right] \quad (6.3)$$

The subscript zero indicates values at $P=0$. With the help of equations (6.1) to (6.3), we get the following relation in the manner

$$\begin{aligned} P &= - \left[\frac{\partial \phi}{\partial f} \right]_T \left[\frac{\partial f}{\partial V} \right]_T \\ &= 3K_0 f (1 + 2f)^{5/2} (1 + af + bf^2) \end{aligned} \quad (6.4)$$

The isothermal bulk modulus is defined as

$$K = -V \left[\frac{\partial P}{\partial V} \right]_T \quad (6.5)$$

Taking the volume derivative of P with the help of equation (6.5), we get

$$K = K_0 \left[1 + 2f \right]^{-5/2} \left[1 + (7 + 2a)f + (9a + 3b)f^2 + 11bf^3 \right] \quad (6.6)$$

The first pressure derivative of the bulk modulus is obtained by differentiating equation (6.5) with respect to pressure as follows:

$$K' = \left[\frac{\partial K}{\partial P} \right]_T = -1 - V \frac{P''}{P'} \tag{6.7}$$

Where

$$P' = \left[\frac{\partial P}{\partial V} \right]_T \quad \text{and} \quad P'' = \left[\frac{\partial^2 P}{\partial V^2} \right]_T$$

are obtained by taking the volume derivative of P using equation (6.4) thus we get

$$P'' = -\frac{K_0}{V_0} (1 + 2f)^{-4} [1 + 2a\bar{f} + 3a + 3b\bar{f}^2 + 11bf^3] \tag{6.8}$$

$$P''' = \frac{K_0}{3V_0^2} (1 + 2f)^{-11/2} [45 + 2a + (70 + 38a + 6b)f + (108a + 69b)f^2 + 154bf^3] \tag{6.9}$$

Substituting equation, (6.8) and (6.9) into equation (6.7), we obtain

$$K' = \frac{12 + 2a + 49 + 32a + 6b\bar{f} + 81a + 60b\bar{f}^2 + 121bf^3}{31 + 2a\bar{f} + 3a + 3b\bar{f}^2 + 11bf^3} \tag{6.10}$$

By taking the second order pressure derivative of the bulk modulus with the help of equation (6.5), we get

$$K'' = \left[\frac{\partial^2 K}{\partial P^2} \right]_T = -\frac{P''}{(P')^2} - V \frac{P'''}{(P')^2} + V \frac{P''^2}{(P')^3} \tag{6.11}$$

Where

$P''' = (\partial^3 P / \partial V^3)_T$ is determined by taking the third order volume derivative of P with The help of equation (6.4). Thus

$$P''' = -\frac{B_0}{9V_0^3} (1 + 2f)^7 [35 + 60a + 6b + 10 + 710a + 216b\bar{f} + 620a + 1497b\bar{f}^2 + 2618f^3] \tag{6.12}$$

The values of parameters a and b can be determined in terms of K'_0 and K''_0 (values of K' and K'' at $P=0$) by substituting $f=0$ in equation (6.10) and (6.11). Thus one obtains

$$a = \frac{3}{2} K'_0 - 4 \tag{6.13}$$

$$b = \frac{1}{6} [9K'_0 K''_0 + 6K_0'^2 - 63K'_0 + 143] \tag{6.14}$$

For determining the values of a and b from equations (6.13) and (6.14), we need to know K'_0 and K''_0 . Values of K'_0 have been measured ultrasonically [2,78,79,80] and are available for all crystals under study. Values of K''_0 have not yet been measured for all the crystals. Moreover,

the experimental values of K_0'' available for some crystals [81-83] are subject to considerable uncertainties. Freund and Ingalls [6] made a detailed study based on different existing forms of isothermal equation of state and determined the values of K_0' and K_0'' by the method of curve fitting. The resulting values were found to be quite uncertain and K_0'' in particular, have errors of the order of 100%. In fact, the values of K_0' and K_0'' determined from the fitting of compression data [9] depend on the choice of the equation of state and the maximum pressure considered. In view of the large uncertainties in the values of K_0'' , Freund and Ingalls emphasized the need to develop alternative methods for determining the values of K_0'' . We therefore adopt the method based on interionic potentials for determining K_0'' .

PROPOSED RESEARCH WORK

In the present work, we have made a comprehensive study of the various thermodynamic relations, critically analyzing their validity and applicability to Alkali halide crystals. A thermodynamic relation involving pressure, volume, and temperature is often quoted as an equation of state. The high pressure equation of state has been a subject of wide investigations [3-6] since the pioneering studies made by Bridgman [7]. Among various phenomenological equations proposed so far, the two most widely used equations are the Murnaghan equation of state [8] and the Birch equation of state [9]. The Murnaghan equation is based on the assumption that the bulk modulus K_T depends linearly on pressure. This may be a good approximation but does not hold strictly true as it implies the second pressure derivative of bulk modulus K_0'' to be zero. However, K_0'' is related to the second-order elastic constants which are of sufficiently higher magnitudes than even first-order elastic constants [10-13]. Thus for an adequate formulation, the higher order terms in the Murnaghan equation of state must be included.

CONCLUSION

In the present thesis, we have investigated thermodynamic relations and approximations used in various equations of state and high pressure, high temperature behavior of elastic constants, bulk modulus and thermal expansion coefficients for alkali halides. First of all we have used 1st and 2nd order Birch equation of state and Murnaghan equation of state.

Here the second order Birch equation of state derived from the theory of finite strain [9] has been used, to calculate the pressure versus compression (V/V_0) data at room temperature for alkali halide crystals, viz., LiF, LiCl, LiBr, LiI, NaF, NaCl, NaBr, NaI and CsCl. These crystals can be compressed to rather high pressures without appearance of any structural phase transformation.

The parameters of the Birch equation of state are determined from the ultrasonically measured experimental values of bulk modulus and its first pressure derivative [2, 34, 58,59] and the calculated values of second pressure derivative of bulk modulus derived from interionic potential models [14,15]. The experimental values of K_0'' are not available for all the crystals under study and the experimental values available for some crystals [81-83] are subject to considerable uncertainties of the order of 100% [6]. We have therefore used interionic potentials with inverse-power function and exponential function for the overlap repulsive energy to evaluate K'' . The resulting P-V data for all the crystals have been found to compare well with the corresponding experimental values reported by Vaidya- Kennedy [55] and by Yogi [45]. The deviation between the calculated and the experimental values is insignificant in the low pressure region but becomes significant as the pressure is increased. The calculated values of V/V_0 agree closely with the experimental values, the maximum deviation at the highest pressure considered being only 2% in case of LiI.

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