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## **Analytical study of metals at high temperature and pressure**

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**Abstract**

In current investigation the P-V-T relationship based on various equations of state pressure & temperature dependence of compression ratio ( $V/V_0$ ), Bulk modulus (K) and of Thermal expansivity ( $\alpha$ ) has been found. Most of the experimental data reported in the literature are available for various crystals. We have found a good agreement b/w theory and experiment. Comparisons of experimental data and calculated values have provided a useful insight regarding the nature of variations of Anderson - Gruneisen parameter. The modules used & developed in present study are expected to yield reliable data for other ionic solids as well as for which experimental data are not yet available. The present study may thus be useful to understand the behaviour of solids under the effect of light pressure & high temperature.

**Keywords:** Analytical study, metals, Temperature, Pressure, Anderson-Gruneisen parameter etc.

**Introduction**

Experimental studies conducted so far have not been able to attain the high 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 & temperature 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. The high pressure equation of state has been a subject of wide investigations Bridgman was the one to make such studies and later many of them followed him. Among various phenomenological equations proposed so far, the two most widely used equations are the Murnaghan equation of state and the Birch equation of state.

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.

**Research Objectives**

1. To investigate thermodynamic relations & approximations used in various equation of state.
2. To analyze the comprehensive study of the various thermodynamic relations for the calculations and investigate the superconducting behavior of the metals by applying Tallon's Equation.

**Research Methodology & Hypothesis**

Various parameter, data collection, various tools, primary and secondary source were used for the calculation of results. Literature survey was done to know the advancement, technology, significance, appl.

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## Results & Findings

Experimental studies conducted so far have not been able to attain the high 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 & temperature 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.

Alkali metal halides (also known as alkali halides) are the family of inorganic compounds with the chemical formula MX, where M is an alkali metal and X is a halogen. These compounds are the often commercially significant sources of these metals and halides. The best known of these compounds is sodium chloride, table salt. The alkali metal halides exist as colourless crystalline solids, although as finely ground powders appear white. They melt at high temperature, usually several hundred degrees to colorless liquids. Their high melting point reflects their high lattice energies. At still higher temperatures, these liquids evaporate to give gases composed of diatomic molecules.

The high pressure equation of state has been a subject of wide investigations Bridgman was the one to make such studies and later many of them followed him. Among various phenomenological equations proposed so far, the two most widely used equations are the Murnaghan equation of state and the Birch equation of state.

The Murnaghan equation is based on the assumption that the bulk modulus is linearly proportional to pressure. This may be a good approximation but does not hold strictly true as it implies the second order pressure derivative of bulk modulus to be zero, the first-order Birch equation included terms containing the first pressure derivative of bulk modulus at zero pressure alone where as the second-order Birch equation contains terms involving both first & second pressure derivative of bulk modulus and we shall make use of both the equations of state.

Theoretically the trends of Bulk modulus with change in pressure up to range of 0-300 k bar for rest crystals have similarity with the trends of NaCl crystal (Experimental). For determination of effect of pressure on volume thermal expansion coefficient ( $\alpha_T$ ), we have used only Tallon's eq (6.2.15) for all seventeen crystals but the experimental values [45] of thermal expansion coefficient ( $\alpha_T$ ) are available for NaF, NaCl, LiF & for CsCl crystals & shows disagreement with - 3.6% deviation for NaCl, -30% for NaF, - 24% for LiF & 164.6% for CsCl crystal but calculated values of  $\alpha_T$  decreased on increasing pressure at room temperature. The all values of  $\alpha_T$  are multiplied with.

We have used various equations of state viz. Tallon's equations of state, Kumar equations of state, Fei-Saxena equations of state and Raju *et al.* equations of state. For calculating compression ratio ( $V/V_0$ ), Bulk modulus ( $K_P$ ) and volume thermal expansion coefficient ( $\alpha_P$ ) with the variation of temperature range from (298-1073K) at various pressures from 0-300 k bar for NaF, NaCl, NaBr NaI, LiF, LiCl, LiBr, LiI, KF, KCl, KBr, KI, RbF, RbCl, RbBr, RbI and for CsCl Crystals.

The input data are compiled in table at initial temperature 298 K & are used in present Calculations as are responded by Tallon, Dhoble Chauhan & Yamamoto *et. Al.* Initially we have used Tallon's eq, Raju's equations, Kumar equations Fei & Saxena equations (6.3.18) for calculating the effect of temperature on compression for halides of Na, Li, K, Rb and for CsCl crystal with the range 298-1073 K & with pressure range 0-300 k bar.

Experimentally it is observed that compression ratio ( $V/V_0$ ) increases one increasing temperature at a constant pressure. The experimental data [23] is available only for NaCl crystal So with the help of calculated values and experimental data [23] it is found that Tallon's equations shows better agreement with -1.05% deviation, Raju equation 3.28%, Kumar equations with 3.3% deviation & Fei & Saxena equations with 1.7% deviation. So Tallon's equations are much nearer to experimental values for NaCl crystal at their maximum temperature 1073 K. Thus the present calculations, for which experimental values are not available, are capable of predicting successfully, the temp dependency of comparison ratio up to 298-1073K.

Experimentally it is found that bulk modulus ( $K_P$ ) decreases linearly on increasing temperature at a constant given pressure. Therefore for NaCl crystal, Kumar equation has least 9.5% variation; Tallon's equation has 18% while a Raju equation has maximum variation - 32% with available experimental data.

Now volume thermal expansion coefficient ( $\alpha_P$ ) also increases on increasing temperature experimentally only for NaCl crystal. So for it we have used only Tallon's equation and Kumar equation & equation) has - 6.9% variation, while equation has 36.8% variation with experimental value respectively at maximum temperature 1073K.

So from isobaric section of work & from table we can conclude that most of cases Tallon's equation of state is much better & capable of predicating successfully the temperature dependence of compression ratio ( $V/V_0$ ), Bulk modulus ( $K_P$ ) and isobaric thermal expansion coefficient ( $\alpha_P$ ) as compare to others as Kumar equations of state, Raju *et al.* equation of state & Fei - Saxena equations of state for theoretical value for 17 crystals of alkali halide at 1073k.

Phenomenological models have been developed by Slater, Tallon, others to study the temperature dependency of elastic constants to understand the thermoelasticity of solids. To know the pressure volume relation of crystals we have to know the interionic potentials, and to evaluate pressure and volume derivatives of bulk modulus.

The crystals considered in the present study to estimate the pressure versus compression ( $V/V_0$ ) values using the from 2<sup>nd</sup> order Birch equation of state are LiF, LiCl, LiBr, LiI, NaBr, NaI, NaF, NaCl (of NaCl structure), and CsCl, (of CsCl Structure). The crystals selected are those which do not exhibit a structural phase transition under the effect of high pressure upto 300 K bar considered in the present work.

## Values of P (K bar) Calculated

In accordance with the 2<sup>nd</sup> order Birch equation of state at room-temperature for alkali halides

**Table 1:** Values of P (K bar) Calculated

V/V <sub>0</sub>	LiF	LiCl	LiBr	LiI	NaF	NaCl	NaBr	NaI	CsCl
1.00	0	0	0	0	0	0	0	0	0
0.98	14.2	6.4	5.0	3.7	9.9	5.1	4.3	3.2	3.9
0.96	30.3	13.6	10.8	8.0	21.2	10.9	9.1	6.9	8.3
0.94	48.8	22.0	17.4	12.9	33.9	17.6	14.6	11.1	13.4
0.92	69.6	31.5	25.0	18.7	48.4	25.1	20.9	15.9	19.2
0.90	93.5	42.5	33.7	25.4	64.9	33.7	28.0	21.4	26.0
0.88	120.8	55.1	43.7	33.1	83.8	43.5	36.2	27.7	33.7
0.86	152.1	69.7	55.3	42.1	105.2	54.7	45.6	35.0	42.7
0.84	188.0	86.5	68.6	52.7	129.8	67.5	56.3	43.2	53.0
0.82	229.4	105.9	84.1	65.0	157.9	82.3	78.7	52.8	65.0

### A comparative study of the second order birch and Murnaghan equations of state for alkali halide crystals:

In the present study, we make a comparative analysis of the Birch and Murnaghan equations of state by retaining the third order terms involving in both the equations of state. As stated earlier, the Birch equation of state is derived from the theory of finite strain by considering Eulerian strain of an elastic isotropic medium under isothermal hydrostatic compression. The form of strain energy adopted here to derive an expression for P is Where only terms up to third order are retained. The Eulerian strain component “f” is defined as The pressure P obtain using the thermodynamic relation.

It should be remarked that the Birch equation of state is applicable up to any value of high pressure whereas the Murnaghan equation of state can be applied only upto such pressures which are well below the critical pressure given by At  $P=P_c$ , the bulk modulus as well as  $V/V_0$  become zero. We have calculated  $P_c$  from equation, using  $K_0$ ,  $K_0'$  and for the crystals under study. The values of  $P_c$  are much higher than the corresponding values of bulk modulus. They are also considerable higher than the transition pressures for structural phase transformation. We can, therefore, apply Murnaghan equation of state up to pressures well below  $P_c$ . In order to obtain the results for the pressure P versus compression ( $V/V_0$ ) with the help of Birch and Murnaghan equations of state, we need and as input data for alkali halides, and alkaline earth oxides. Experimental values of have been compiled from the literature for various ionic solids. For alkali halides the values of have already been reported in Table 6.1. Values of are determined from interionic potentials using the Born-Mayer exponential form  $\exp(-r/a)$  as well as inverse power form  $A/r^n$  for the overlap repulsive energy. The method of calculation and expressions for determining the potential parameters (A, n, C, and) and the pressure' derivative of bulk modulus.

Values of calculated from the two potential forms are rather close to each other as compared to large uncertainties in the experimental values. In the present calculation, we have taken an average of the values of estimated from the two potential functions.

The values of calculated from the interionic potentials along with the ultrasonically measured values of have been used in the present study to compute the pressure versus compression values for five ionic solids using the second order Birch equation of state and the modified Murnaghan equation of state. The crystals chosen for the present study have NaCl, CsCl structures. They do not show any structural phase transition up-to the highest pressure considered in the present work. The P-V data obtained from both the equations of state are considered.

### Conclusion

In the present work, 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 1<sup>st</sup> and 2<sup>nd</sup> 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 has been used, to calculate the pressure versus compression ( $V/V_0$ ) data at room temperature for alkali halide crystals,. These crystals can be compressed to rather high pressures without appearance of any structural phase transformation. We have therefore used interionic potentials with inverse-power function and exponential function for the overlap repulsive energy to evaluate. The resulting P-V data for all the crystals have been found to compare well with the corresponding experimental values. 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.

We have also presented a detailed comparative study of the Birch equations of state and Murnaghan equations of state. First order equations (containing only and second order equations (also containing) for the Birch equations of state as well as the first and second order Murnaghan equations of state have been studied and used to obtain P-V data up to a considerably higher pressure range for Nine alkali halides, It should be remarked that the second order Birch equation of state is applicable to any value of high pressure, whereas the second order Murnaghan equation of state can be applied only up to such pressures which are well below the critical pressure given by. However, this prediction is contradicted by the experimental data. Thus, one has to be careful while applying the second order Murnaghan equation in the higher pressure range approaching  $P_c$ . The results obtained from the second order Murnaghan equation of state and second order Birch equation of state have been found to present close agreement with each other as well as with experimental values for LiF and NaF up to nearly 100 k bar. The results deviate significantly from each other at higher pressure. The results obtained from the second order Birch equation present better agreement with experimental values as compared to the first order Birch equation. On the other hand, the results obtained from the Murnaghan equations deviate significantly in the high pressure region. The data obtained from the first order Murnaghan equation of state are significantly higher, whereas those obtained from the second order Murnaghan equation of state are significantly

lower than the experimental values. Thus, the second order Birch equation of state yields the closest agreement with the experimental data.

The main contribution of present study into predict the P-V-T data as well as the thermal expansivity ( $\alpha$ ) for NaCl crystal at simultaneously elevated temperature and pressure using temperature corrected modified Murnaghan equation of state<sup>[50]</sup>, involving five parameters. The five parameters are  $a_0$  and  $b_0$ , where subscripts '0' implies values of the parameter at initial temperature ( $T_0$ ) and initial pressure ( $P_0$ ). Fei and Saxena have used this equation to predict molar values of NaCl at elevated temperature and pressures up to 773K and 35 k bar respectively and compared it with the experimental data reported to Boehler-Kennedy.

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