

Thermal and elastic properties of sodium chloride at high temperature

S. K. SRIVASTAVA AND PALLAVI SINHA

*Geeta Institute of Management and Technology,
Kanipla, Kurukshetra, 136 118 Haryana, India
Phone: +91-8059521027; Fax: +91-1744-279801*

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In the present study, the Anderson-Isaak approximation for volume dependence of the Anderson-Grüneisen parameter is modified with the addition of an assumption regarding the volume dependence of thermoelastic parameter (k). New expressions for volume dependence of δ_T and thermal expansivity are obtained; those follow the constraints of high pressure thermodynamics in the limit of infinite pressure. The modified expression is used to estimate temperature dependence of elastic moduli for NaCl. A close agreement between theory and experiment reveals the validity of present approach.

Keywords: Anderson-Grüneisen parameter; thermal expansivity; elastic constants.

1 INTRODUCTION

Thermal expansivity is a very important physical parameter to understand the high temperature and high pressure behaviour of solids. It is also used to solve many problems of material science and condensed matter physics. Thermal expansivity is directly related to many thermal and elastic parameters of thermal physics. It is found that the uncertainty in many thermodynamic functions arises due to uncertainty in thermal expansivity. Various attempts [1–5] have been made to find the values of thermal expansivity for minerals at high pressure. In these studies the computation of volume dependence of thermal

*Corresponding author: sanjeevsrivastava1980@rediffmail.com

expansivity is done with the help of the volume dependence of the Anderson-Grüneisen parameter (δ_T).

The ceramic science requires the knowledge of temperature dependence of elastic properties of materials. The knowledge of temperature dependence of elastic moduli is of central importance for understanding the thermo elastic behaviour of solids in high temperature region. The elasticity provides more information than the volume to understand the temperature dependence of equations of state because the bulk modulus is defined by the derivative of pressure. A variety of attempts [6–11] have been made to study elastic constants of solids. Some phenomenological, semi phenomenological and empirical formulations have been developed to understand the change in elastic constants with the change in temperature at atmospheric pressure. Besides being the considerable theoretical interests there is still no complete general theory that should be used for precise calculations of elasticity. In the present study, we have developed a new model to understand the pressure or volume dependence of thermal expansivity along an isotherm for NaCl. The material NaCl is used as best test bed for the study because the Sodium Chloride (NaCl) is one of the most studied inorganic material and a typical ionic solid. In laboratory measurement of compression data, the material NaCl is used as a pressure gauge. This is one of the most widely used internal pressures standard in high-pressure diffraction experiment. The resulted expression is obtained with the help of modification in Anderson- Isaak expression [2] for volume dependence of the Anderson-Grüneisen parameter. The newly developed expression is also used along isobaric condition at $P = 0$ and applied to estimate the temperature dependence of elastic constants. The method of analysis is shown in Section 2 and results are discussed in Section 3.

2 METHOD OF ANALYSIS

The Anderson-Grüneisen parameter is an important physical quantity for understanding the thermo elastic properties of solids at high pressures and high temperatures [12,13]. The isothermal Anderson-Grüneisen parameter (δ_T) is defined as follows [12,13];

$$\delta_T = -\frac{1}{\alpha K_T} \left(\frac{\partial K_T}{\partial T} \right)_P \quad (1)$$

where α is the volume thermal expansion coefficient or thermal expansivity and K_T is the isothermal bulk modulus. These parameters are expressed as follows;

$$\alpha = \frac{1}{V} \left(\frac{\partial V}{\partial T} \right)_P \quad (2)$$

and

$$K_T = -V \left(\frac{\partial P}{\partial V} \right)_T \quad (3)$$

Using the following thermodynamic identity [13];

$$\left(\frac{\partial \alpha}{\partial P} \right)_T = \frac{1}{K_T^2} \left(\frac{\partial K_T}{\partial T} \right)_P \quad (4)$$

in eq. (1), we get

$$\delta_T = \frac{V}{\alpha} \left(\frac{\partial \alpha}{\partial V} \right)_T \quad (5)$$

Relationship (5) is very important to understand the behaviour of thermal expansivity under the change in volume or compression along an isotherm. Thus, to investigate the volume dependence of thermal expansivity, it is required to know the volume dependence of the Anderson-Grüneisen parameter. Various expressions for volume dependence of the Anderson-Grüneisen parameter are available in literature [1,2,4,5]. Anderson and Isaak [2] approximated following power law for variation of δ_T with volume, along an isotherm;

$$\delta_T = \delta_T^0 \left(\frac{V}{V_0} \right)^k \quad (6)$$

where $\delta_T = \delta_T^0$ at $V = V_0$. The k is a thermoelastic constant. With the help of eqs. (5) and (6). Anderson-Isaak [2] obtained next expression for volume dependence of thermal expansivity.

$$\frac{\alpha}{\alpha_0} = \exp \left[-\frac{\delta_T^0}{k} \left\{ 1 - \left(\frac{V}{V_0} \right)^k \right\} \right] \quad (7)$$

Now, According to high pressure thermodynamics [14–16] the Anderson-Grüneisen parameter remains finite and thermal expansivity tends to zero at infinite pressure or at zero volume ($P \rightarrow \infty, V \rightarrow 0$). Unfortunately, neither eq. (6) nor eq. (7) follow the above boundary conditions at infinite pressure ($P \rightarrow \infty, V \rightarrow 0$). Such deficiency in relationships (6) and (7) may be due to the invariant nature of k with respect to volume. Therefore, we assume that k is not a volume independent term but varies with the change in volume as follows, as a simple choice;

$$k = k_0 \left(\frac{V}{V_0} \right) \quad (8)$$

where $k = k_0$ at $V = V_0$. Now using the next relationship [2,13]

$$k = \left(\frac{\partial \ln \delta_T}{\partial \ln V} \right)_T \quad (9)$$

we acquire subsequently expression for volume dependence of the Anderson-Grüneisen parameter;

$$\delta_T = \delta_T^0 \exp \left[k_0 \left\{ \left(\frac{V}{V_0} \right) - 1 \right\} \right] \quad (10)$$

The corresponding expression for volume dependence of thermal expansivity (α) can be obtained with the help of eqs. (5) and (10), as given below;

$$\ln \left(\frac{\alpha}{\alpha_0} \right) = \int_{V_0}^V \frac{\delta_T^0}{V} \exp \left[k_0 \left\{ \left(\frac{V}{V_0} \right) - 1 \right\} \right] dV \quad (11)$$

Since the value of $[(V/V_0)-1]$ is less than 1, therefore, we can expand the exponential term up to second order only, as higher order terms are insignificant. Thus, the solution of eq. (11) is given by following relationship

$$\left(\frac{\alpha}{\alpha_0} \right) = \left(\frac{V}{V_0} \right)^{\delta_T^0 \left(1 - k_0 + \frac{k_0^2}{2} \right)} \exp \left[\delta_T^0 k_0 \left\{ (1 - k_0) \left(\frac{V}{V_0} - 1 \right) + \frac{k_0}{4} \left[\left(\frac{V}{V_0} \right)^2 - 1 \right] \right\} \right] \quad (12)$$

3 RESULTS AND DISCUSSION

Here, we get finite value of δ_T and zero value of α at infinite pressure ($P \rightarrow \infty, V \rightarrow 0$), with the help of relationship (8). In other sense, the resulted expressions (10) and (12) follow the constraints of high pressure thermodynamics [14–16] in the limit of infinite pressure. Therefore, the deficiency in relationships (6) and (7) is removed in the present study with the help of an approximation given by eq. (8).

Now, to check the suitability of newly developed expression (12), we require the value of δ_T^0 and k_0 . To investigate the value of k_0 , we used the infinite pressure behaviour of the Anderson-Grüneisen parameter. The infinite pressure value of the Anderson-Grüneisen parameter ($\delta_{T\infty}$) can be obtained with the help of eq. (10). Putting $V = 0$ in eq. (10), we get

$$\delta_{T\infty} = \delta_T^0 \exp(-k_0) \quad (13)$$

The inter-relationship between infinite pressure value of the first pressure derivative of isothermal bulk modulus (K'_{∞}) and $\delta_{T\infty}$ is given by following expression [5];

$$\delta_{T\infty} = K'_{\infty} - 1 \quad (14)$$

Therefore, eq. (13) can also be written as follows;

$$(K'_{\infty} - 1) = \delta_T^0 \exp(-k_0) \quad (15)$$

Following the Thomas-Fermi model, according to which $K'_{\infty} = (5/3)$, we get $k_0 = 2$ for NaCl, as the value of δ_T^0 is equal to 5.3 [17]. It should be included that the Thomas-Fermi model is used extensively in literature [18–23].

Again, the experimental data on volume dependence of thermal expansivity are available for NaCl in literature [17]. These data are obtained by combination of the several kinds of experimental data and used by Anderson [13] in further analysis of the volume dependence of the Anderson-Grüneisen parameter (δ_T) and thermal expansivity (α) of NaCl. Such experimentally determined values are used to judge the suitability of newly developed expression for volume dependence of thermal expansivity. Under the condition $k_0 = 2$, relationship (12) converts in following format;

$$\left(\frac{\alpha}{\alpha_0}\right) = \left(\frac{V}{V_0}\right)^{\delta_T^0} \exp \left[2\delta_T^0 \left\{ \left(1 - \frac{V}{V_0}\right) + \frac{1}{2} \left[\left(\frac{V}{V_0}\right)^2 - 1 \right] \right\} \right] \quad (16)$$

The relationship (16) provides a way to compute volume dependence of thermal expansivity for NaCl. Thus, we predicted compression dependence of thermal expansivity for NaCl, with the help of eq. (16). The predicted values are compared with available experimental data [17] in Table 1. An excellent agreement between theory and experiment reveals the validity of present approach.

Deng and Yan [24] analyzed P-V-T relationships and thermodynamic properties of some alkali halides including NaCl. They considered Anderson-Isaak approximation {eq. (6)} along isobaric expansion and shown the validity of their assumption. In the similar manner, we expect that the newly developed relationship (10) is also valid along an isobar, especially at atmospheric pressure. Under this condition, the relationship (10) can also be expressed as follows for NaCl;

$$\delta(T, P) = \delta(T_0, P) \exp \left[2 \left\{ \frac{V(T, P)}{V(T_0, P)} - 1 \right\} \right] \quad (17)$$

TABLE 1

A comparison of computed values of thermal expansivity with available experimental data.

$P(\text{GPa})$	$\left(\frac{V}{V_0}\right)$	$\alpha \left(10^{-5} \text{ K}^{-1}\right)$	
		Eq. (16)	Exp. (17)
0	1.0000	11.9	11.9
1	0.9627	9.8	9.8
2	0.9324	8.4	8.5
3	0.9067	7.4	7.5
4	0.8845	6.7	6.7
5	0.8649	6.1	6.1
10	0.7910	4.3	4.3
15	0.7397	3.4	3.4
20	0.7004	2.9	2.9
25	0.6685	2.5	2.5
30	0.6416	2.2	2.2

Following relationship is applicable, along an isobar [13];

$$\delta_T = -\frac{V}{K_T} \left(\frac{dK_T}{dV} \right)_P \quad (18)$$

With the help of eqs. (17) and (18), we get following expression for volume dependence of isothermal bulk modulus at atmospheric pressure;

$$\left(\frac{K_T}{K_T^0} \right) = \left(\frac{V}{V_0} \right)^{-\delta_T^0} \exp \left[2\delta_T^0 \left\{ \left(\frac{V}{V_0} - 1 \right) + \frac{1}{2} \left(1 - \left(\frac{V}{V_0} \right)^2 \right) \right\} \right] \quad (19)$$

Using the method of generalization [25] we get next relationship for variance of elastic constants with the change in volume expansion at $P = 0$. The generalized form of eq. (19) can be written as follows;

$$\left(\frac{C_{ij}}{C_{ij}^0} \right) = \left(\frac{V}{V_0} \right)^{-\delta_{ij}^0} \exp \left[2\delta_{ij}^0 \left\{ \left(\frac{V}{V_0} - 1 \right) + \frac{1}{2} \left(1 - \left(\frac{V}{V_0} \right)^2 \right) \right\} \right] \quad (20)$$

where C_{ij} is a second order elastic constant and δ_{ij} is the associated Anderson-Grüneisen parameter. To check the validity of eq. (20), we computed values of temperature dependence of elastic constants for NaCl and compared with available experimental data [12] in Figure 1. The values of temperature dependence of volume expansion ratio are extracted from the experimental

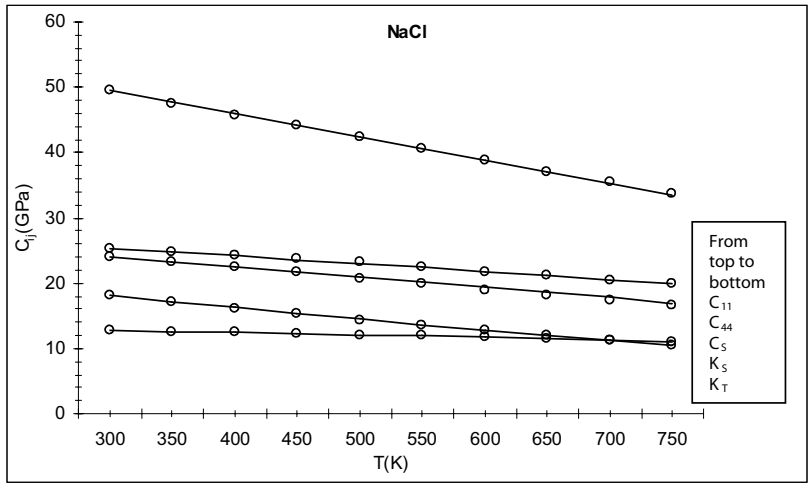


FIGURE 1
Temperature dependence of elastic moduli of NaCl. Calculated values are shown by line and experimental data [12] are represented with the help of points.

TABLE 2
Input parameters used in computational process.

Elastic Constant (C_{ij})	C_{ij}^0 (Gpa) [12]	δ_{ij}^0
C_{11}	49.5	6.0
C_{14}	12.79	2.2
C_s	18.1	8.5
K_s	25.3	3.7
K_T	24.0	5.3

data [12,13] and other required parameters are shown in Table 2. A close agreement is obtained between calculated and experimentally determined values.

Thus, we studied the thermal and elastic properties of Sodium chloride. The study is based on an assumption that the thermo-elastic constant is a volume dependent term, which modifies the Anderson-Isaak approximation of volume dependence of the Anderson-Grüneisen parameter. This approximation is forced to accept because the existing formulations do not satisfy the boundary conditions of extreme pressure or fundamentally not consistent with high pressure thermodynamics [14–16]. A new expression for volume dependence of thermal expansivity is obtained and applied successfully on the material of interest. It is also found that the newly developed expression for volume dependence of the Anderson-Grüneisen parameter is also applicable for isobaric expansion, especially at atmospheric pressure, and used to

estimate the temperature dependence of elastic constants of NaCl. A close agreement between theory and experiment is found, which in turn reveals the validity of our approach.

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