

Analysis of volume dependence of thermal expansivity for NaCl

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Received 28 January 2016; revised 2 September 2016; accepted 27 February 2017

In the present paper, a suitable model to evaluate the volume dependence of thermal expansivity α by using the reciprocal form of volume dependence of Anderson-Grüneisen parameter (δ_T) has been proposed. The newly developed relationship has satisfied the constraints of infinite pressure behavior, i.e., $P \rightarrow \infty$ or $V \rightarrow 0$. The results obtained through the present model show the consistency with the experimental data for NaCl.

Keywords: Thermal Expansivity, Grüneisen parameter, Anderson-Grüneisen parameter, NaCl

1 Introduction

Thermal expansivity α is very important thermodynamic parameter for modelling the equation of state of the Earth's interior at high temperatures and high pressures. It is a necessary parameter for solving many materials science problems and is useful for understanding the nature of stress in materials. Thermal expansivity has been related to other thermodynamic parameters through Grüneisen parameter. It is an important factor in the equations interpreting many important properties of solids, i.e., infinite pressure behavior of thermodynamic and thermoelastic properties of solids¹, because it has been emphasized² that most of the serious errors in the calculations of thermodynamic functions arise due to uncertainty of thermal expansivity. Various attempts³⁻¹⁴ have been made to find the high temperatures and pressures data of thermal expansivity for solids.

Because of the necessity to understand the high temperatures and high pressures properties for NaCl which is one of the most studied inorganic crystal and a typical ionic solid. This solid has been used as a pressure gauge in laboratory measurements of compression data by many researchers^{15,16}. NaCl has a stable B1 (rocksalt) structure up to a pressure of about 30 GPa, and its melting temperature is nearly 1074 K. This may explain the stability of rocksalt NaCl under normal temperature and pressure. Besides, NaCl exhibits phase transition under high pressure because B1 phase becomes less stable with decreased cell volume. Thus we have a wide range of pressures and

temperatures for studying the equations of state and thermoelastic and thermodynamic properties of NaCl.

In the present study, we have made an attempt to derive a new relationship for volume dependence of thermal expansivity on the basis of the reciprocal form for volume dependence of the isothermal Anderson-Grüneisen parameter. NaCl is used to check the validity of the present formulation.

2 Thermal Expansivity

2.1 Theory of thermal expansivity

The isothermal Anderson-Grüneisen parameter δ_T is defined as¹⁷:

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

where α is volume thermal expansivity which is defined as¹⁷:

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

and K_T is isothermal bulk modulus which is given by¹⁷:

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

In addition, for describing the temperature dependence of the isothermal bulk modulus δ_T has been used for the discussion of pressure dependence of thermal expansivity. We can understand the

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pressure dependence of α through Maxwell's relation as:

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

Using this thermodynamic identity (Eq. (4)) in Eq. (1), we get:

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

2.2 Formulation for thermal expansivity

Al'tshuler *et al.*¹⁸ has given the following expression for Grüneisen parameter:

$$\gamma = \gamma_\infty + (\gamma_0 - \gamma_\infty) \left(\frac{V}{V_0}\right)^\beta \quad \dots (6)$$

where γ_0 and γ_∞ are, respectively, the values of Grüneisen parameter γ at $P=0$ or $V \rightarrow V_0$ and $P \rightarrow \infty$ or $V \rightarrow 0$ and β is an adjustable parameter.

Shanker *et al.*¹⁰ pointed out the similarity for the volume dependence of γ and δ_T as:

$$\delta_T = \delta_{T_\infty} + (\delta_{T_0} - \delta_{T_\infty}) \left(\frac{V}{V_0}\right)^n \quad \dots (7)$$

where δ_{T_0} and δ_{T_∞} are, respectively, the values of δ_T at $P=0$ or $V \rightarrow V_0$ and $P \rightarrow \infty$ or $V \rightarrow 0$ and n is an adjustable parameter.

Sharma¹³ has given a simple choice for reciprocal form for the volume dependence of isothermal Anderson-Grüneisen parameter (δ_T) as:

$$\frac{1}{\delta_T} = \frac{1}{\delta_{T_\infty}} + \left(\frac{1}{\delta_{T_0}} - \frac{1}{\delta_{T_\infty}}\right) \left(\frac{V}{V_0}\right)^m \quad \dots (8)$$

where m is a dimensionless fitting parameter.

Using Eq. (8) with Eq. (5) one can get the following equation:

$$\frac{\alpha}{\alpha_0} = \left(\frac{V}{V_0}\right)^{\delta_{T_\infty}} \left(\frac{\delta_T}{\delta_{T_0}}\right)^{\delta_{T_\infty}/m} \quad \dots (9)$$

where α_0 , δ_{T_0} are, respectively, the values of α , δ_T at $P=0$ however, δ_{T_∞} is the value of δ_T at $P \rightarrow \infty$ or $V \rightarrow 0$.

3 Results and Discussion

Chopelas-Boehler⁴, Anderson-Isaak⁵ and Srivastava *et al.*¹⁹ have used the following expressions to evaluate the volume dependence of thermal expansivity, respectively:

$$\frac{\alpha}{\alpha_0} = \left(\frac{V}{V_0}\right)^{-1} \exp\left[-(\delta_{T_0} + 1)\left(1 - \frac{V}{V_0}\right)\right] \quad \dots (10)$$

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

where κ is an dimensionless thermoelastic parameter:

$$\frac{\alpha}{\alpha_0} = \frac{1}{\left[1 + \frac{\delta_{T_0}}{\delta_{T_\infty}} \left\{\left(\frac{V}{V_0}\right)^{-\delta_{T_\infty}} - 1\right\}\right]} \quad \dots (12)$$

The value of δ_{T_∞} is calculated by using the well known thermodynamic identity²⁰:

$$\delta_T = K_T' + q - 1 + C_T' \quad \dots (13)$$

where K_T' is the first-order pressure derivative of isothermal bulk modulus (K_T) which is defined as:

$$K_T' = \left(\frac{\partial K_T}{\partial P}\right)_T \quad \dots (14)$$

The last term in Eq. (13) is:

$$C_T' = \left(\frac{\partial \ln C_V}{\partial \ln V}\right)_T \quad \dots (15)$$

C_V is the specific heat at constant volume and q , the second Grüneisen parameter which are respectively defined as¹⁷:

$$C_V = \left(\frac{dU}{dT}\right)_V \quad \dots (16)$$

$$q = \left(\frac{d \ln \gamma}{d \ln V}\right)_T \quad \dots (17)$$

At infinite pressure ($P \rightarrow \infty$) or $V \rightarrow 0$, Eq. (13) becomes:

Table 1 — The values of Input parameters used in calculations

| Solid NaCl | K'_0 | δ_{T_0} | K'_∞ | δ_{T_∞} | m | $\alpha_0 (10^{-5}K^{-1})$ | κ |
|---------------|---------------------------|---------------------------|-------------|---------------------|-------|----------------------------|--------------------------|
| | 5.5 (Ref. ²⁸) | 5.3 (Ref. ²⁸) | 3.3 | 2.3 | 1.856 | 11.9 (Ref. ²⁸) | 1.4 (Ref. ⁵) |

$$\delta_{T_\infty} = K'_\infty + q_\infty - 1 + C'_{T_\infty} \quad \dots (18)$$

Since²¹ at $P \rightarrow \infty$ or $V \rightarrow 0, q \rightarrow 0$ in high temperature and high pressure region²¹, $C'_{T_\infty} \rightarrow 0$ at $P \rightarrow \infty$ or $V \rightarrow 0$, Now Eq. (18) becomes:

$$\delta_{T_\infty} = K'_\infty - 1 \quad \dots (19)$$

To discuss δ_{T_∞} , we must keep in our mind the following thermodynamic identities²⁰:

$$\left[\frac{\partial \ln(\alpha K_T)}{\partial \ln V} \right]_T = \delta_T - K'_T \quad \dots (20)$$

and

$$\left[\frac{\partial \ln(\alpha K_T)}{\partial \ln V} \right]_S = q - 1 \quad \dots (21)$$

Equation (20) has been used by many researchers^{9,22-27} to discuss the nature of variation in product αK_T with volume. From Eq. (20), $\alpha K_T \rightarrow \infty$ only when $\delta_T - K'_T$ is negative at $P \rightarrow \infty$ which gives that δ_{T_∞} must be less than K'_∞ . Thus the value of δ_{T_∞} should be constrained by the relationship⁹:

$$0 < \delta_{T_\infty} < K'_\infty \quad \dots (22)$$

Following Stacey-Davis model²¹, i.e., $K'_\infty = \frac{3}{5} K'_0$ where K'_0 is the value of first pressure derivative of isothermal bulk modulus (K'_T) at $P = 0$ and room temperature, i.e., $T_0 = 300$ K. The value of δ_{T_∞} obtained from Eq. (19) for solid under consideration and the calculated value satisfies the constraint (Eq. (22)).

The input parameters used in the present calculations are cited in Table 1. We have estimated the values of thermal expansivity through Eq. (9). For direct vision we have plotted the graph for the values

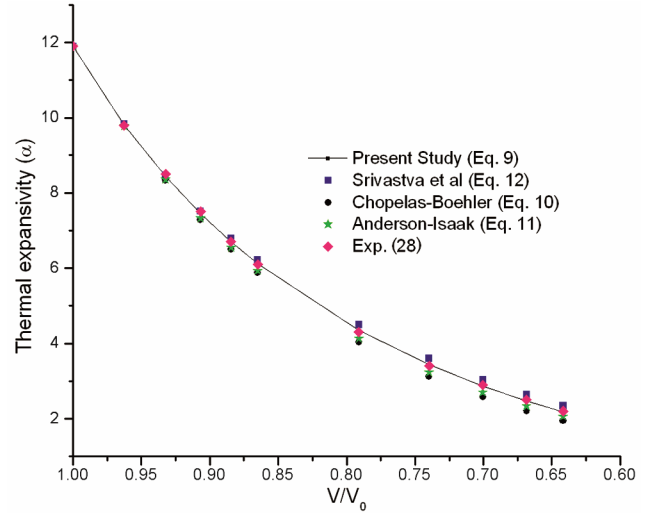


Fig. 1 — Plot for the values of thermal expansivity ($10^{-5}K^{-1}$) versus volume ratios for NaCl

of thermal expansivity versus volume ratios in Fig. 1 along with experimental data²⁸. It is clear that the values of α through Eq. (9) are much better than those values extracted through Eqs (10-12). It is emphasized here that the better competency of proposed relationship as evident from Fig. 1 reveals the support of the present model and also satisfies the thermodynamic constraint^{20,21} i.e. $\alpha \rightarrow 0$ at $P \rightarrow \infty$ or $V \rightarrow 0$.

4 Conclusions

An expression for the volume dependence of Thermal expansivity by using the reciprocal form of volume dependent Anderson- Grüneisen parameter has been proposed. It has been found that the results obtained through Eq. (9) shows the consistency with those values given by Birch²⁸ for NaCl. Thermal expansivity decreases as volume decreases. The present formulation satisfies the thermodynamic constraint^{9,10,20-22}, i.e., $\alpha \rightarrow 0$ at $P \rightarrow \infty$ or $V \rightarrow 0$. Equation (8) also satisfies the thermodynamic constraint^{10,21}, i.e., $\delta_T \rightarrow \delta_{T_\infty}$. The basic thermodynamic assumption supports the validity of Eq. (9). At last, we can say that one can use the reciprocal form of Anderson- Grüneisen parameter; as the most remarkable is the Stacey reciprocal K-primed Equations of State (EOS)²³.

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