A New Simple Model on the Volume and Pressure Dependence of Thermal Expansivity for Sodium Chloride

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Adopting the assumption that the second Grüneisen parameter q is volume-independent, we derived straightforward the volume dependence of the Anderson–Grüneisen parameter $\delta_T(V)$ according to the Anderson relationship and the Tait equation of state. On the basis of this revised $\delta_T(V)$, a simple empirical model on the volume and pressure dependence of the thermal expansivity in solids is developed. The calculated results are in good agreement with the experimental data for sodium chloride. A comparison of our model with the previous was discussed, which confirms that the developed model is slightly superior to Anderson's work [J. Geophys. Res. **72**, 3661 (1967)] and Fang's work [High Temp. – High Press. **31**, 507 (1999)].

Key words: Thermal Expansivity; Equation of State; Anderson–Grüneisen Parameter; Sodium Chloride.

1. Introduction

The thermal expansivity in solids is an interesting physical phenomenon characterizing the anharmonic effect of interaction between atoms or molecules and can be related to some other thermodynamic and mechanic quantities, such as specific heat, elastic constants, Grüneisen parameter, etc. So the theory of thermal expansivity plays a central role in describing the high temperature and high pressure behaviour of solids [1, 2]. Due to the experimental difficulties, the accurate data on volume or pressure dependence of thermal expansivity are often scarce at high temperatures and high pressures. Thus the reliable semiempirical or theoretical models are useful for evaluating and predicting high temperature and high pressure thermal expansivity. For many years researchers have developed theoretical models to evaluating the volume and pressure dependence of thermal expansivity in solids, and obtained some good theoretical results agreeing with the experimental data [3, 4].

Anderson presented a simple expression on the volume thermal expansivity suitable for several materials of geophysical interest [3],

$$\alpha = \alpha_0 \eta^{\delta_{T_0}}, \tag{1}$$

which is useful for analyzing the thermal expansivity of solids [5 – 8]. Where α_0, δ_{T_0} are the values of thermal expansion coefficient α and Anderson–Grüneisen parameter δ_T at pressure $P = 0$, respectively, and $\eta = V/V_0$ is the compression ratio of volume V. Equation (1) comes from the integration of the isothermal Anderson–Grüneisen parameter $\delta_T = (\partial \ln \alpha / \partial \ln \eta)_T$ when taking δ_T as a volume or pressure independent constant. The predicted results of Anderson's theory agreed with the experimental data for alpha quartz, spinel, garnet, MgO, and Al_2O_3 [3].

Fang proposed an expression on the pressure dependence of thermal expansivity [4] as

$$\alpha = \alpha_0 \left(1 + \frac{B_0' P}{B_0}\right)^{\frac{1-q-B_0'}{B_0'}}, \tag{2}$$

where B_0 and B_0' are the values of the isothermal bulk modulus B_T and its first pressure derivative B_T' at pressure $P = 0$, respectively, and q is the second Grüneisen parameter. Equation (2) is derived from the relationship for the variation of the Grüneisen parameter γ with pressure [9],

$$\frac{\gamma}{\gamma_0} = \left(1 + \frac{B_0' P}{B_0}\right)^{-\frac{q}{B_0'}}, \tag{3}$$

where γ_0 is the initial value of the Grüneisen parameter at zero pressure. Equation (2) gives a good description of the pressure dependence of thermal expansivity for sodium chloride at 300 K, 550 K, and 800 K. In the present paper, firstly a new volume dependence of the Anderson–Grüneisen parameter $\delta_T(\eta)$ is derived according to the assumption of volume-independent q; based on this revised $\delta_T(\eta)$, a model for evaluating the volume and pressure dependence of thermal expansivity in solids is developed. The comparison between the calculated results and experimental data of sodium chloride at three temperatures indicates that the new computing formula for α is superior to (1) and (2).

2. Method of Analysis

Anderson [10] pointed out the relationship between the Anderson–Grüneisen parameter δ_T, B'_T, and q, in the quasi-harmonic approximation and at high temperatures, which might be described as the Anderson relationship

$$\delta_T = B'_T + q - 1, \tag{4}$$

with which we investigated the Grüneisen parameter [11, 12] and bulk modulus [13] at high temperature and high pressure. q in (4) has been reported experimentally to be approximately constant for many solids [14, 15], and the treatment of volume-independent q is adopted frequently to study the pressure dependence of the Grüneisen parameter [9] and other thermodynamical properties [16]. So q in the following text is also considered as volume-independent.

The pressure derivative of the Tait equation of state (EOS) [17]

$$\eta = 1 - \frac{1}{B'_0 + 1} \ln\left(1 + \frac{B'_0 + 1}{B_0} P\right) \tag{5}$$

gives

$$B'_T = \left(B'_0 + 1\right)\eta - 1. \tag{6}$$

Combing (4) and (6) yields

$$\delta_T = \left(B'_0 + 1\right)\eta + q - 2, \tag{7}$$

which is a new expression to predict the volume dependence of the Anderson–Grüneisen parameter. Integrating the Anderson–Grüneisen parameter $\delta_T = (\partial \ln \alpha / \partial \ln \eta)_T$, we obtain immediately

$$\alpha = \alpha_0 \eta^{q-2} \exp\left[\left(B'_0 + 1\right)\left(\eta - 1\right)\right]. \tag{8}$$

Equation (8) is a new computing formula which can be used to predict the volume dependence of thermal expansivity. The volume compression ratio η in (8) can be obtained with the help of EOS. In view of (6), the basis of (8), being derived from (5), η is calculated by using Tait EOS (5). To test the validity of this new computing model, we have applied (8) to the experimental data of sodium chloride at 300 K, 550 K, and 800 K, respectively. For the sake of comparison, the experimental data of the thermal expansion coefficient were taken from [15] and [18], as is done by Fang [4], and the parameters B_0, B'_0, and q used in computing are the same as Fang's. The calculated results are plotted in Figures 1–3. Meanwhile, we also calcu-
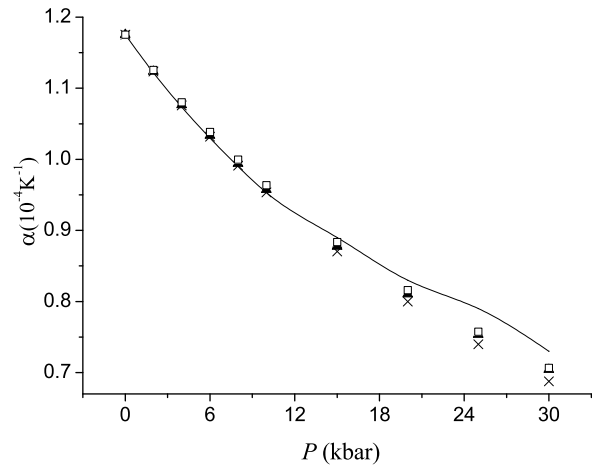

Fig. 1. Pressure dependence of thermal expansion coefficient for sodium chloride at 300 K. □: Anderson's work (1); ×: Fang's work (2); ▲: this work (8); —: experimental ([15] and [18])
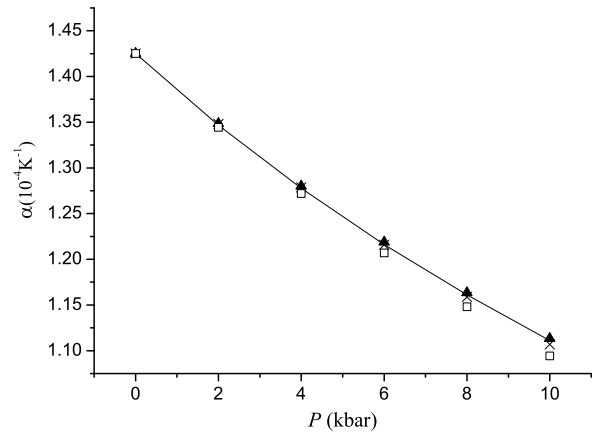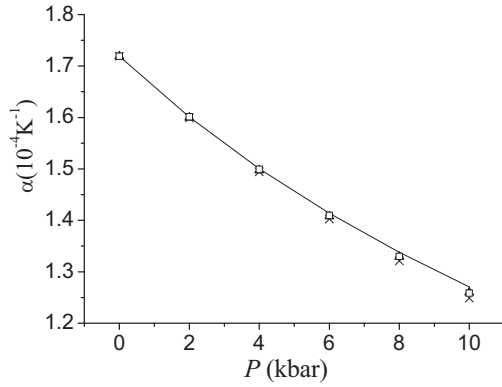

Fig. 2. The same as in Figure 1, at 550 K.

Fig. 3. The same as in Figure 1, at 800 K.

Table 1. Root mean square deviation (10^{-6} K^{-1}) between the values calculated with the three equations [(1), (2), and (8)] and experimental values of the thermal expansion coefficient for sodium chloride.

Temperature (K)	Anderson's work (1)	Fang's work (2)	This work (8)
300	1.5	2.4	1.6
550	1.0	0.2	0.2
800	0.6	1.2	0.6

lated the root mean square deviation (RMSD) between the theoretical values with the three equations [(1), (2), and (8)] and experimental values of the thermal expansion coefficient at three temperatures, as shown in Table 1.

3. Results and Discussion

(i) According to Figures 1 – 3 and the corresponding RMSD listed in Table 1, all the calculated results with (1), (2), and (8) agree with the experimental data. However, comparatively speaking, it can be seen that (8) is slightly superior to (1) and (2) on the degree of agreement with experiment. The calculated results of this work are slightly superior to those yielded by (1) and (2) although (8) and the other two equations have an identical deviation at a certain temperature (to see RMSDs in Tab. 1). Especially in the case of higher pressure or smaller volume compression ratio V/V_0, this work seems to be more valid, as shown in Figures 1 – 3. So the new theoretical model proposed here on the volume and pressure dependence of the Anderson–Grüneisen parameter and the thermal expansivity, i.e. (7) and (8) respectively, are justified at least for sodium chloride.

(ii) The term $\exp(\eta - 1)$ in (8) can be expanded as

$$\exp(\eta - 1) = \eta + \frac{1}{2}(\eta - 1)^2 + \frac{1}{6}(\eta - 1)^3 + \cdots. \tag{9}$$

At low pressures, the higher orders (≥ 2) of $(\eta - 1)$ can be left out. Then (8) gives

$$\alpha = \alpha_0 \eta^{q-2} \eta^{B'_0+1}, \tag{10}$$

i. e.,

$$\alpha = \alpha_0 \eta^{B'_0+q-1}. \tag{11}$$

In view of $B'_0 + q - 1 = \delta_{T_0}$, (11) is just (1), which suggests that Anderson's work [3] could be considered as one case of (8) at low pressure.

Additionally, Equation 2 of Fang's work [4] is on the basis of the well-known Murnaghan EOS,

$$\eta = \left(1 + \frac{B'_0}{B_0}P\right)^{-\frac{1}{B'_0}}. \tag{12}$$

According to (12), (2), and $B'_0 + q - 1 = \delta_{T_0}$, it is not difficult to find that (1) and (2) are identical in physics although they are expressed in two different formula. So (1) and (2) could be considered as an approximation of (8) at low pressure, which may be the reason why (8) is superior to (1) and (2).

(iii) The experimental values of the second Grüneisen parameter q are close to unity for many solids including sodium chloride [14, 19, 20]. If we take $q = 1$, then (4) changes into

$$\delta_T = B'_T, \tag{13}$$

according to which Kumar derived a useful general isothermal equation, which gives a good description on the $P - V$ relationship for alkaline halide [21].

In view of the definition $\delta_T = (\partial \ln \alpha / \partial \ln \eta)_T$ and $B'_T = -(\partial \ln B_T / \partial \ln \eta)_T$, one can easily get

$$\left(\frac{\partial \ln(\alpha B_T)}{\partial \ln \eta}\right)_T \equiv \delta_T - B'_T. \tag{14}$$

Equation (13) considers δ_T as B'_T, which means

$$\alpha B_T = \text{const} \tag{15}$$

along an isotherm, which has been found to be a good approximation for many solids at high temperatures [10, 12, 22 – 24]. So the consideration of volume-independent q is useful for analyzing the thermodynamic properties, and thus the adoption of volume-independent q in the present paper seems to be reasonable.

We also note that (7) can be rewritten as the Chopelas relationship [11, 25] with the help of (13), i. e. $q = 1$,

$$\delta_T = \left(\delta_{T_0} + 1\right) \eta - 1 \,. \tag{16}$$

Using (16) in $\delta_T = (\partial \ln \alpha / \partial \ln \eta)_T$, the volume dependence of the thermal expansivity becomes

$$\alpha = \alpha_0 \eta^{-1} \exp \left[(B'_0 + 1)(\eta - 1) \right] \,, \tag{17}$$

which is Kumar's work [25]. Obviously (17) is just our work (8) at $q = 1$. The results calculated with (17) are in agreement with the available experimental data for sodium chloride [25], which reveals thus a wider application range of this work (8).

In brief, we have proposed straightforward a simple and useful model on the volume and pressure dependence of thermal expansivity, which is suitable for sodium chloride. It should be pointed out that, although (8) gives a better description for thermal expansivity of sodium chloride, we suggest that this model is applied under medium pressure ranges because of the limit of the Tait EOS which dose not satisfy the infinite pressure behaviour limit. To obtain the thermodynamic properties of very high pressure case $P \rightarrow \infty$, a suitable EOS is needed. Stacey and Davis [26] and Sharma and Sharma [27] suggested an approach introducing new parameters at extremely high pressure, also this is another interesting topic but not the aim of the present paper.

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