

THERMAL EXPANSIVITY OF SODIUM CHLORIDE AND MAGNESIUM OXIDE AT HIGH PRESSURES AND HIGH TEMPERATURES

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ABSTRACT

We have developed a new model for determining the thermal expansivity of solids at high pressures and high temperatures up to the melting points. The model has been applied to determine values of thermal expansivity of NaCl and MgO for a wide range of pressures and temperatures. The main finding is that the thermal expansivity decreases with the increase in pressure, and increases with the increase in temperature. The rate of increase of thermal expansivity with temperature calculated along different isobars is found to decrease rapidly with the increase in pressure. This finding is consistent with the thermodynamic constraint according to which the thermal expansivity must approach zero in the limit of extreme compression.

Keywords: Thermal Expansivity, NaCl, MgO, Extreme Compression, High Temperatures

1 INTRODUCTION

Thermal expansivity or volume thermal expansion coefficient is an important physical property of materials [1]. It gives us valuable information regarding the variations of volume with temperatures along different isobars, i.e. pressure-volume-temperature relationship of different materials [2, 3].

Thermodynamics of solids in the limit of infinite pressure reveals that the thermal expansivity of solids tends to zero at infinite pressure [4] Shanker et al. The earlier models for the volume dependence of thermal expansivity [5, 6] do not satisfy the infinite-pressure behaviour of thermal expansivity. The expressions for the volume dependence of the isothermal Anderson-Grüneisen parameter (δ_T) considered in the derivation of earlier formulations for the volume dependence of α [7, 8] have been found to be inadequate [4]. A formulation for the volume dependence of (δ_T) is presented here which is similar to the model due Burakovsky and Preston [9] for the volume dependence of Grüneisen parameter (γ). The new formulation for $\alpha(v)$ reveals that (δ_T) in the limit of extreme compression ($V \rightarrow 0$) and ($P \rightarrow \infty$) must be greater than zero for satisfying the thermodynamic result according to which α tends to zero at infinite pressure.

In the present study we calculate thermal expansivity of NaCl and MgO of high pressures using the modified version of the Burakovsky and Preston model [9, 10]. Values of α are then obtained at high temperatures along different isobars at selected pressures using the Anderson formula [1] in the temperature range starting from the Debye temperature θ_D up to the melting temperature (T_m). It should be mentioned that θ_D is nearly below 300K

for NaCl, and nearly 950K for MgO. The melting temperature for NaCl is nearly 1100K whereas that for MgO is approximately 3000 K.

II METHOD OF ANALYSIS

The thermal expansivity or volume thermal expansion coefficient α is defined as

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

The thermal expansivity α of solids at different compressions, i.e. V/V_0 are determined using the thermodynamic constraint developed by Stacey [11] in the limit of extreme compression (volume $V \rightarrow 0$ and pressure $P \rightarrow \infty$). We have formulated expressions for determining values of α as a function of compression and temperature. We have obtained results for α in case of NaCl and MgO along different isobars at selected pressures with increasing temperature.

The Anderson-Grüneisen parameter is an important physical quantity for understanding the thermoelastic properties of solids at high pressures and high temperatures [12 – 14]. In the present paper we study the volume dependence of the Anderson-Grüneisen parameter and derive an improved formula for thermal expansivity of solids which is found to be consistent with the thermodynamic constraint at extreme compression. The isothermal Anderson-Grüneisen parameter δ_T is defined as

$$\delta_T = -\frac{1}{\alpha K_T} \left(\frac{\partial K_T}{\partial T} \right)_p \quad (2)$$

and the isothermal bulk modulus.

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

Using the thermodynamic identity.

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

In Eq. (2) we get

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

Equations (1) and (5) reveals that in the limit $V \rightarrow 0$, α will tend to zero only when δ_T remains finite and positive equal to $\delta_{T\infty}$. According to the model of Burakovsky and Preston [9] we can write

$$\delta_T = \delta_{T\infty} + C_1 \left(\frac{V}{V_0} \right)^{\frac{1}{3}} + C_2 \left(\frac{V}{V_0} \right)^m \quad (6)$$

where C_1 , C_2 and m are constraints depending on the material. Substituting Eq. (5) for δ_T in Eq. (6) and then integrating we find the following expression for the thermal expansivity α

$$\frac{\alpha}{\alpha_0} = \left(\frac{V}{V_0}\right)^{\delta_{T\infty}} \exp \left\{ -3C_1 \left[1 - \left(\frac{V}{V_0}\right)^{\frac{1}{3}} \right] - \frac{C_2}{m} \left[1 - \left(\frac{V}{V_0}\right)^m \right] \right\} \quad (7)$$

Where α_0 is the value of α at $P = 0$.

III RESULTS AND DISCUSSIONS

Thermodynamics of solids at extreme compressions ($V \rightarrow 0$, and $P \rightarrow \infty$), it has been found by Stacy [11] that $\alpha \rightarrow 0$, but $\alpha \rightarrow 0$ only when $\delta_T \rightarrow \delta_\infty$ a finite positive value. The experimental data corresponding to the low compression region and for a limited range of temperature are available in the literature for NaCl [1] and MgO [5, 6]. We use this data to fit equations (6) and (7) in order to determine the parameters, C_1 , C_2 and m . We find $\delta_{T\infty} = 2$, $C_1 = C_2 = 1.78$, $m = 1.5$ for NaCl using $\delta_T^0 = 5.56$ and $\delta_{T\infty} = 2$, $C_1 = C_2 = 1.39$, $m = 1.5$ for MgO using $\delta_T^0 = 4.78$, the zero-pressure value of δ_T . With the help of these parameters, we have calculated α at different compressions using Eq.(7) for NaCl and MgO at initial temperatures 300K and 1000K respectively. The initial temperatures are close to the Debye temperatures θ_D for NaCl (300K) and MgO (1000K). The results are given in Tables 1 and 2. Values of α determined from Eq. (7) are listed at different compressions corresponding to pressures obtained from the modified Rydberg-Vinet EOS used by Singh [15].

Now, we calculate the thermal expansivity along different isobars at pressures given in Tables 1 and 2 using the Anderson formula

$$\alpha = \alpha_0 \left[1 - \alpha_0 \delta_T^0 (T - T_0) \right]^{-1} \quad (8)$$

Equation (8) is valid at high temperatures such that $T \geq \theta_D$. Values of $\alpha(T)$ are obtained from Eq. (8) taking α_0 , δ_T^0 and T_0 at appropriate pressure along an isobar. The results given in Table 1 and 2 reveal that α decreases fast with the increases in pressure or compression, and α increase with the increase in temperature along an isobar. The effect of temperature on thermal expansivity α is reduced considerably at high compressions. At high pressures the anharmonic effects in the solid are suppressed considerably so that the thermal expansivity increases very slowly with the increase in temperature for NaCl as well as MgO.

IV CONCLUSIONS

The formulation of the variation of thermal expansivity of solids with the change in compression used in the present study is consistent with the thermodynamic boundary condition in the limit of extreme compression. This ensures the reliability of the results for thermal expansivity at high pressures. For NaCl and MgO the

results obtained in the present study are in good agreement with the values based on experimental data reported in the literature [8, 16]. Such a comparison is presented in Figures 1 and 2 for the thermal expansivity as a function of pressure and temperature.

Table 1

Values Of Thermal Expansivity Along Different Isobars At Selected Pressures And Temperatures For Nacl.

V/V ₀	P (GPa)	δ_T^0	$\alpha (10^{-5} K^{-1})$ at different temperatures					
			300 K	450 K	600 K	750 K	900 K	1050 K
1.00	0	5.56	11.8	13.0	14.7	16.7	19.4	23.2
0.95	1.42	5.29	8.92	9.59	10.44	11.7	12.5	13.8
0.90	3.36	5.23	6.7	7.07	7.52	8	8.5	9.1
0.85	6.04	5.08	4.99	5.28	5.5	5.72	5.98	6.32
0.80	9.72	4.92	3.69	3.83	4.01	4.24	4.43	4.63
0.75	14.8	4.72	2.7	2.73	2.75	2.8	2.89	2.98
0.70	21.8	4.62	1.95	1.97	1.98	1.99	2	2.1
0.65	31.7	4.47	1.4	1.42	1.43	1.44	1.45	1.46

Table 2

Values Of Thermal Expansivity Along Different Isobars At Selected Pressures And Temperatures For Mgo.

V/V ₀	P (GPa)	δ_T^0	$\alpha (10^{-5} K^{-1})$ at different temperatures				
			1000 K	1500 K	2000 K	2500 K	3000 K
1.00	0	4.78	4.44	4.96	5.63	6.51	7.71
0.95	9.21	4.66	3.47	3.77	4.13	4.58	5.12
0.90	21.1	4.52	2.71	2.88	3.08	3.31	3.58
0.85	36.6	4.40	2.10	2.20	2.31	2.43	2.57
0.80	56.6	4.28	1.61	1.66	1.72	1.79	1.86
0.75	82.7	4.16	1.23	1.26	1.29	1.33	1.37
0.70	117	4.04	0.933	0.950	0.969	0.988	1.01
0.65	163	3.93	0.694	0.703	0.713	0.723	0.734
0.60	224	3.82	0.508	0.512	0.518	0.523	0.528

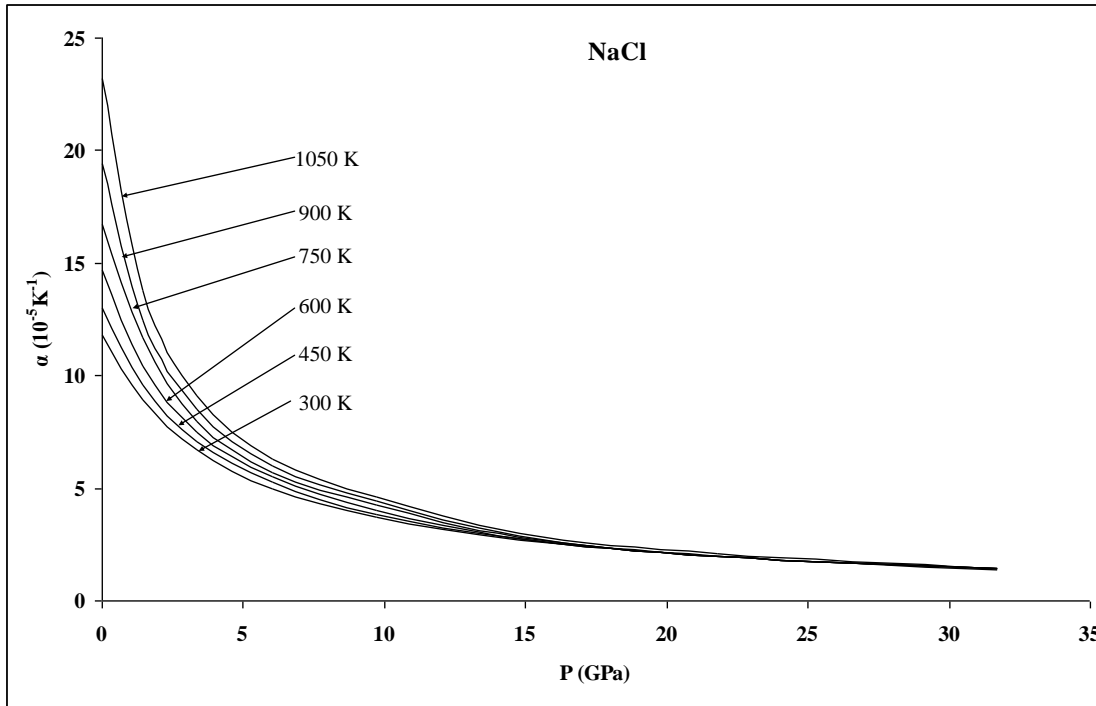


Fig 1: Comparison of the Calculated and Experimental Values [1, 16] Of Thermal Expansivity For Nacl

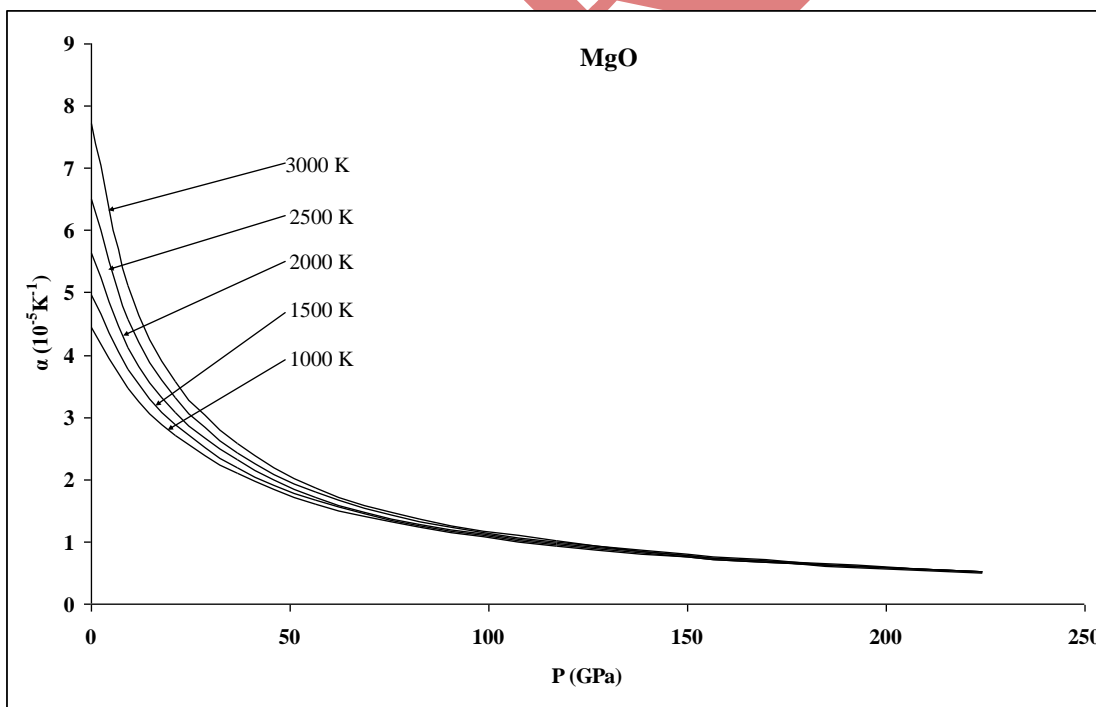


Fig 2: Comparison of the calculated and experimental values [1, 8] of thermal expansivity for MgO

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