

Volume Dependence of Thermodynamic Properties for Solids at high Temperatures

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Z. Naturforsch. **69a**, 532–538 (2014) / DOI: 10.5560/ZNA.2014-0046

Received December 19, 2013 / revised May 22, 2014 / published online July 30, 2014

A new computing model on the volume dependence of the product αK_T of the thermal expansion coefficient α and the isothermal bulk modulus K_T is proposed straightforward in this paper. Based on this revised formula, the volume dependence of Grüneisen parameter, entropy, Anderson–Grüneisen parameter, and first pressure derivative of bulk modulus, respectively, are thus investigated. The calculated results agree well with the previous work for magnesium oxide, sodium chloride, lithium, sodium, and potassium.

Key words: Thermal Expansion; Bulk Modulus; Solid.

1. Introduction

The volume thermal expansion coefficient α and bulk modulus K_T are the important thermodynamic quantum charactering the anharmonic properties of solids under high temperature – high pressure. Also α and K_T play an indispensable role in the research area of equation of state for solid state [1, 2] and thus have been investigated extensively [2–5]. Many efforts [6, 7] are made to study the compression dependence of thermal expansion. And also isothermal bulk modulus versus volume can be predicted by isothermal equation of state or the ab-initio calculation [8]. General knowledge says that the αK_T reveals the contest relation between interaction and thermal motion of lattice points in solids without phase transition, and based on αK_T , the thermal equation of state of solid can be studied easily [9].

An approximation of pressure-independent αK_T is often used, [10, 11]

$$\alpha K_T = \text{const}, \quad (1)$$

according to which the variation of thermal expansion versus pressure was obtained [12, 13]. However, the shortage of constant αK_T has been found by Dass in the case of high pressure. Many researchers [11,

14, 15] have pointed out that αK_T is not independent of pressure over a large pressure range. Many attempts [16, 17] have revealed the temperature and pressure dependence of αK_T for MgO which is an important low mantel material [18]. Also many attempts [19, 20] showed analogous results for MgO according to phenomenological equations about α and K_T versus volume.

Anderson [5] got another equation of αK_T versus volume by analyzing a thermodynamic identity on variation of αK_T versus volume V for isothermal condition

$$\left[\frac{\partial \ln(\alpha K_T)}{\partial \ln V} \right]_T \equiv \delta_T - K'_T, \quad (2)$$

where $\delta_T = -(1/\alpha K_T)(\partial K_T/\partial T)_P$ and $K'_T = (\partial K_T/\partial P)_T$ are the isothermal Anderson–Grüneisen parameter and the pressure P derivative of K_T , respectively. If $\delta_T - K'_T$ is a small number compared to unity, then $\delta_T - K'_T$ can be considered volume independent. So Anderson et al. [21] represented an approximate relation between αK_T and the volume compression ratio $\eta = V/V_0$,

$$\frac{\alpha K_T}{\alpha_0 K_{T_0}} = \eta^{\delta_T - K'_T}, \quad (3)$$

where V_0 , α_0 , and K_{T_0} are, respectively, the values of volume, thermal expansion, and isothermal bulk modulus at zero pressure. Equation (3) can be also obtained from $\alpha/\alpha_0 = \eta^{\delta_T}$ and $K_T/K_{T_0} = \eta^{-K'_T}$, based on that δ_T and K'_T are volume-independent. Equation (3) is only applicable to high temperature and low pressure. However, a strong volume dependence of $\delta_T - K'_T$ is revealed for MgO under high pressure in [16]. Furthermore, a remarkable minimum of αK_T versus volume were observed [16, 17, 19, 20] and so far has not been explained. So a better model for evaluating the volume dependence of αK_T is needed to analyze these phenomena mentioned above.

In this paper, a new model on volume dependence of αK_T is developed. Based on this revised formula, the volume dependence of Grüneisen parameter, entropy, Anderson–Grüneisen parameter, and first pressure derivative of bulk modulus can be predicted easily for MgO, NaCl, Li, Na, and K.

2. Theoretical Formulation

2.1. αK_T Versus Volume at High Temperature

In order to obtain the more precise evaluation of αK_T versus volume at high temperature, we start from revising (3). In view of the facts of (i) existence of positive or negative $\delta_T - K'_T$ at different temperatures and (ii) observation of the minimum volume in αK_T , an assumption of volume dependence of αK_T is accordingly proposed as $\frac{\alpha K_T}{\alpha_0 K_{T_0}} = A\eta^{-B} + C\eta^B$, where A and B are the volume-independent parameters introduced newly for the selected solids. The initial condition without compression, $\alpha K_T = \alpha_0 K_{T_0}$, indicates $C = (1 - A)$. Hence a new equation is derived immediately as following:

$$\frac{\alpha K_T}{\alpha_0 K_{T_0}} = A\eta^{-B} + (1 - A)\eta^B. \quad (4)$$

According to (2) and (4), $\delta_T - K'_T$ can be expressed as

$$\delta_T - K'_T = B \frac{-A + (1 - A)\eta^{2B}}{A + (1 - A)\eta^{2B}}. \quad (5)$$

Equation (5) at $\eta = 1$ (i. e., zero pressure) yields an equation on the parameters A and B :

$$B(1 - 2A) = \delta_{T_0} - K'_{T_0}, \quad (6)$$

where δ_{T_0} and K'_{T_0} are, respectively, the values of δ_T and K'_T at zero pressure. The derivative of (5) with respect to η at $P = 0$ gives

$$\left[\frac{\partial(\delta_T - K'_T)}{\partial\eta} \right]_{\eta=1} = 4A(1 - A)B^2. \quad (7)$$

By solving (6) and (7), one can obtain easily the parameter A and B as

$$A = \frac{1}{2} \left(1 - \frac{\delta_{T_0} - K'_{T_0}}{\sqrt{(\delta_{T_0} - K'_{T_0})^2 + [\partial(\delta_T - K'_T)/\partial\eta]_{\eta=1}}} \right), \quad (8)$$

$$B = \sqrt{(\delta_{T_0} - K'_{T_0})^2 + [\partial(\delta_T - K'_T)/\partial\eta]_{\eta=1}}. \quad (9)$$

To simplify (8) and (9), the knowledge of δ_T and K'_T are needed. Anderson et al. [22] has described δ_T as a power law with η ,

$$\delta_T = \delta_{T_0} \eta^\kappa, \quad (10)$$

where κ is a dimensionless and temperature-dependent parameter. We [23] have represented a relation between K'_T versus η ,

$$K'_T = K'_{T_0} \eta^s, \quad (11)$$

where $s = -K_{T_0} K''_{T_0} / K'_{T_0}$ is also a dimensionless parameter varying with temperature. According to (8)–(11), the specific expression of parameter A and B can be obtained:

$$A = \frac{1}{2} \left(1 - \frac{\delta_{T_0} - K'_{T_0}}{\sqrt{(\delta_{T_0} - K'_{T_0})^2 + (\delta_{T_0} \kappa + K_{T_0} K''_{T_0})}} \right), \quad (12)$$

$$B = \sqrt{(\delta_{T_0} - K'_{T_0})^2 + (\delta_{T_0} \kappa + K_{T_0} K''_{T_0})}. \quad (13)$$

So the parameters A and B can be got immediately if the values of K_{T_0} , K'_{T_0} , K''_{T_0} , δ_{T_0} , and κ are known according to (12) and (13).

2.2. The Volume Dependence of Grüneisen Parameter γ at High Temperature

The Grüneisen parameter is defined as

$$\gamma = \frac{\alpha K_T V}{C_V}. \quad (14)$$

Chopelas [15] has pointed out that the effect of pressure on C_V at high temperatures (higher than Debye

temperature) is very small, which can be verified for MgO by Figure 3 in [17]. Obviously C_V is held constant when $T \geq 1000$ K (Debye temperature of MgO ~ 940 K [24]), so (14) yields

$$\frac{\gamma}{\gamma_0} = \frac{\alpha K_T \eta}{\alpha_0 K_{T_0}}, \quad (15)$$

where γ_0 is the Grüneisen parameter at $\eta = 1$ for the considered isotherm. Combining (4) with (15), we get

$$\gamma/\gamma_0 = A\eta^{-B+1} + (1-A)\eta^{B+1}, \quad (16)$$

which is a new computing formula on the volume dependence of the Grüneisen parameter.

2.3. The Volume Dependence of Entropy

The Maxwell relation gives an equation on entropy S , V , T , P , and αK_T as following:

$$(\partial S/\partial V)_T = (\partial P/\partial T)_V = \alpha K_T. \quad (17)$$

The integration of (17) versus volume for isothermal condition yields

$$S(\eta) = S(1) + V_0 \int_1^\eta \alpha K_T d\eta. \quad (18)$$

Substituting (4) into (18), we obtain the entropy per gram

$$S(\eta) = S(1) + \frac{\alpha_0 K_{T_0}}{\rho_0} \left[\frac{A}{-B+1} (\eta^{-B+1} - 1) + \frac{1-A}{B+1} (\eta^{B+1} - 1) \right], \quad (19)$$

where $\rho_0 = 1/V_0$ is the density at $\eta = 1$. Equation (19) could be used to evaluate the volume dependence of the entropy along a certain isotherm.

3. Results and Discussion

To test the validity of the new model, we applied (4) on MgO, respectively, at 300 K, 500 K, 1000 K, 1500 K, and 2000 K by employing Cynn's data [16]. The values of parameters A and B were obtained by fitting Cynn's data [16] and were listed in Table 1. The calculated values through (4) are shown

in Figure 1 along with the results obtained by Anderson et al. [17] and Isaak et al. (Table 3.1 and Table 4.1 in [5]) for the sake of comparison. According to Figure 1, one can find that the calculated values through (4) are in good agreement with the previous results for MgO of many researchers [5, 16, 17], which justify our new model on the volume dependence of αK_T .

The calculated A and B through (12) and (13) for MgO are shown in Table 2 along with the parameters K_{T_0} , K'_{T_0} , K''_{T_0} , δ_{T_0} , and κ taken from [7, 17, 22, 25]. It can be found that the difference between the fitted values (Table 1) and calculated values (Table 2) of A and B is very small, which also reveals that (4) is reliable.

The comparison between the calculated values of $\delta_T - K'_T$ through (5) and the previous data for MgO are plotted in Figure 2. A good agreement is observed, which reveals that (5) seems to be reliable at least for MgO. Equation (4) is the basis of (5), so the validity of (4) is tested again.

Under quasiharmonic approximation at high temperature, the volume dependence of the heat capacity can be omitted and the following equation is obtained [7] according to the Grüneisen relation:

$$\delta_T = K'_T + q - 1, \quad (20)$$

Table 1. Fitted values of parameter A and B through (4) for MgO.

Temperature	300 K	500 K	1000 K	1500 K	2000 K
A	0.172	0.246	0.305	0.329	0.359
B	1.90	1.64	1.58	1.41	1.14

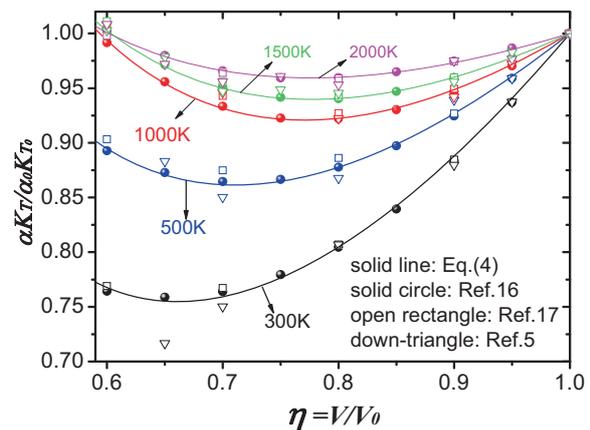


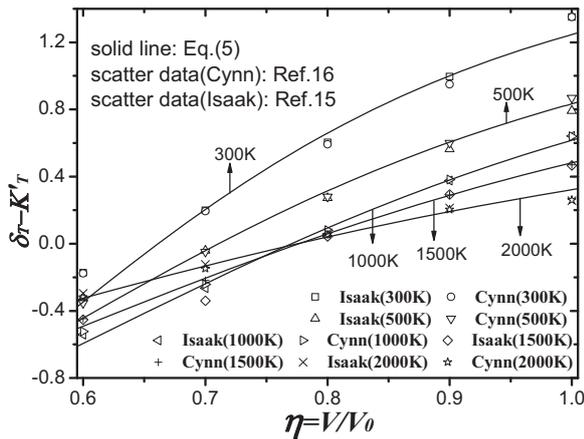
Fig. 1 (colour online). Volume dependence of $\alpha K_T/\alpha_0 K_{T_0}$ for MgO at various temperatures.

Table 2. Calculated values of A and B through (12) and (13) along with parameters of K_{T_0} , K'_{T_0} , K''_{T_0} , δ_{T_0} , and κ for MgO.

Temperaturec	300 K	500 K	1000 K	1500 K	2000 K
A	0.195	0.237	0.299	0.339	0.346
B	2.21	1.66	1.59	1.46	0.84
K_{T_0} (Gpa) [17]	180	175	160	144	128
K'_{T_0} [17]	4.15	4.21	4.36	4.53	4.74
K''_{T_0} (Gpa ⁻¹) [25]	-0.026	-0.029	-0.033	-0.035	-0.043
δ_{T_0} [7]	5.50	5.08	5.00	5.00	5.00
κ [22]	1.41	1.39	1.48	1.39	1.23

Table 3. Volume dependence of the Grüneisen parameter for MgO at high temperatures.

$\eta = V/V_0$	1000 K		1500 K		2000 K	
	[16]	(16)	[16]	(16)	[16]	(16)
1.00	1.540	1.540	1.517	1.517	1.476	1.476
0.95	1.423	1.422	1.406	1.409	1.380	1.382
0.90	1.319	1.315	1.308	1.311	1.290	1.293
0.85	1.229	1.220	1.220	1.222	1.205	1.210
0.80	1.151	1.136	1.141	1.141	1.130	1.134
0.75	1.086	1.065	1.073	1.070	1.062	1.063
0.70	1.031	1.004	1.013	1.009	0.998	0.998
0.65	0.985	0.955	0.960	0.956	0.940	0.939
0.60	0.950	0.918	0.913	0.913	0.884	0.886
RMSD		0.019		0.003		0.003

Fig. 2. Volume dependence of $\delta_T - K'_T$ for MgO.

where $q = (\partial \ln \gamma / \partial \ln \eta)_T$, called the second Grüneisen parameter. According to the isothermal derivative of (20) with respect to η , (8) and (9) can be rewritten as, respectively,

$$A = \frac{1}{2} \left(1 - \frac{\delta_{T_0} - K'_{T_0}}{\sqrt{(\delta_{T_0} - K'_{T_0})^2 + (\partial q / \partial \eta)_{\eta=1}}} \right) \quad (21)$$

and

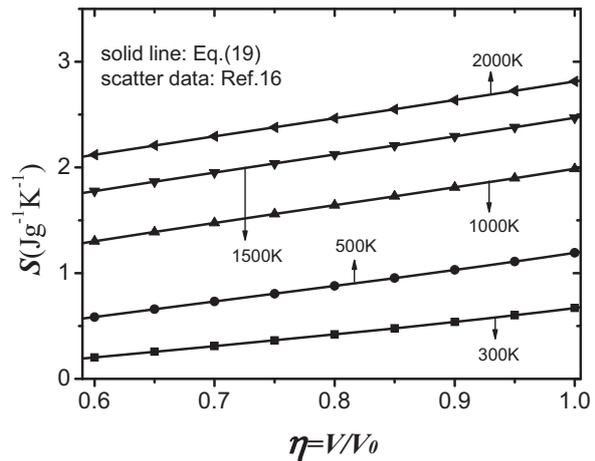


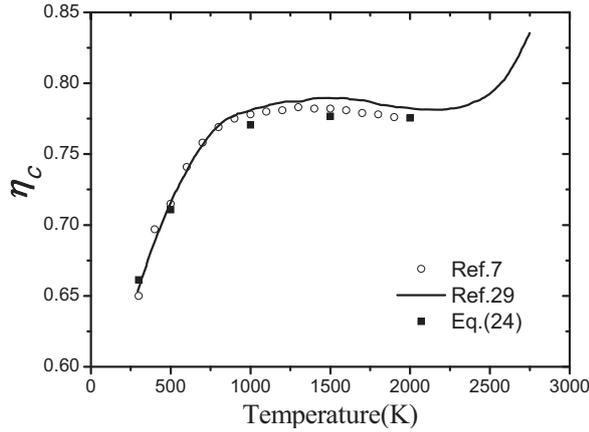
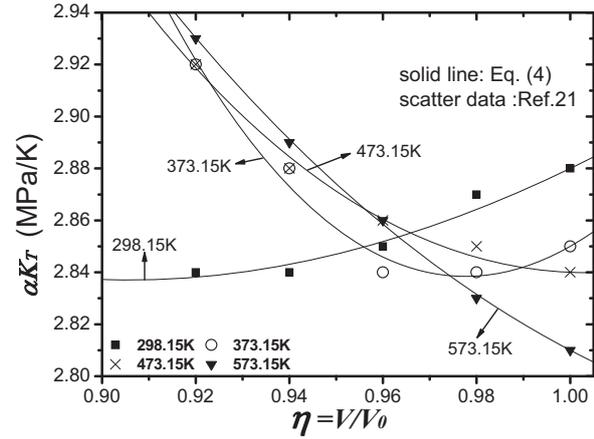
Fig. 3. Volume dependence of entropy for MgO.

$$B = \sqrt{(\delta_{T_0} - K'_{T_0})^2 + (\partial q / \partial \eta)_{\eta=1}}. \quad (22)$$

The logarithmic derivative of q ,

$$q' = \left(\frac{\partial \ln q}{\partial \ln V} \right)_T, \quad (23)$$

is assumed to be constant by Jeanloz [26]. Equation (23) is equal to $q = q_0 \eta^{q'}$, which could be used to get $(\partial q / \partial \eta)_{\eta=1}$ by fitting a set of data (η, q) . Thus

Fig. 4. Volume minimum η_c versus temperature for MgO.Fig. 5. Volume dependence of αK_T for NaCl at various temperatures.Table 4. Volume dependence of the Grüneisen parameter γ for Li, Na, and K at 298 K.

η	Li		η	Na		η	K	
	[27]	(16)		[27]	(16)		[27]	(16)
1.000	0.980	0.980	1.000	1.210	1.210	1.000	1.270	1.270
0.958	0.900	0.913	0.931	1.050	1.073	0.878	1.020	1.037
0.922	0.850	0.865	0.878	1.000	1.001	0.802	0.920	0.920
0.891	0.840	0.831	0.837	0.980	0.965	0.747	0.860	0.848
0.864	0.820	0.806	0.803	0.960	0.949	0.704	0.810	0.799
0.841	0.800	0.789	0.775	0.940	0.944	0.669	0.760	0.764
0.819	0.760	0.776	0.750	0.940	0.948	0.640	0.730	0.738
RMSD		0.012			0.012			0.010

Table 5. Fitted values of parameter A and B through (16) for Li, Na, and K at 298 K.

Solids	Li	Na	K
A	0.345	0.332	0.275
B	2.52	2.82	1.51

we obtained the values of $(\partial q/\partial \eta)_{\eta=1}$ 4.37, 4.29, 3.89, 2.95, and 1.89 at 400 K, 500 K, 1000 K, 1500 K, and 1900 K, respectively, for MgO by using Cynn's data [16]. It is not difficult to found that $(\partial q/\partial \eta)_{\eta=1}$ decreases with the rise of temperature. Under very high temperature, if both $\delta_{T_0} - K'_{T_0}$ and $(\partial q/\partial \eta)_{\eta=1}$ tend to be quite small, and then parameter $A \rightarrow 0.5$ and $B \rightarrow 0$,

Table 6. Values of ρ_0 ($\text{g} \cdot \text{cm}^{-3}$) and $\alpha_0 K_{T_0}$ ($\text{MPa} \cdot \text{K}^{-1}$) for MgO.

Temperature	300 K	500 K	1000 K	1500 K	2000 K
ρ_0 [28]	3.585	3.559	3.486	3.405	3.319
$\alpha_0 K_{T_0}$ [28]	5.042	6.000	6.320	6.150	5.920

according to which (4) suggests that αK_T keep nearly constant over a large pressure range. So (1) is only the specific case of high temperature for (4), which indicates that our work is more universal.

The Grüneisen parameters calculated through (16) for MgO are shown in Table 3 along with those data compiled by Cynn et al. [16]. In order to test the validity of (16) widely, we have applied it on lithium, sodium, and potassium at 298 K, and results obtained through (16) are cited in Table 4 along with experimental data [27]. The fitted parameters A and B are listed in Table 5. The very small room mean square deviation (RMSD) in Tables 3–4 reveals a good agreement be-

Table 7. Fitted values of A and B of NaCl through (4).

Temperature	298 K	373 K	473 K	573 K
A	0.414	0.455	0.505	0.582
B	1.76	3.98	2.70	2.05

tween (16) and the previous works of Cynn [16] and Boehler [27], respectively.

The entropy calculated through (19) for MgO is consistent with Cynn's data [16], as shown in Figure 3. The calculation-required values ρ_0 and $\alpha_0 K_{T_0}$ are taken from [28], and listed in Table 6. So (19) seems to be reliable for predicting the volume dependence of entropy.

As the pressure increases, the thermal expansion coefficient α decreases but the isothermal bulk modulus

K_T increases accordingly because of solid stiffening, which suggests a possible minimum of αK_T . Anderson [17] and Cynn [16] have found that αK_T performs a remarkable minimum value η_c from 0.6 to 1.0 corresponding to different temperatures for MgO. The value of η_c increases with temperature until a certain temperature above the Debye temperature.

According to (4), (12), and (13), we obtained immediately

$$\eta_c = \left(1 - \frac{2(\delta_{T_0} - K'_{T_0})}{\sqrt{(\delta_{T_0} - K'_{T_0})^2 + (\delta_{T_0} \kappa + K_{T_0} K''_{T_0}) + (\delta_{T_0} - K'_{T_0})}} \right)^{\frac{1}{2\sqrt{(\delta_{T_0} - K'_{T_0})^2 + (\delta_{T_0} \kappa + K_{T_0} K''_{T_0})}}}. \quad (24)$$

Equation (2) gives

$$\left[\frac{\partial(\alpha K_T / \alpha_0 K_{T_0})}{\partial \eta} \right]_T \equiv \frac{\alpha K_T \eta}{\alpha_0 K_{T_0}} (\delta_T - K'_T), \quad (25)$$

which indicates that the value of η at $\delta_T = K'_T$ is exactly η_c . So the values of η at $\delta_T = K'_T$ versus temperature were taken from [7, 29] to compare with our calculated results of η_c through (24), as shown in Figure 4. The comparison shows that (24) can predict validly the minimum behaviour of αK_T versus η .

Parameter $A \rightarrow 0.5$ indicates $\eta_c \rightarrow 1$ in view of (24), which reveals thus αK_T increases as η decrease at quite high temperature. In order to test the validity of this theoretical prediction, we applied (4) on NaCl with Debye temperatures 320 K [30] and almost identical K'_{T_0} and δ_{T_0} ($K'_{T_0} = 5.5$, $\delta_{T_0} = 5.3$) over a larger compression range [14]. The experimental data of αK_T are taken from [21] for NaCl at 298 K, 373 K, 473 K, and 573 K. The required parameters of A and B are fitted through (4) and are shown in Table 7. For the sake of comparison, the calculated results through (4) and experimental data of αK_T are plotted in Figure 5. A good agreement between experimental results and ours are found in Figure 5, which justify (4) for NaCl. Also Figure 5 shows that $\eta_c \rightarrow 1$ in the cases of 473 K and 573 K, which confirms the prediction of this paragraph head.

In summary, we have proposed straightforward a new simple model on the volume dependence of the product αK_T of thermal expansion coefficient α and isothermal bulk modulus K_T . This new model is useful for evaluating easily and precisely the thermodynamic properties of solids, such as the volume dependence of the Grüneisen parameter, entropy, and the difference between the Anderson–Grüneisen parameter and the first pressure derivative of bulk modulus. Also the minimum behaviour of αK_T versus η caused by solid stiffening can be explained according to this new model. In addition, it could be used to study the volume dependence of thermal pressure, which is in investigation.

Acknowledgements

This work was supported by the National Natural Science Foundation of China under Grant No. 21373011 and 61106011, Anhui Provincial Natural Science Foundation No. 10040606Q31 and 1308085QF109, Anhui Provincial College Natural Science Foundation No. KJ2012A137, the open project of National Key Laboratory of Solid State Microstructures M25002, and The National Basic Research Programme of China under Grant No. 2011CB933400.

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