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Thermal Expansion and Elastic Constants[1]

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We give a simple, useful relationship between thermal expansion, $\Delta V/V$, and elastic constants. The relationship permits estimation of thermal expansion from only elastic constants (second order and third order) and atomic volume. Elastic-constant temperature dependence is not required. We test the relationship for a variety of crystalline solids. Considering the 0–293 K region, measurement–calculation disagreement ranges from less than 1 to 15%. The model permits extrapolation of high-temperature (near-linear) thermal expansion to zero temperature.

KEY WORDS: crystals; Debye temperature; Einstein temperature; elastic constants; Grüneisen parameter; low temperatures; thermal expansion; thermal expansivity; zero-point energy.

1. INTRODUCTION

This study focuses on the volume change that occurs when a solid's temperature increases from zero to some temperature near the Einstein or Debye temperature:

$$\frac{\Delta V}{V} = \frac{V(T) - V(0)}{V(0)} \tag{1}$$

Usually, one calculates $\Delta V/V$ by integration:

$$\Delta V/V = \int_0^T \beta(T)\, dT \tag{2}$$

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Here, β denotes the usual volume thermal expansivity:

$$\beta(T) = (1/V)(\partial V/\partial T)_P \tag{3}$$

The present study provides an alternative approach to estimating $\Delta V/V$. It requires knowing C_{ij} and C_{ijk}, the second-order and third-order elastic constants, but not their temperature dependences. It extends ideas given by Sheard [1].

2. THEORY

In discussing simple statistical-mechanical models of solids, Slater [2] gave an expression for the volume thermal expansivity:

$$\beta = (k/BV_0) \sum_j \gamma_j (hv_j/kT)^2 \exp(hv_j/kT)/[\exp(hv_j/kT) - 1]^2 \tag{4}$$

Here k denotes Boltzmann's constant, h Planck's constant, B the bulk modulus, V_0 the total volume of solid at zero temperature, v the vibrational frequency, and j the jth oscillator ($j = 1 - 3N$ for a crystal containing N atoms), and γ_j, the mode Grüneisen parameter, is given by

$$\gamma_j = -d \ln v_j / d \ln V \tag{5}$$

Following Einstein, we take all $v_j = v$; following Grüneisen, we take all $\gamma_j = \gamma$, where v and γ represent average values. We introduce the Einstein characteristic temperature $\Theta_E = hv/k$ and the atomic volume $V_a = V_0/N$. Thus simplified, Eq. (4) becomes

$$\beta = (3k\gamma/BV_a)(\Theta_E/T)^2 \exp(\Theta_E/T)/[\exp(\Theta_E/T) - 1]^2 \tag{6}$$

Here, the sum over j in Eq. (4) is $3N$.

For simplicity, we ignore the small temperature dependences of γ, B, Θ, and V_a. Integrating Eq. (6), we get

$$\Delta V/V(T) = (3k\gamma\Theta_E/BV_a)/[\exp(\Theta_E/T) - 1] \tag{7}$$

Equations (6) and (7) contain four parameters: B, γ, Θ_E, and V_a. Below, we describe how B depends only on the C_{ij}, γ only on the C_{ij} and C_{ijk}, and Θ_E only on the C_{ij} and V_a. Thus, we can estimate both $\beta(T)$ and $\Delta V/V(T)$ from the elastic constants and atomic volume.

For simplicity, we also consider only cubic-symmetry materials, which possess three independent second-order elastic constants: C_{11}, C_{12}, and C_{44}. [To extend the approach to noncubic symmetry would require more

general expressions for Eqs. (9), (14), and (15).] From the general expression for the bulk modulus [3],

$$B = \tfrac{1}{9} \sum_{i,j=1,2,3} C_{iijj} \tag{8}$$

we obtain

$$B = \tfrac{1}{3}(C_{11} + 2C_{12}) \tag{9}$$

We can calculate the Einstein temperature, $\Theta_E = (3/4)\,\Theta_D$, where Θ_D denotes Debye temperature, by first calculating the mean sound velocity v_m [4]:

$$\Theta_E = (3/4)(h/k)(3/4\pi V_a)^{1/3}\, v_m \tag{10}$$

Here V_a denotes atomic volume and v_m the mean sound velocity obtained by numerical integration over all directions:

$$3v_m^{-3} = (1/4\pi) \int \sum_{\alpha=1,3} v_\alpha^{-3}\, d\Omega \tag{11}$$

Here v_1 denotes the quasilongitudinal sound velocity, v_2 and v_3 the quasitransverse sound velocities, and $d\Omega$ the increment of solid angle. Phase sound velocities v_α are roots of the Christoffel equations:

$$\det(C_{ijkl} n_j n_k - \rho v^2 \delta_{il}) = 0 \tag{12}$$

Here, ρ denotes mass density, n_i components of unit wave vector, and δ_{il} the Kronecker delta. As discussed by Blackman [4], various methods exist for solving Eq. (11), but direct numerical integration provides the simplest approach. We used seventy vectors distributed over 1/48 of space.

We used the high-temperature limit of the thermodynamic Grüneisen parameter [5]:

$$\gamma_H = \frac{1}{3N} \sum_{j=1}^{3N} \gamma_j \tag{13}$$

To calculate the mode Grüneisen parameters, γ_j, we used the following relationship [6, 7]:

$$\begin{aligned}\gamma_j = -\left(\frac{1}{6w}\right) \{&2w + C_{11} + 2C_{12} + (C_{111} + 2C_{112})(N_1^2 U_1^2 + N_2^2 U_2^2 + N_3^2 U_3^2) \\ &+ (C_{144} + 2C_{166})[(N_2 U_3 + N_3 U_2)^2 \\ &+ (N_3 U_1 + N_1 U_3)^2 + (N_1 U_2 + N_2 U_1)^2] \\ &+ 2(C_{123} + 2C_{112})(N_2 N_3 U_2 U_3 + N_3 N_1 U_3 U_1 + N_1 N_2 U_1 U_2)\}\end{aligned} \tag{14}$$

Here

$$w = C_{11}(N_1^2U_1^2 + N_2^2U_2^2 + N_3^2U_3^2) + C_{44}[(N_2U_3 + N_3U_2)^2 + (N_3U_1 + N_1U_3)^2 + (N_1U_2 + N_2U_1)^2] + 2C_{12}^{S}(N_2N_3U_2U_3 + N_3N_1U_3U_1 + N_1N_2U_1U_2) \quad (15)$$

The vectors **N** and **U** refer to propagation and polarization vectors of the jth normal mode. The elastic constants are expressed in Voigt's contracted notation.

Table I shows the input information and the calculated $\Delta V/V$ results for nine materials: five metallic elements, a covalent element, a covalent compound, and two ionic compounds (valence 1 and valence 2). The calculation–measurement comparison shows differences ranging from 1 to 15%. The smallest disagreements seem to occur in close-packed high-Einstein-temperature materials.

For copper, Fig. 1 shows the curve predicted by Eq. (7) together with measured values [8]. We could achieve an exact (to the eye) fit by reducing Θ_E from 248 to 243 K. The dashed line in Fig. 1 represents a linear extrapolation from high temperatures, where from Eq. (7) the slope equals $3k\gamma/BV_a$. The intercept at $T=0$ gives the zero-point vibration-induced volume increase:

$$(\Delta V/V)_{zp} = 3k\gamma\Theta_E/2BV_a \quad (16)$$

We note that $(\Delta V/V)_{zp}$ equals approximately the volume change caused by warming from 0 to 293 K. Indeed, for $\Theta_E = 293$ K, a typical Einstein temperature, Eqs. (7) and (16) show that

$$(\Delta V/V)_{0\text{–}293}/(\Delta V/V)_{zp} = 1.16 \quad (17)$$

Table I. The 0–293 K Thermal Dilatation Predicted for Various Materials

Material	γ	B (10^{11} N·m^{-2})	V_a (Å^3)	Θ_D (K)	Θ_E (K)	$\Delta V/V$ (%) Theory	$\Delta V/V$ (%) Observed	Ratio theory: observed
Al	2.22	0.759	16.60	408	306	1.21	1.25	0.97
Cu	2.03	1.353	11.81	330	248	0.98	0.98	1.00
Ag	2.50	1.012	17.06	216	162	1.31	1.24	1.06
Au	2.57	1.735	16.96	155	116	0.86	0.98	0.88
Fe	1.81	1.669	11.70	464	348	0.59	0.59	0.99
Ge	0.76	0.754	22.64	371	278	0.32	0.28	1.13
GaAs	0.65	0.755	22.50	345	259	0.29	0.27	1.06
NaCl	1.46	0.252	22.41	303	227	2.26	2.32	0.97
MgO	1.60	1.533	9.35	946	710	0.35	0.41	0.86

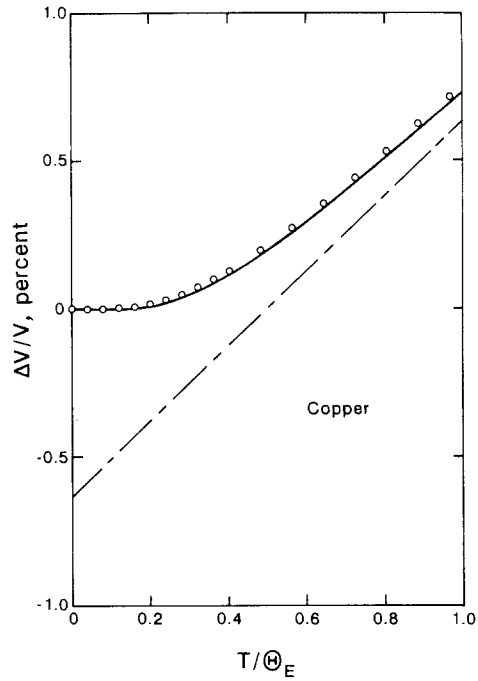

Fig. 1. For copper, a theoretical curve corresponding to Eq. (7). Open circles represent observed values recommended in Ref. 8. The dashed line represents linear extrapolation from high temperatures. Its intercept at $T=0$ gives the zero-point energy contribution to volume. Lowering the Θ_E from 248 to 243 K gives exact agreement between theory and measurement.

Finally, we want to emphasize the possibility of using Eq. (7) to extrapolate higher-temperature near-linear $\Delta V/V$ measurements to zero temperature. For this purpose, one needs good estimates of B, γ, Θ_E, and V_a for the material considered.

3. SUMMARY

In summary, we derived a simple four-parameter relationship for $\Delta V/V(T)$. All four parameters have simple physical meanings: bulk modulus, Einstein (or Debye) temperature, Grüneisen parameter, and atomic volume. This relationship permits easy understanding of inter-

connections among these variables and the thermal expansivity, $\beta(T)$. Especially for high-Debye temperature close-packed metals, the relationship predicts a $\Delta V/V$ that agrees well with observation.

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