Thermal Expansion and Elastic Constants\textsuperscript{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; Grünneisen 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:

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

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

$$\frac{\Delta V}{V} = \int_{0}^{T} \beta(T) \, dT$$  \hspace{1cm} (2)

\textsuperscript{1} Paper presented at the Tenth International Thermal Expansion Symposium, June 6–7, 1989, Boulder, Colorado, U.S.A.

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Here, \( \beta \) denotes the usual volume thermal expansivity:

\[
\beta(T) = \frac{1}{V} \left( \frac{\partial V}{\partial T} \right)_T.
\]

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:

\[
\beta = \frac{k}{BV_0} \sum_j \gamma_j (h\nu_j/kT)^2 \frac{\exp(h\nu_j/kT)}{[\exp(h\nu_j/kT) - 1]^2}
\]

Here \( k \) denotes Boltzmann’s constant, \( h \) Planck’s constant, \( B \) the bulk modulus, \( V_0 \) the total volume of solid at zero temperature, \( \nu \) the vibrational frequency, and \( j \) the \( j \)th oscillator \( (j=1-3N \text{ for a crystal containing } N \text{ atoms}) \), and \( \gamma_j \), the mode Grüneisen parameter, is given by

\[
\gamma_j = -\frac{d\ln v_j}{d\ln V}
\]

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

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

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

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

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

Equations (6) and (7) contain four parameters: \( B \), \( \gamma \), \( \Theta_E \), and \( V_a \). Below, we describe how \( B \) depends only on the \( C_{ij} \), \( \gamma \) only on the \( C_{ij} \) and \( C_{ijk} \), and \( \Theta_E \) 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],

\[ B = \frac{1}{6} \sum_{i,j=1,2,3} C_{iij} \]  

we obtain

\[ B = \frac{1}{3}(C_{11} + 2C_{12}) \]  

(9)

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

\[ \Theta_E = (3/4)(h/k)^3(3/4\pi V_a)^{1/3} v_m \]  

(10)

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

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

(11)

Here \( v_1 \) denotes the quasilongitudinal sound velocity, \( v_2 \) and \( v_3 \) the quasi-transverse sound velocities, and \( d\Omega \) the increment of solid angle. Phase sound velocities \( v_\alpha \) are roots of the Christoffel equations:

\[ \det(C_{ijkl} n_j n_k - \rho v^2 \delta_{il}) = 0 \]  

(12)

Here, \( \rho \) denotes mass density, \( n_i \) components of unit wave vector, and \( \delta_{il} \) 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]:

\[ \gamma_{HI} = \frac{1}{3N} \sum_{j=1}^{3N} \gamma_j \]  

(13)

To calculate the mode Grüneisen parameters, \( \gamma_j \), we used the following relationship [6, 7]:

\[ \gamma_j = -\left(\frac{1}{6w}\right) \left\{ 2w + C_{11} + 2C_{12} + (C_{111} + 2C_{112})(N_1^2 U_1^2 + N_2^2 U_2^2 + N_3^2 U_3^2) \right. \]

\[ + (C_{144} + 2C_{166})[(N_2 U_3 + N_3 U_2)^2 \]

\[ + (N_3 U_1 + N_1 U_3)^2 + (N_1 U_2 + N_2 U_1)^2] \]

\[ + 2(C_{123} + 2C_{112})(N_2 N_3 U_2 U_3 + N_3 N_1 U_3 U_1 + N_1 N_2 U_1 U_2) \} \]  

(14)
Here
\[ w = C_{11}(N_1^2 U_1^2 + N_2^2 U_2^2 + N_3^2 U_3^2) \]
\[ + C_{44}[(N_2 U_3 + N_3 U_2)^2 + (N_3 U_1 + N_1 U_3)^2 + (N_1 U_2 + N_2 U_1)^2] \]
\[ + 2C_{12}^S(N_2 N_3 U_2 U_3 + N_3 N_1 U_3 U_1 + N_1 N_2 U_1 U_2) \]  
(15)

The vectors \( \mathbf{N} \) and \( \mathbf{U} \) refer to propagation and polarization vectors of the \( j \)th 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 \( \Theta_E \) 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 \( 3kT/BV_a \). The intercept at \( T=0 \) gives the zero-point vibration-induced volume increase:
\[ \frac{\Delta V}{V}_{zp} = \frac{3k\gamma}{2BV_a} \]  
(16)

We note that \( \frac{\Delta V}{V}_{zp} \) 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
\[ \frac{\Delta V}{V}_{0-293}/\frac{\Delta V}{V}_{zp} = 1.16 \]  
(17)

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

<table>
<thead>
<tr>
<th>Material</th>
<th>( \gamma )</th>
<th>( B ) ((10^{11} \text{ N} \cdot \text{m}^{-2}))</th>
<th>( V_a ) ((\text{Å}^3))</th>
<th>( \Theta_D ) (K)</th>
<th>( \Theta_E ) (K)</th>
<th>( \Delta V/V ) (%)</th>
<th>Ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al</td>
<td>2.22</td>
<td>0.759</td>
<td>16.60</td>
<td>408</td>
<td>306</td>
<td>1.21</td>
<td>1.25</td>
</tr>
<tr>
<td>Cu</td>
<td>2.03</td>
<td>1.353</td>
<td>11.81</td>
<td>330</td>
<td>248</td>
<td>0.98</td>
<td>0.98</td>
</tr>
<tr>
<td>Ag</td>
<td>2.50</td>
<td>1.012</td>
<td>17.06</td>
<td>216</td>
<td>162</td>
<td>1.31</td>
<td>1.24</td>
</tr>
<tr>
<td>Au</td>
<td>2.57</td>
<td>1.735</td>
<td>16.96</td>
<td>155</td>
<td>116</td>
<td>0.86</td>
<td>0.98</td>
</tr>
<tr>
<td>Fe</td>
<td>1.81</td>
<td>1.669</td>
<td>11.70</td>
<td>464</td>
<td>348</td>
<td>0.59</td>
<td>0.59</td>
</tr>
<tr>
<td>Ge</td>
<td>0.76</td>
<td>0.754</td>
<td>22.64</td>
<td>371</td>
<td>278</td>
<td>0.32</td>
<td>0.28</td>
</tr>
<tr>
<td>GaAs</td>
<td>0.65</td>
<td>0.755</td>
<td>22.50</td>
<td>345</td>
<td>259</td>
<td>0.29</td>
<td>0.27</td>
</tr>
<tr>
<td>NaCl</td>
<td>1.46</td>
<td>0.252</td>
<td>22.41</td>
<td>303</td>
<td>227</td>
<td>2.26</td>
<td>2.32</td>
</tr>
<tr>
<td>MgO</td>
<td>1.60</td>
<td>1.533</td>
<td>9.35</td>
<td>946</td>
<td>710</td>
<td>0.35</td>
<td>0.41</td>
</tr>
</tbody>
</table>
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 $\Theta_E$ 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 $B, \gamma, \Theta_E$, 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.

REFERENCES