

1. TENSORIAL ASPECTS OF PHYSICAL PROPERTIES

It should be mentioned that the true situation is more complicated. The grain boundaries of anisotropic polycrystalline solids are subject to considerable stresses because the neighbouring grains have different amounts of expansion or contraction. These stresses may cause local plastic deformation and cracks may open up between or within the grains. These phenomena can lead to a hysteresis behaviour when the sample is heated up or cooled down. Of course, in polycrystals of a cubic crystal species, these problems do not occur.

If the polycrystalline sample exhibits a texture, the orientation distribution function (ODF) has to be considered in the averaging process. The resulting overall symmetry of a textured polycrystal is usually  $\frac{\infty}{m}$  (see Section 1.1.4.7.4.2), showing the same tensor form as hexagonal crystals (Table 1.4.1.1), or *mmm*.

1.4.2. Grüneisen relation

Thermal expansion of a solid is a consequence of the anharmonicity of interatomic forces (see also Section 2.1.2.8). If the potentials were harmonic, the atoms would oscillate (even with large amplitudes) symmetrically about their equilibrium positions and their mean central position would remain unchanged. In order to describe thermal expansion, the anharmonicity is most conveniently accounted for by means of the so-called ‘quasiharmonic approximation’, assuming the lattice vibration frequencies  $\omega$  to be independent of temperature but dependent on volume  $[(\partial\omega/\partial V) \neq 0]$ . Anharmonicity is taken into account by letting the crystal expand, but it is assumed that the atoms vibrate about their new equilibrium positions harmonically, *i.e.* lattice dynamics are still treated in the harmonic approximation. The assumption  $(\partial\omega/\partial V) = 0$ , which is made for the harmonic oscillator, is a generalization of the postulate that the frequency of a harmonic oscillator does not depend on the amplitude of vibration.

This approach leads, as demonstrated below, to the Grüneisen relation, which combines thermal expansion with other material constants and, additionally, gives an approximate description of the temperature dependence of thermal expansion (*cf.* Krishnan *et al.*, 1979; Barron, 1998).

For isotropic media, the volume expansion  $\beta$  [ $= 3\alpha = \alpha_{11} + \alpha_{22} + \alpha_{33}$ ], *cf.* (1.4.1.2), can be expressed by the thermodynamic relation

$$\beta = \frac{1}{V} \left( \frac{\partial V}{\partial T} \right)_p = -\frac{1}{V} \left( \frac{\partial V}{\partial p} \right)_T \left( \frac{\partial p}{\partial T} \right)_V = \kappa \left( \frac{\partial p}{\partial T} \right)_V, \quad (1.4.2.1)$$

$\kappa$  being the isothermal compressibility. To obtain the quantity  $(\partial p/\partial T)_V$ , the pressure  $p$  is deduced from the free energy  $F$ , whose differential is  $dF = -S dT - p dV$ , *i.e.* from

$$p = -(\partial F/\partial V)_T. \quad (1.4.2.2)$$

In a crystal consisting of  $N$  unit cells with  $p$  atoms in each unit cell, there are  $3p$  normal modes with frequencies  $\omega_s$  (denoted by an index  $s$  running from 1 to  $3p$ ) and with  $N$  allowed wavevectors

Table 1.4.1.1. Shape of the quadric and symmetry restrictions

System	Quadric		No. of independent components	Nonzero components
	Shape	Direction of principal axes		
Triclinic	General ellipsoid or hyperboloid	No restrictions	6	
Monoclinic		One axis parallel to twofold axis ( <b>b</b> )	4	
Orthorhombic		Parallel to crystallographic axes	3	
Trigonal, tetragonal, hexagonal	Revolution ellipsoid or hyperboloid	<i>c</i> axis is revolution axis	2	
Cubic, isotropic media	Sphere	Arbitrary, not defined	1	

$\mathbf{q}_t$  (denoted by an index  $t$  running from 1 to  $N$ ). Each normal mode  $\omega_s(\mathbf{q}_t)$  contributes to the free energy by the amount

$$f_{s,t} = \frac{\hbar}{2} \omega_s(\mathbf{q}_t) + kT \ln \left[ 1 - \exp \left( -\frac{\hbar \omega_s(\mathbf{q}_t)}{kT} \right) \right]. \quad (1.4.2.3)$$

The total free energy amounts, therefore, to

$$F = \sum_{s=1}^{3p} \sum_{t=1}^N f_{s,t} = \sum_{s=1}^{3p} \sum_{t=1}^N \left\{ \frac{\hbar}{2} \omega_s(\mathbf{q}_t) + kT \ln \left[ 1 - \exp \left( -\frac{\hbar \omega_s(\mathbf{q}_t)}{kT} \right) \right] \right\}. \quad (1.4.2.4)$$

From (1.4.2.2)

$$p = -\left( \frac{\partial F}{\partial V} \right)_T = -\sum_{s=1}^{3p} \sum_{t=1}^N \left\{ \frac{\hbar}{2} \frac{\partial \omega_s}{\partial V} + \frac{\exp(-\hbar \omega_s/kT) \hbar (\partial \omega_s/\partial V)}{1 - \exp(-\hbar \omega_s/kT)} \right\}. \quad (1.4.2.5)$$

The last term can be written as

$$\frac{\hbar (\partial \omega_s/\partial V)}{\exp(\hbar \omega_s/kT) - 1} = \hbar n(\omega_s, T) \frac{\partial \omega_s}{\partial V}, \quad (1.4.2.6)$$

where  $n(\omega_s, T)$  is the Bose–Einstein distribution

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$$n(\omega_s, T) = \frac{1}{\exp(\hbar\omega_s/kT) - 1}. \quad (1.4.2.7)$$

Differentiation of (1.4.2.5) and (1.4.2.6) with respect to temperature at constant volume [see (1.4.2.1)] yields

$$\begin{aligned} \left(\frac{\partial p}{\partial T}\right)_V &= - \sum_s \sum_t \hbar \frac{\partial n(\omega_s, T)}{\partial T} \frac{\partial \omega_s(\mathbf{q}_t)}{\partial V} \\ &= - \sum_s \sum_t c_{s,t}^V \frac{1}{\omega_s(\mathbf{q}_t)} \frac{\partial \omega_s(\mathbf{q}_t)}{\partial V} \end{aligned} \quad (1.4.2.8)$$

with

$$c_{s,t}^V = \hbar\omega_s(\mathbf{q}_t) \frac{\partial n(\omega_s, T)}{\partial T} = k \frac{(\hbar\omega_s/kT)^2 \exp(\hbar\omega_s/kT)}{[\exp(\hbar\omega_s/kT) - 1]^2}. \quad (1.4.2.9)$$

This quantity,  $c_{s,t}^V$  (the Einstein function), is the well known contribution of the normal mode  $\omega_s(\mathbf{q}_t)$  to the specific heat (at constant volume):

$$c^V = \sum_s \sum_t c_{s,t}^V = \sum_s \sum_t \hbar\omega_s(\mathbf{q}_t) \frac{\partial n(\omega_s, T)}{\partial T}. \quad (1.4.2.10)$$

Equation (1.4.2.8) can be simplified by the introduction of an ‘individual Grüneisen parameter’  $\gamma_{s,t}$  for each normal mode  $\omega_s(\mathbf{q}_t)$ :

$$\gamma_{s,t} = - \frac{V}{\omega_s(\mathbf{q}_t)} \frac{\partial \omega_s(\mathbf{q}_t)}{\partial V} = - \frac{\partial[\ln \omega_s(\mathbf{q}_t)]}{\partial(\ln V)}. \quad (1.4.2.11)$$

Equation (1.4.2.8) then reads [with (1.4.2.1)]

$$\left(\frac{\partial p}{\partial T}\right)_V = \frac{1}{V} \sum_s \sum_t c_{s,t}^V \gamma_{s,t} = \frac{\beta}{\kappa}. \quad (1.4.2.12)$$

Based on these individual parameters  $\gamma_{s,t}$ , an average (or overall mode-independent) Grüneisen parameter  $\bar{\gamma}$  can be defined as

$$\bar{\gamma} = \frac{\sum_s \sum_t \gamma_{s,t} c_{s,t}^V}{\sum_s \sum_t c_{s,t}^V} = \frac{\sum_s \sum_t \gamma_{s,t} c_{s,t}^V}{c^V}. \quad (1.4.2.13)$$

In this averaging process, the contribution of each normal mode to  $\bar{\gamma}$  is weighted in the same way as it contributes to the specific heat  $c^V$  [see (1.4.2.10)]. Equations (1.4.2.12) and (1.4.2.13) lead to the Grüneisen relation

$$\beta = \bar{\gamma} \frac{\kappa c^V}{V}. \quad (1.4.2.14)$$

The above derivation was made for isotropic media. For anisotropic media,  $\Delta V/V$  is replaced by the strain  $u_{kl}$  and  $\kappa^{-1}$  is replaced by the stiffness tensor  $c_{ijkl}$  [cf. Chapter 2.1 and equation (2.1.2.75)]. Then the Grüneisen parameter turns out to be a second-rank tensor  $\gamma_{ij}$ :

$$\gamma_{ij} = \frac{V}{c^V} c_{ijkl}^T \alpha_{kl}. \quad (1.4.2.15)$$

In the Debye approximation, the mode frequencies scale linearly with the cut-off frequency  $\omega_D$ . Therefore, with  $\hbar\omega_D = kT_D$ , the average isotropic Grüneisen parameter is calculated to be

$$\gamma_D = - \frac{V}{\omega_D} \frac{\partial \omega_D}{\partial V} = - \frac{V}{T_D} \frac{\partial T_D}{\partial V} = - \frac{\partial(\ln T_D)}{\partial(\ln V)}.$$

Since, in the Debye theory,  $T_D$  is independent of temperature,  $\gamma_D$  turns out to be independent of temperature. As  $\kappa$  and  $V$  are only weakly temperature dependent, the thermal expansion  $\beta$  should then, according to (1.4.2.14), roughly behave like  $c^V$ , *i.e.*  $\beta$  should be proportional to  $T^3$  at very low temperatures, and should be approximately constant for  $T \gg T_D$  (the Dulong–Petit law). This

behaviour is found to be approximately satisfied for many compounds, even with different types of interatomic interaction, and  $\gamma$  takes values roughly between 1 and 2. Even in the case of crystals with highly anisotropic elastic and thermal behaviour, the three principal values of the tensor  $\gamma_{ij}$  [(1.4.2.15)] are comparably uniform, having values of about 2 (Küppers, 1974).

Effectively,  $\gamma$  shows a certain more or less pronounced dependence on temperature. The individual  $\gamma_{s,t}$  are assumed to be temperature independent. However, being an average over the whole spectrum of excited modes [cf. (1.4.2.13)],  $\bar{\gamma}$  will not necessarily have the same value at low temperatures (when only low frequencies are excited) as at high temperatures (when all modes are excited). Two limiting cases can be considered:

(1) At very high temperatures, all normal modes contribute by an equal amount and the overall  $\bar{\gamma}$  becomes simply the mean value of all  $\gamma_{s,t}$ .

$$\gamma_\infty = \frac{1}{3pN} \sum_s \sum_t \gamma_{s,t}.$$

(2) At very low temperatures, only the lower frequencies contribute. If only the acoustic branches are considered,  $\bar{\gamma}$  can be related to the velocities of elastic waves. In the long-wavelength limit, dispersion is neglected, *i.e.*  $|\mathbf{q}_t|$  is proportional to  $\omega$ :

$$|\mathbf{q}_t| = \frac{\omega_s(\mathbf{q}_t)}{v_s(\varphi, \vartheta)}, \quad (1.4.2.16)$$

where  $v_s(\varphi, \vartheta)$  ( $s = 1, 2, 3$ ) describes the velocities of the three elastic waves propagating in a direction  $(\varphi, \vartheta)$ . The density of vibrational states for each acoustic branch in reciprocal space increases with  $q^2 dq$ . From (1.4.2.16), it follows that the number of normal modes in an increment of solid angle in  $\mathbf{q}$  space,  $d\Omega = \sin \vartheta d\vartheta d\varphi$ , within a frequency interval  $\omega$  to  $\omega + d\omega$ , is proportional to  $(\omega^2 d\omega d\Omega)/v^3$ . The summation over  $t$  can be converted into an integration over  $\omega$  and  $\Omega$ , leading to

$$\gamma_0 = \frac{\sum_{s=1}^3 \int \frac{\gamma_s(\vartheta, \varphi) d\Omega}{v_s^3(\vartheta, \varphi)}}{\sum_{s=1}^3 \int \frac{d\Omega}{v^3(\vartheta, \varphi)}}.$$

The  $v_s(\varphi, \vartheta)$  can be calculated if the elastic constants are known. For isotropic solids, the term  $\sum v_s^{-3}$  can be replaced (as done in Debye’s theory of heat capacity) by  $(v_l^{-3} + 2v_{tr}^{-3})$ , with  $v_l$  being the velocity of the longitudinal wave and  $v_{tr}$  the velocity of the transverse waves.

In metals, the conduction electrons and magnetic interactions yield contributions to the free energy and to the specific heat. Accordingly, expression (1.4.2.14) can be augmented by introduction of an ‘electronic Grüneisen parameter’,  $\gamma_e$ , and a ‘magnetic Grüneisen parameter’,  $\gamma_m$ , in addition to the ‘lattice Grüneisen parameter’,  $\gamma_l$ , considered so far:

$$\beta = \frac{\kappa}{V} (\gamma_l c_l^V + \gamma_e c_e^V + \gamma_m c_m^V).$$

### 1.4.3. Experimental methods

#### 1.4.3.1. General remarks

Although the strain tensor  $u_{ij}$  and the thermal expansion tensor  $\alpha_{ij}$  in general contain components with  $i \neq j$  (shear strains), in practice only longitudinal effects, *i.e.* relative length changes  $\Delta l/l$  with temperature changes  $\Delta T$ , are measured along different directions and the results are later transformed to a common coordinate system. Diffraction methods directly yield this ratio  $\Delta l/l$ . Other measuring techniques require separate measurements of  $\Delta l$  and  $l$ . The error in the measurement of  $l$  can