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 $\frac{\infty}{m}m$ (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 ω 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 β $[= 3\alpha = \alpha_{11} + \alpha_{22} + \alpha_{33}]$, *cf.* (1.4.1.2), can be expressed by the thermodynamic relation

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

κ 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 ω_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**)		4	
Orthorhombic		Parallel to crystallographic axes		3	
Trigonal, tetragonal, hexagonal	Revolution ellipsoid or hyperboloid	*c* 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

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

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

references