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1.4. Thermal expansion

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1.4.1. Definition, symmetry and representation surfaces

If the temperature T of a solid is raised by an amount ΔT, a deformation takes place that is described by the strain tensor u_{ij}:

$$u_{ij} = \alpha_{ij} \Delta T. \qquad (1.4.1.1)$$

The quantities α_{ij} are the coefficients of thermal expansion. They have dimensions of T^{-1} and are usually given in units of $10^{-6}\ \mathrm{K}^{-1}$. Since u_{ij} is a symmetrical polar tensor of second rank and T is a scalar, α_{ij} is a symmetrical polar tensor of second rank ($\alpha_{ij} = \alpha_{ji}$). According to the properties of the strain tensor u_{ij} (*cf.* Section 1.3.1.3.2), the 'volume thermal expansion', β, is given by the (invariant) trace of the 'linear' coefficients α_{ij}.

$$\beta = \frac{1}{V}\frac{\Delta V}{\Delta T} = \alpha_{11} + \alpha_{22} + \alpha_{33} = \text{trace } (\alpha_{ij}). \qquad (1.4.1.2)$$

The magnitudes of thermal expansion in different directions, α'_{11}, can be visualized in the following ways:

(1) The representation quadric (*cf.* Section 1.1.3.5.2)

$$\alpha_{ij} x_i x_j = C \qquad (1.4.1.3)$$

can be transformed to principal axes X_1, X_2 and X_3 with principal values α_1, α_2 and α_3:

$$\alpha_1 X_1^2 + \alpha_2 X_2^2 + \alpha_3 X_3^2 = C.$$

The length of any radius vector leading to the surface of the quadric ($C = 1$) represents the reciprocal of the square root of thermal expansion along that direction, $\alpha'_{11} = a_{1i} a_{1j} \alpha_{ij}$ (a_{kl} are the direction cosines of the particular direction).

If all α_i are positive, the quadric ($C = +1$) is represented by an ellipsoid, whose semiaxes have lengths $1/\sqrt{\alpha_i}$. In this case, the square of the reciprocal length of radius vector $\mathbf{r}$, r^{-2}, represents the amount of positive expansion in the particular direction, *i.e.* a *dilation* with increasing temperature. If all α_i are negative, C is set to -1. Then, the quadric is again an ellipsoid, and r^{-2} represents a negative expansion, *i.e.* a *contraction* with increasing temperature.

If the α_i have different signs, the quadric is a hyperboloid. The asymptotic cone represents directions along which no thermal expansion occurs ($\alpha'_{11} = 0$).

If one of the α_i is negative, let us first choose $C = +1$. Then, the hyperboloid has one (belt-like) sheet (*cf.* Fig. 1.3.1.3) and the squares of reciprocal lengths of radius vectors leading to points on this sheet represent positive expansions (dilatations) along the particular directions. Along directions where the hyperboloid has no real values, negative expansions occur. To visualize these, C is set to -1. The resulting hyperboloid has two (cap-like) sheets (*cf.* Fig. 1.3.1.3) and r^{-2} represents the amount of contraction along the particular direction.

If two of the α_i are negative, the situation is complementary to the previous case.

(2) A crystal sample having spherical shape (radius = 1 at temperature T) will change shape, after a temperature increase ΔT, to an ellipsoid with principal axes $(1 + \alpha_1 \Delta T)$, $(1 + \alpha_2 \Delta T)$ and $(1 + \alpha_3 \Delta T)$. This 'strain ellipsoid' is represented by the formula

$$\frac{X_1^2}{(1+\alpha_1 \Delta T)^2} + \frac{X_2^2}{(1+\alpha_2 \Delta T)^2} + \frac{X_3^2}{(1+\alpha_3 \Delta T)^2} = 1.$$

Whereas the strain quadric (1.4.1.3) may be a real or imaginary ellipsoid or a hyperboloid, the strain ellipsoid is always a real ellipsoid.

(3) The magnitude of thermal expansion in a certain direction (the longitudinal effect), α'_{11}, if plotted as radius vector, yields an oval:

$$(\alpha_1 X_1^2 + \alpha_2 X_2^2 + \alpha_3 X_3^2)^2 = (X_1^2 + X_2^2 + X_3^2)^3.$$

If spherical coordinates (φ, ϑ) are used to specify the direction, the length of $\mathbf{r}$ is

$$|\mathbf{r}| = \alpha'_{11} = (\alpha_1 \cos^2 \varphi + \alpha_2 \sin^2 \varphi) \sin^2 \vartheta + \alpha_3 \cos^2 \vartheta. \qquad (1.4.1.4)$$

Sections through this representation surface are called polar diagrams.

The three possible graphical representations are shown in Fig. 1.4.1.1.

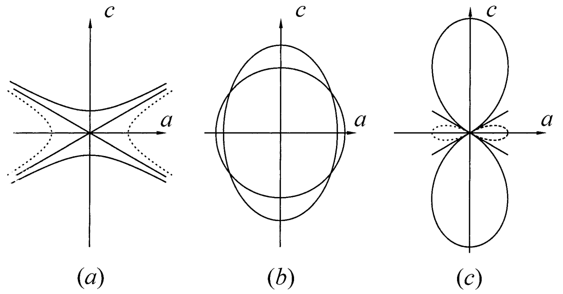
The maximum number of independent components of the tensor α_{ij} is six (in the triclinic system). With increasing symmetry, this number decreases as described in Chapter 1.1. Accordingly, the directions and lengths of the principal axes of the representation surfaces are restricted as described in Chapter 1.3 (*e.g.* in hexagonal, trigonal and tetragonal crystals, the representation surfaces are rotational sheets and the rotation axis is parallel to the n-fold axis). The essential results of these symmetry considerations, as deduced in Chapter 1.1 and relevant for thermal expansion, are compiled in Table 1.4.1.1.

The coefficients of thermal expansion depend on temperature. Therefore, the directions of the principal axes of the quadrics in triclinic and monoclinic crystals change with temperature (except the principal axis parallel to the twofold axis in monoclinic crystals).

The thermal expansion of a polycrystalline material can be approximately calculated if the α_{ij} tensor of the single crystal is known. Assuming that the grains are small and of comparable size, and that the orientations of the crystallites are randomly distributed, the following average of α'_{11} [(1.4.1.4)] can be calculated:

$$\bar{\alpha} = \frac{1}{4\pi} \int_0^{2\pi} \int_0^{\pi} \alpha'_{11} \sin \vartheta \, \mathrm{d}\vartheta \, \mathrm{d}\varphi = \tfrac{1}{3}(\alpha_1 + \alpha_2 + \alpha_3).$$

If the polycrystal consists of different phases, a similar procedure can be performed if the contribution of each phase is considered with an appropriate weight.



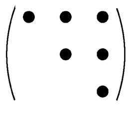
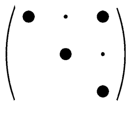
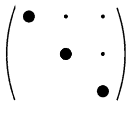
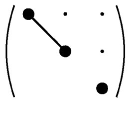
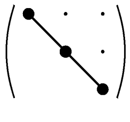
(*a*) (*b*) (*c*)

Fig. 1.4.1.1. Sections (*ac* plane) of representation surfaces for a trigonal (or tetragonal or hexagonal) crystal with $\alpha_{11} = \alpha_{22} = -1$ and $\alpha_{33} = +3 \times 10^{-5}\ \mathrm{K}^{-1}$ (similar to calcite). (*a*) Quadric, (*b*) strain ellipsoid (greatly exaggerated), (*c*) polar diagram. The *c* axis is the axis of revolution. Sectors with negative expansions are dashed.

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*.

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	

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

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

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 $\mathrm{d}F=-S\,\mathrm{d}T-p\,\mathrm{d}V$, *i.e.* from

$$p=-(\partial F/\partial V)_T. \tag{1.4.2.2}$$

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 $\mathbf{q}_t$ (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

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

The total free energy amounts, therefore, to

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

From (1.4.2.2)

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

The last term can be written as

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

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