1. TENSORIAL ASPECTS OF PHYSICAL PROPERTIES

usually be neglected. Thus, the accuracies of Δl and ΔT limit the accuracy of thermal expansion coefficients. The temperature interval ΔT is determined by two measurements of temperatures $T_2 > T_1$, with $T_2 - T_1 = \Delta T$. To increase the accuracy of the difference ΔT, this interval should be large. The measured thermal expansion $\Delta l/(l\Delta T)$ is usually assigned to a temperature at the midpoint of the temperature interval, $T_0 = (T_2 - T_1)/2$. This procedure is only justified if thermal expansion does not depend on temperature.

Since, in fact, thermal expansion depends on temperature, in principle, smaller intervals should be chosen, which, in turn, enlarge the error of ΔT. Here, a compromise has to be made. Sometimes, after completion of a first run and after reviewing the preliminary course of $\alpha(T)$, it is necessary to repeat some measurements using smaller temperature intervals in temperature ranges with large curvatures.

The more-or-less curved course of $\alpha_{ij}(T)$ is usually fitted by polynomials in powers of temperature. Here, those T terms should be selected that are physically meaningful in the particular temperature range. For the low-temperature behaviour of a metal, a polynomial of type $\alpha = AT + BT^3 + CT^5$ should be chosen. For minerals at higher temperatures, a polynomial $\alpha = \alpha_0 + AT + BT^{-1} + CT^{-2}$ is used (Saxena & Shen, 1992).

Temperature is usually measured by thermocouples and, in the cases of optical or electrical measurements (Sections 1.4.3.3 and 1.4.3.4) and at low temperatures also by platinum resistance thermometers. Above 1100 K, optical pyrometers can be used.

In order to measure the thermal expansion of a crystal, at least as many independent measurements are necessary as the tensor has independent components (fourth column in Table 1.4.1.1). It is advisable, however, to carry out more measurements than are necessary. In this case (of redundancy), a 'best' set of tensor components is to be determined by least-squares methods as described below.

Let us assume the most general case of a triclinic crystal, where $m > 6$ independent measurements of thermal expansions b_k ($k = 1, \ldots, m$) were performed along m different directions with direction cosines $(\alpha_{1j})_k$ ($j = 1, 2, 3$) with respect to the chosen coordinate system. Each measurement b_k is related to the six unknown tensor components α_{ij} (to be determined) by

$$b_k = (\alpha'_{11})_k = (\alpha_{1i})_k(\alpha_{1j})_k\alpha_{ij}. \qquad (1.4.3.1)$$

If the α_{ij} are replaced by α_γ ($\gamma = 1, \ldots, 6$), using Voigt's one-index notation (Section 1.1.4.10.2), then $b_k = C_{k\gamma}\alpha_\gamma$ represents an overdetermined inhomogeneous system of m linear equations for the six unknowns α_γ. The coefficients $C_{k\gamma}$, forming an $m \times 6$ matrix, are products containing direction cosines according to (1.4.3.1). The solution is obtained after several matrix calculations which are indicated by the formula (Nye, 1985)

$$\alpha_\gamma = \left\{ \left[(C_{l\delta}^t \cdot C_{l\varepsilon})^{-1} \right]_{\gamma\eta} C_{k\eta}^t \right\} b_k$$
$$(\gamma, \delta, \varepsilon, \eta = 1, \ldots, 6; \quad l, k = 1, \ldots, m),$$

where a superscript 't' means transposed.

Instead of determining the tensor components of a triclinic or monoclinic crystal in a direct way, as outlined above, it is also possible to determine first the temperature change of the crystallographic unit cell and then, by formulae given *e.g.* by Schlenker *et al.* (1978), to deduce the tensor components α_{ij}. The direct approach is recommended, however, for reasons of the propagation of errors (Jessen & Küppers, 1991).

The experimental techniques of measuring relative length changes $\Delta l/l$ that are most widely used include diffraction, optical interferometry, pushrod dilatometry and electrical capacitance methods. If the specimens available are very small and/or irregular in shape, only diffraction methods can be used. The other methods require single-crystal parallelepipedal samples with at least 5 mm side lengths.

1.4.3.2. *Diffraction*

Thermal expansion expresses itself, on a microscopic scale, by a change of the interplanar spacings of lattice planes. These can be measured by use of diffraction methods from changes of Bragg angles θ. Differentiation of the Bragg equation $2d\sin\theta = \lambda$, giving $\Delta d/d = -\cot\theta\Delta\theta$, yields the thermal expansions α'_{11} in directions normal to lattice planes (hkl) (*i.e.* along $\mathbf{h} = h\mathbf{a}^* + k\mathbf{b}^* + l\mathbf{c}^*$) and, if $\mathbf{h}$ has direction cosines $a_{1j}^{(hkl)}$ with respect to the chosen Cartesian coordinate system,

$$\alpha_{11}'^{(hkl)} = a_{1i}^{(hkl)}a_{1j}^{(hkl)}\alpha_{ij} = \frac{1}{d^{(hkl)}}\frac{\partial d^{(hkl)}}{\partial T} = -\cot\theta\frac{\partial\theta}{\partial T}.$$

The coefficient $\cot\theta$ permits a tremendous increase of sensitivity and accuracy if $\theta \to 90°$. That means, if possible, high-angle ($\theta > 70°$) reflections should be used for measurement because, for a given Δd, the changes of Bragg angles $|\Delta\theta|$ to be measured increase with $(\cot\theta)^{-1} = \tan\theta$.

The most important diffraction techniques (X-radiation is preferentially used) are: the rotating-crystal method, the Weissenberg method and diffractometers with counter recording. If small single crystals ($>$ approximately 50 µm) are not available, powder methods (using a Debye–Scherrer film camera or powder diffractometer) must be used, although the advantage of the highly accurate back-reflections, in general, cannot be used.

Experimental aspects of measuring absolute d-values are discussed in detail in Volume C of *International Tables for Crystallography* (1999), Part 5. Since only relative displacements are to be measured in the present case, many complications connected with the determination of absolute values do not apply for thermal expansion measurements, such as zero-point correction, eccentricity of the mounted sample, refraction, absorption and diffraction profile.

1.4.3.3. *Optical methods (interferometry)*

The basic principle of measuring thermal expansion by interferometry consists of converting sample-length changes into variations of optical path differences of two coherent monochromatic light beams, which are reflected from two opposite end faces of the sample (or planes corresponding to them). An He–Ne laser usually serves as a light source. A beam expander produces a parallel beam and interference by two planes, which are slightly inclined to each other, produces fringes of equal thickness. Thermal expansion causes a movement of this fringe pattern, which is detected by photodiodes. The number of fringes passing a reference mark is counted and gives a measure of the relative movement of the two planes.

As examples for various realizations of interferometric devices (Hahn, 1998), two basic designs will be described.

(i) *Fizeau interferometer* (Fig. 1.4.3.1). The sample S is covered by a thin plate P_2 (with a polished upper surface and a coarsely ground and non-reflecting lower surface) and is placed in between a bottom plate P_3 and a wedge-shaped plate P_1 (wedge angle of about 1°). The upper surface of P_1 reflects the incident beam (*i*) to a reflected beam (*r*) so that it is removed from the interference process. The relevant interference takes place between ray (1) reflected by the lower surface of P_1 and ray (2) reflected by the upper surface of P_2. A cylindrical tube T, which defines the distance between P_1 and P_3 as well as P_2, is usually made of fused silica, a material of low and well known thermal expansion. The measured dilatation is caused, therefore, by the difference between thermal expansion of the sample and a portion of the fused silica tube of equal length. The whole apparatus is mounted in a thermostat.

(ii) *Michelson interferometer* (Fig. 1.4.3.2). The reference mirror M and the beam-splitter B are placed outside the thermostat. The upper face of the sample S is one interference plane and the upper surface of the bottom plate is the other. The