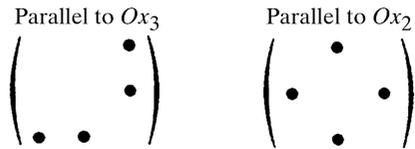


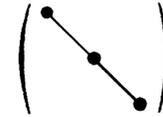
1. TENSORIAL ASPECTS OF PHYSICAL PROPERTIES

(b) Group m :



(v) Cubic and spherical systems

(a) Groups 23, 432 and ∞A_∞ :



(c) Group $2/m$: all components are equal to zero.

(iii) Orthorhombic system

(a) Group 222:



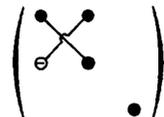
(b) Group $mm2$:



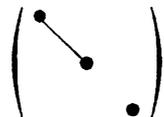
(c) Group mmm : all components are equal to zero.

(iv) Trigonal, tetragonal, hexagonal and cylindrical systems

(a) Groups 3, 4, 6 and A_∞ :



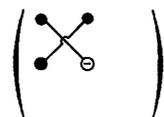
(b) Groups 32, 42, 62 and $A_\infty \infty A_2$:



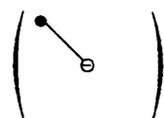
(c) Groups $3m$, $4m$, $6m$ and $A_\infty \infty M$:



(d) Group $\bar{4}$:



(e) Group $\bar{4}2m$:



(f) Groups $\bar{3}$, $4/m$, $\bar{6}2m$, $\bar{3}m$, $4/m\bar{m}$ and $6/m\bar{m}$: all components are equal to zero.

The axial tensor is reduced to a pseudoscalar.

(b) Groups $m\bar{3}$, $\bar{4}3m$, $m\bar{3}m$ and $\infty(A_\infty/M)C$: all components are equal to zero.

1.1.4.10.7.2. Independent components of symmetric axial tensors according to the following point groups

Some axial tensors are also symmetric. For instance, the optical rotatory power of a gyrotropic crystal in a given direction of direction cosines $\alpha_1, \alpha_2, \alpha_3$ is proportional to a quantity G defined by (see Section 1.6.5.4)

$$G = g_{ij}\alpha_i\alpha_j,$$

where the gyration tensor g_{ij} is an axial tensor. This expression shows that only the symmetric part of g_{ij} is relevant. This leads to a further reduction of the number of independent components:

(i) Triclinic system

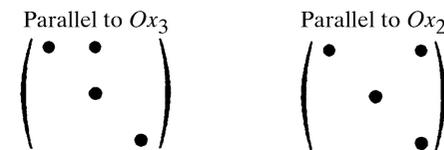
(a) Group 1:



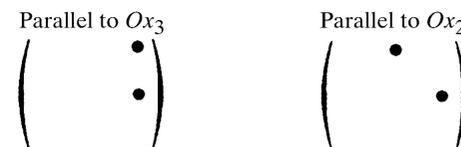
(b) Group $\bar{1}$: all components are equal to zero.

(ii) Monoclinic system

(a) Group 2:



(b) Group m :



(c) Group $2/m$: all components are equal to zero.

(iii) Orthorhombic system

(a) Group 222:



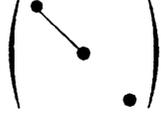
(b) Group $mm2$:



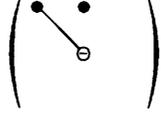
(c) Group mmm : all components are equal to zero.

1.1. INTRODUCTION TO THE PROPERTIES OF TENSORS

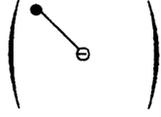
- (iv) *Trigonal, tetragonal and hexagonal systems*
 (a) Groups 3, 32, 4, 42, 6, 62:



- (b) Group $\bar{4}$:

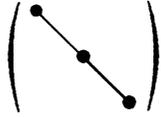


- (c) Group $\bar{4}2m$:



- (d) Groups $\bar{3}$, $3m$, $\bar{3}m$, $4/m$, $4mm$, $4/mmm$, $\bar{6}$, $\bar{6}2m$ and $6/mmm$: all components are equal to zero.

- (v) *Cubic and spherical systems*
 (a) Groups 23, 432 and $A_\infty \infty A_2$:



- (b) Groups $m\bar{3}$, $\bar{4}3m$, $m\bar{3}m$ and $\infty(A_\infty/M)C$: all components are equal to zero.

In practice, gyrotropic crystals are only found among the enantiomorphic groups: 1, 2, 222, 3, 32, 4, 422, 6, 622, 23, 432. Pasteur (1848*a,b*) was the first to establish the distinction between 'molecular dissymmetry' and 'crystalline dissymmetry'.

1.1.5. Thermodynamic functions and physical property tensors

[The reader may also consult Mason (1966), Nye (1985) or Sirotnin & Shaskol'skaya (1982).]

1.1.5.1. Isothermal study

The energy of a system is the sum of all the forms of energy: thermal, mechanical, electrical *etc.* Let us consider a system whose only variables are these three. For a small variation of the associated extensive parameters, the variation of the internal energy is

$$dU = E_n dD_n + T_{kl} dS_{kl} + \Theta d\sigma,$$

where Θ is the temperature and σ is the entropy; there is summation over all dummy indices; an orthonormal frame is assumed and variance is not apparent. The mechanical energy of deformation is given by $T_{kl} dS_{kl}$ (see Section 1.3.2.8). Let us consider the Gibbs free-energy function \mathcal{G} defined by

$$\mathcal{G} = U - E_n D_n - T_{kl} S_{kl} - \Theta \sigma.$$

Differentiation of \mathcal{G} gives

$$d\mathcal{G} = -D_n dE_n - S_{kl} dT_{kl} - \sigma d\Theta.$$

The extensive parameters are therefore partial derivatives of the free energy:

$$S_{kl} = -\frac{\partial \mathcal{G}}{\partial T_{kl}}; \quad D_n = -\frac{\partial \mathcal{G}}{\partial E_n}; \quad \sigma = -\frac{\partial \mathcal{G}}{\partial \Theta}.$$

Each of these quantities may be expanded by performing a further differentiation in terms of the intensive parameters, T_{kl} , E_n and Θ . We have, to the first order,

$$\begin{aligned} dS_{kl} &= \left[\frac{\partial S_{kl}}{\partial T_{ij}} \right]_{E, \Theta} dT_{ij} + \left[\frac{\partial S_{kl}}{\partial E_n} \right]_{T, \Theta} dE_n + \left[\frac{\partial S_{kl}}{\partial \Theta} \right]_{E, T} \delta\Theta \\ dD_n &= \left[\frac{\partial D_n}{\partial T_{kl}} \right]_{E, \Theta} dT_{kl} + \left[\frac{\partial D_n}{\partial E_m} \right]_{T, \Theta} dE_m + \left[\frac{\partial D_n}{\partial \Theta} \right]_{E, T} \delta\Theta \\ d\sigma &= \left[\frac{\partial \sigma}{\partial T_{ij}} \right]_{E, \Theta} dT_{ij} + \left[\frac{\partial \sigma}{\partial E_m} \right]_{T, \Theta} dE_m + \left[\frac{\partial \sigma}{\partial \Theta} \right]_{E, T} \delta\Theta. \end{aligned}$$

To a first approximation, the partial derivatives may be considered as constants, and the above relations may be integrated:

$$\left. \begin{aligned} S_{kl} &= (s_{klj})^{E, \Theta} T_{ij} + (d_{kln})^{T, \Theta} E_n + (\alpha_{kl})^{E, T} \delta\Theta \\ D_n &= (d_{nkl})^{E, \Theta} T_{kl} + (\varepsilon_{nm})^{T, \Theta} E_m + (p_n)^{E, T} \delta\Theta \\ \delta\sigma &= (\alpha_{ij})^E T_{ij} + (p_m)^T E_m + (\rho C^{E, T} / \Theta) \delta\Theta. \end{aligned} \right\} \quad (1.1.5.1)$$

This set of equations is the equivalent of relation (1.1.1.6) of Section 1.1.1.3, which gives the coefficients of the matrix of physical properties. These coefficients are:

(i) For the principal properties: $(s_{klj})^{E, \Theta}$: elastic compliances at constant temperature and field; $(\varepsilon_{nm})^{T, \Theta}$: dielectric constant at constant temperatures and stress; $\rho C^{T, E}$: heat capacity per unit volume at constant stress and field (ρ is the specific mass and $C^{T, E}$ is the specific heat at constant stress and field).

(ii) For the other properties: $(d_{kln})^{T, \Theta}$ and $(d_{nkl})^{E, \Theta}$ are the components of the piezoelectric effect and of the converse effect. They are represented by 3×9 and 9×3 matrices, respectively. One may notice that

$$d_{kln} = \frac{\partial S_{kl}}{\partial E_n} = -\frac{\partial^2 \mathcal{G}}{\partial E_n \partial T_{kl}} = -\frac{\partial^2 \mathcal{G}}{\partial T_{kl} \partial E_n} = \frac{\partial D_n}{\partial T_{kl}} = d_{nkl},$$

which shows again that the components of two properties that are symmetric with respect to the leading diagonal of the matrix of physical properties are equal (Section 1.1.1.4) and that the corresponding matrices are transpose to one another.

In a similar way,

(a) the matrices $(\alpha_{kl})^{E, T}$ of the thermal expansion and $(\alpha_{ij})^E$ of the piezocalorific effect are transpose to one another;

(b) the components $(p_n)^T$ of the pyroelectric and of the electrocalorific effects are equal.

Remark. The piezoelectric effect, namely the existence of an electric polarization \mathbf{P} under an applied stress, is always measured at zero applied electric field and at constant temperature. The second equation of (1.1.5.1) becomes under these circumstances

$$P_n = D_n = (d_{nkl})^\Theta T_{kl}.$$

Remark. Equations (1.1.5.1) are, as has been said, first-order approximations because we have assumed the partial derivatives to be constants. Actually, this approximation is not correct, and in many cases it is necessary to take into account the higher-order terms as, for instance, in:

(a) nonlinear elasticity (see Sections 1.3.6 and 1.3.7);

(b) electrostriction;

(c) nonlinear optics (see Chapter 1.7);

(d) electro-optic and piezo-optic effects (see Sections 1.6.6 and 1.6.7).