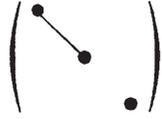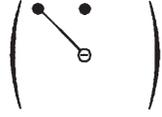## 1.1. INTRODUCTION TO THE PROPERTIES OF TENSORS

(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 $\bar{3}$, $3m$, $\bar{3}m$, $4/m$, $4mm$, $4/mm$, $\bar{6}$, $\bar{6}2m$ and $6/mm$: 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 Sirotin & 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

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

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

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

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:

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

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,

$$dS_{kl} = \left[\frac{\partial S_{kl}}{\partial T_{ij}}\right]_{E,\Theta} dT_{ij} + \left[\frac{\partial S_{kl}}{\partial E_n}\right]_{T,\Theta} dE_n + \left[\frac{\partial S_{kl}}{\partial \Theta}\right]_{E,T} \delta\Theta$$

$$dD_n = \left[\frac{\partial D_n}{\partial T_{kl}}\right]_{E,\Theta} dT_{kl} + \left[\frac{\partial D_n}{\partial E_m}\right]_{T,\Theta} dE_m + \left[\frac{\partial D_n}{\partial \Theta}\right]_{E,T} \delta\Theta$$

$$d\sigma = \left[\frac{\partial \sigma}{\partial T_{ij}}\right]_{E,\Theta} dT_{ij} + \left[\frac{\partial \sigma}{\partial E_m}\right]_{T,\Theta} dE_m + \left[\frac{\partial \sigma}{\partial \Theta}\right]_{E,T} \delta\Theta.$$

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

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

$$(1.1.5.1)$$

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: $\left(s_{klij}\right)^{E,\Theta}$: 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 electrocaloric effects are equal.

Remark. The piezoelectric effect, namely the existence of an electric polarization **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).

1.1.5.2. *Other forms of the piezoelectric constants*

We use here another Gibbs function, the electric Gibbs function, $\mathcal{G}_2$, defined by

$$\mathcal{G}_2 = \mathcal{U} - E_n D_n - \Theta\sigma.$$

Differentiation of $\mathcal{G}$ gives

$$d\mathcal{G}_2 = -D_n \, dE_n + T_{ij} \, dS_{ij} - \sigma \, d\Theta.$$

It follows that

$$T_{ij} = \frac{\partial\mathcal{G}_2}{\partial S_{ij}}; \quad D_n = -\frac{\partial\mathcal{G}_2}{\partial E_n}; \quad \sigma = -\frac{\partial\mathcal{G}_2}{\partial\Theta}$$

and a set of relations analogous to (1.1.5.1):

$$\left.\begin{array}{llll}
T_{ij} = (c_{ijkl})^{E,\Theta} S_{kl} & -(e_{ijn})^{S,\Theta} E_n & -(\lambda_{ij})^{E,S} \, \delta\Theta \\
D_n = (e_{nij})^{E,\Theta} S_{ij} & +(\varepsilon_{nm})^{S,\Theta} E_m & +(p_n)^S \, \delta\Theta \\
\delta\sigma = (\lambda_{ij})^E S_{ij} & +(p_n)^S E_n & +\rho C^{E,S} \, \delta\Theta/\Theta,
\end{array}\right\} \quad (1.1.5.2)$$

where the components $(c_{ijkl})^{E,\Theta}$ are the isothermal elastic stiffnesses at constant field and constant temperature,

$$e_{ijn} = -\frac{\partial T_{ij}}{\partial E_n} = -\frac{\partial^2\mathcal{G}_2}{\partial E_n \partial S_{ij}} = -\frac{\partial^2\mathcal{G}_2}{\partial S_{ij}\partial E_n} = \frac{\partial D_n}{\partial S_{ij}} = e_{nij}$$

are the piezoelectric stress coefficients at constant strain and constant temperature,

$$\lambda_{ij} = -\frac{\partial T_{ij}}{\partial\Theta} = -\frac{\partial^2\mathcal{G}_2}{\partial\Theta\partial S_{ij}} = -\frac{\partial^2\mathcal{G}_2}{\partial S_{ij}\partial\Theta} = \frac{\partial\delta\sigma}{\partial S_{ij}}$$

are the temperature-stress constants and

$$p_n = \frac{\partial D_n}{\partial\Theta} = -\frac{\partial^2\mathcal{G}_2}{\partial\Theta\partial E_n} = -\frac{\partial^2\mathcal{G}_2}{\partial E_n\partial\Theta} = \frac{\partial\delta\sigma}{\partial D_n}$$

are the components of the pyroelectric effect at constant strain.

The relations between these coefficients and the usual coefficients d_{kln} are easily obtained:

(i) At constant temperature and strain: if one puts $\delta\Theta = 0$ and $S_{kl} = 0$ in the first equation of (1.1.5.1) and (1.1.5.2), one obtains, respectively,

$$0 = s_{klij} T_{ij} + d_{kln} E_n$$
$$T_{ij} = -e_{ijn} E_n,$$

from which it follows that

$$d_{kln} = s_{klij} e_{ijn}$$

at constant temperature and strain.

(ii) At constant temperature and stress: if one puts $\delta\Theta = 0$ and $T_{ij} = 0$, one obtains in a similar way

$$S_{kl} = d_{kln} E_n$$
$$0 = c_{ijkl} S_{kl} - e_{ijn} E_n,$$

from which it follows that

$$e_{ijn} = c_{ijkl} d_{kln}$$

at constant temperature and stress.

1.1.5.3. *Relation between the pyroelectric coefficients at constant stress and at constant strain*

By combining relations (1.1.5.1) and (1.1.5.2), it is possible to obtain relations between the pyroelectric coefficients at constant stress, p_n^T, and the pyroelectric coefficients at constant strain, p_n^S,

also called *real* pyroelectric coefficients, p_n^S. Let us put $T_{ij} = 0$ and $E_n = 0$ in the first equation of (1.1.5.1). For a given variation of temperature, $\delta\Theta$, the observed strain is

$$S_{kl} = \left[\alpha_{kl}\right]^{E,T} \delta\Theta.$$

From the second equations of (1.1.5.1) and (1.1.5.2), it follows that

$$D_n = p_n^T \delta\Theta$$
$$D_n = e_{nkl} S_{kl} + p_n \delta\Theta.$$

Substituting the expression S_{kl} and eliminating D_n, it follows that

$$p_n^T = e_{nkl}\left[\alpha_{kl}\right]^{E,T} + p_n^S. \quad (1.1.5.3)$$

This relation shows that part of the pyroelectric effect is actually due to the piezoelectric effect.

1.1.5.4. *Adiabatic study*

Piezoelectric resonators usually operate at a high frequency where there are no heat exchanges, and therefore in an adiabatic regime ($\Theta\delta\sigma = 0$). From the third equation of (1.1.5.1), we obtain a relation between the temperature variation, the applied stress and the electric field:

$$(\alpha_{ij})^E T_{ij} + (p_m)^T E_m + \frac{\rho C^{T,E}}{\Theta}\delta\Theta = 0.$$

If we substitute this relation in the two other relations of (1.1.5.1), we obtain two equivalent relations, but in the *adiabatic* regime:

$$S_{kl} = (s_{klij})^{E,\sigma} T_{ij} + (d_{klm})^{T,\sigma} E_m$$
$$D_n = (d_{nij})^{E,\sigma} T_{ij} + (\varepsilon_{nm})^{T,\sigma} E_m.$$

By comparing these expressions with (1.1.5.1), we obtain the following relations between the adiabatic and the isothermal coefficients:

$$(s_{ijkl})^{E,\sigma} = (s_{ijkl})^{E,\theta} - \frac{(\alpha_{ij})^E (\alpha_{kl})^E \Theta}{\rho C^{T,E}}$$

$$(d_{nij})^{E,\sigma} = (d_{nij})^{E,\theta} - \frac{(p_n)^T (\alpha_{kl})^E \Theta}{\rho C^{T,E}}$$

$$(\varepsilon_{mn})^{T,\sigma} = (\varepsilon_{mn})^{T,\theta} - \frac{(p_n)^T (p_m)^T \Theta}{\rho C^{T,E}}.$$

1.1.6. Glossary

$\mathbf{e}_i$	basis vectors in direct space (covariant)
$\mathbf{e}^i$	basis vectors in reciprocal space (contravariant)
x^i	components of a vector in direct space (contravariant)
x_i	components of a vector in reciprocal space (covariant)
g_{ij}	components of the metric tensor
$t_{i_1\ldots i_p}^{j_1\ldots j_q}$	components of a tensor of rank n, p times covariant and q times contravariant ($n = p + q$)
A^T	transpose of matrix A
$\otimes$	tensor product
$\bigwedge$	outer product
$\wedge$	vector product
∂_i	partial derivative with respect to x_i
δ_i^j	Kronecker symbol
ε_{ijk}	permutation tensor