An Introduction to Crystal Physics

(Description of the Physical Properties of Crystals)

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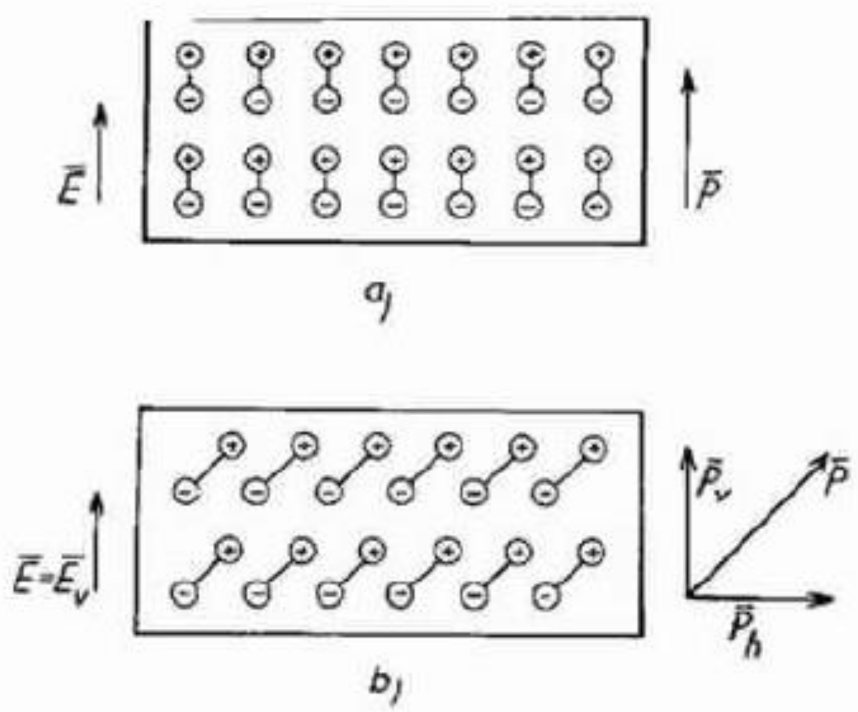

Fig. 1. Formation of dipoles (a) in isotropic, (b) in anisotropic insulators.

$$\bar{P} = \chi \bar{E}.$$

$$P_1 = \chi_{11} E_1 + \chi_{12} E_2 + \chi_{13} E_3$$

$$P_2 = \chi_{21} E_1 + \chi_{22} E_2 + \chi_{23} E_3$$

$$P_3 = \chi_{31} E_1 + \chi_{32} E_2 + \chi_{33} E_3.$$

Accordingly if the $[B_{ijk...n}]$ and $[A_{pqr...u}]$ tensors represent physical quantities the general form of the relation between these quantities may be written (in first-order approximation) using the Einstein's convention as follows

$$B_{ijk...n} = a_{ijk...npqr...u} \cdot A_{pqr...u} \qquad (i, j, k \ldots n, p, q, r, \ldots u = 1, 2, 3) \quad (2.1)$$

where the tensor $[a_{ijk...npqr...u}]$ denotes the physical property connecting the two physical quantities.

It follows from the tensor algebra that if $[A_{pqr...u}]$ denotes an f-rank and $[B_{ijk...n}]$ a g-rank tensor the $[a_{ijk...npq...u}]$, denoting the physical property, must be an $(f+g)$-rank tensor.

Table 1. Tensors representing physical properties

Property or effect	Tensor notation	Tensor rank	Maximum no. of independent components	Defining equation	Physical quantities in the defining equation	
Density	ρ	0	1	$\Delta m = \rho \, \Delta V$	Δm mass	ΔV volume
Specific heat	c	0	1	$\Delta S = \frac{c}{T} \Delta T$	ΔS entropy	T temperature
Pyroelectricity	$[p_i]$	1	3	$\Delta P_i = p_i \cdot \Delta T$	$[P_i]$ dielectric polarization	T temperature
Electrocaloric effect	$[p_i]$	1	3	$\Delta S = p_i \, \Delta E_i$	ΔS entropy	$[E_i]$ electric field
Dielectric permittivity	$[\varepsilon_{ij}]$	2	6	$D_i = \varepsilon_{ij} E_j$	$[D_i]$ electric displacement	$[E_j]$ electric field
Magnetic permeability	$[\mu_{ij}]$	2	6	$B_i = \mu_{ij} H_j$	$[B_i]$ magnetic induction	$[H_j]$ magnetic field
Electrical conductivity	$[\sigma_{ik})$	2	6	$j_i = \sigma_{ik} E_k$	$[j_i]$ current density	$[E_k]$ electric field
Electrical resistivity	$[\rho_{ik}]$	2	6	$E_i = \rho_{ik} \cdot j_k$	$[E_i]$ electric field	$[j_k]$ current density
Thermal conductivity	$[k_{ij}]$	2	6	$h_i = -k_{ij}(\partial T/\partial x_j)$	$[h_i]$ heat flux	$[\partial T/\partial x_j]$ temperature gradient
Thermal expansion	$[\alpha_{ij}]$	2	6	$\varepsilon_{ij} = \alpha_{ij} \, \Delta T$	$[\varepsilon_{ij}]$ strain	T temperature
Seebeck-effect	$[\beta_{ik}]$	2	9	$E_i = -\beta_{ik}(\partial T/\partial x_k)$	$[E_i]$ electric field	$[\partial T/\partial x_k]$ temperature gradient
Peltier-effect	$[\pi_{ik}]$	2	9	$h_i = \pi_{ik} j_k$	$[h_i]$ heat flux	$[j_k]$ current density
Hall-effect	$[\rho_{ikl}]$	3	9	$E_i = \rho_{ikl} \cdot j_k \cdot H_l$	$[E_i]$ electric field	$[j_k]$ current density $[H_l]$ magn. field
Direct piezo-electric effect	$[d_{ijk}]$	3	18	$P_i = d_{ijk} \cdot \sigma_{jk}$	$[P_i]$ dielectric polarization	$[\sigma_{jk}]$ stress

Converse piezo-electric effect	$[d_{ijk}]$	3	18	$\varepsilon_{jk} = d_{ijk}E_i$	$[\varepsilon_{jk}]$ strain	$[E_i]$ electric field
Piezomagnetic effect	$[q_{lij}]$	3	18	$M_l = q_{lij}\sigma_{ij}$	$[M_l]$ magnetic polarization	$[\sigma_{ij}]$ stress
Electro-optical effect	$[r_{ijk}]$	3	18	$\Delta a_{ij} = r_{ijk}E_k$	$[a_{ij}]$ dielectric impermeability	$[E_k]$ electric field
Second Harmonic Generation	$[d_{ijk}]$	3	18	$P_i^{2\omega} = d_{ijk}E_jE_k$	$[P_i^{2\omega}]$ dielectric polarization at frequency 2ω	$[E_j]$, $[E_k]$ electric field
Second-order elastic stiffnesses	$[c_{ijkl}]$	4	21	$\sigma_{ij} = c_{ijkl}\varepsilon_{kl}$	$[\sigma_{ij}]$ stress	$[\varepsilon_{kl}]$ strain
Second-order elastic compliances	$[s_{ijkl}]$	4	21	$\varepsilon_{ij} = s_{ijkl}\sigma_{kl}$	$[\varepsilon_{ij}]$ strain	$[\sigma_{kl}]$ stress
Piezooptic effect	$[\pi_{ijkl}]$	4	36	$\Delta a_{ij} = \pi_{ijkl}\sigma_{kl}$	$[a_{ij}]$ dielectric impermeability	$[\sigma_{kl}]$ stress
Quadratic electrooptic effect	$[R_{ijkl}]$	4	36	$\Delta a_{ij} = R_{ijkl}E_kE_l$	$[a_{ij}]$ dielectric impermeability	$[E_k]$, $[E_l]$ electric field
Electrostriction	$[\gamma_{iljk}]$	4	36	$\varepsilon_{jk} = \mu_{iljk}E_iE_l$	$[\varepsilon_{jk}]$ strain	$[E_i]$, $[E_l]$, electric field
Third-order elastic stiffnesses	$[c_{ijklmn}]$	6	56	$\Phi = \frac{1}{2}c_{ijkl}\cdot\eta_{ij}\cdot\eta_{kl} + \frac{1}{6}c_{ijklmn}\cdot\eta_{ij}\cdot\eta_{kl}\cdot\eta_{mn}$	Φ, energy of deformation, $[c_{ijkl}]$ second-order stiffnesses	$[\eta_{ij}]$, $[\eta_{ij}]$, $[\eta_{mn}]$ the Lagrange finite strain components

are investigated simultaneously. Independent variables should be the stress $[\sigma_{kl}]$, the electric field $[E_k]$, the magnetic field $[H_l]$ and temperature $[T]$ whereas the deformation $[\varepsilon_{ij}]$, the polarization $[P_i]$, the magnetization $[M_i]$ and the entropy $[S]$ are selected as dependent variables. The differentials of the former quantities are obviously connected with the following relationships:

$$d\varepsilon_{ij} = \underset{1.}{\left(\frac{\partial \varepsilon_{ij}}{\partial \sigma_{kl}}\right)} d\sigma_{kl} + \underset{2.}{\left(\frac{\partial \varepsilon_{ij}}{\partial E_k}\right)} dE_k + \underset{3.}{\left(\frac{\partial \varepsilon_{ij}}{\partial H_l}\right)} dH_l + \underset{4.}{\left(\frac{\partial \varepsilon_{ij}}{\partial T}\right)} dT$$

$$dP_i = \underset{5.}{\left(\frac{\partial P_i}{\partial \sigma_{kl}}\right)} d\sigma_{kl} + \underset{6.}{\left(\frac{\partial P_i}{\partial E_k}\right)} dE_k + \underset{7.}{\left(\frac{\partial P_i}{\partial H_l}\right)} dH_l + \underset{8.}{\left(\frac{\partial P_i}{\partial T}\right)} dT$$

$$dM_i = \underset{9.}{\left(\frac{\partial M_i}{\partial \sigma_{kl}}\right)} d\sigma_{kl} + \underset{10.}{\left(\frac{\partial M_i}{\partial E_k}\right)} dE_k + \underset{11.}{\left(\frac{\partial M_i}{\partial H_l}\right)} dH_l + \underset{12.}{\left(\frac{\partial M_i}{\partial T}\right)} dT$$

$$dS = \underset{13.}{\left(\frac{\partial S}{\partial \sigma_{kl}}\right)} d\sigma_{kl} + \underset{14.}{\left(\frac{\partial S}{\partial E_k}\right)} dE_k + \underset{15.}{\left(\frac{\partial S}{\partial H_l}\right)} dH_l + \underset{16.}{\left(\frac{\partial S}{\partial T}\right)} dT$$

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The partial derivatives are characteristic of the following effects:

1. Elastic deformation.
2. Reciprocal (or converse) piezo-electric effect.
3. Reciprocal (or converse) piezo-magnetic effect.
4. Thermal dilatation.
5. Piezo-electric effect.
6. Electric polarization.
7. Magneto-electric polarization.
8. Pyroelectricity.
9. Piezo-magnetic effect.
10. Reciprocal (or converse) magneto-electric polarization.
11. Magnetic polarization.
12. Pyromagnetism.
13. Piezo-caloric effect.
14. Electro-caloric effect.
15. Magneto-caloric effect.
16. Heat transmission.

In order to recognize the relationships among the partial derivatives of the equation-system (3.1) let us discuss the Gibb's potential of the system

$$G = U - \sigma_{ij}\varepsilon_{ij} - E_k P_k - H_l M_l - TS. \tag{3.2}$$

Remembering that the total differential of the internal energy according to the first and second law of thermodynamics is

$$dU = \sigma_{ij}\, d\varepsilon_{ij} + E_k\, dP_k + H_l\, dM_l + T\, dS \tag{3.3}$$

one obtains for the total differential of the Gibbs' potential the expression

$$dG = -\varepsilon_{ij}\, d\sigma_{ij} - P_k\, dE_k - M_l\, dH_l - S\, dT. \tag{3.4}$$

At the same time one may describe the total differential of the Gibbs' potential with the partial derivatives of the independent variables:

$$dG = \left(\frac{\partial G}{\partial \sigma_{ij}}\right) d\sigma_{ij} + \left(\frac{\partial G}{\partial E_k}\right) dE_k + \left(\frac{\partial G}{\partial H_l}\right) dH_l + \left(\frac{\partial G}{\partial T}\right) dT \tag{3.5}$$

$$\left(\frac{\partial G}{\partial \sigma_{ij}}\right) = -\varepsilon_{ij} \qquad \left(\frac{\partial G}{\partial E_k}\right) = -P_k \qquad \left(\frac{\partial G}{\partial H_l}\right) = -M_l \qquad \left(\frac{\partial G}{\partial T}\right) = -S.$$

Some tensors are symmetrical

$$-\left(\frac{\partial^2 G}{\partial \sigma_{kl}\partial \sigma_{ij}}\right)=\frac{\partial \varepsilon_{ij}}{\partial \sigma_{kl}}=s_{ijkl}=-\left(\frac{\partial^2 G}{\partial \sigma_{ij}\partial \sigma_{kl}}\right)=\frac{\partial \varepsilon_{kl}}{\partial \sigma_{ij}}=s_{klij}$$

$$-\left(\frac{\partial^2 G}{\partial E_j\partial E_k}\right)=\frac{\partial P_k}{\partial E_j}=\chi_{kj}=-\left(\frac{\partial^2 G}{\partial E_k\partial E_j}\right)=\frac{\partial P_j}{\partial E_k}=\chi_{jk}$$

Tensors representing the direct and reciprocal effects are related to each other:

$$-\left(\frac{\partial^2 G}{\partial \sigma_{ij}\,\partial E_k}\right)=\left(\frac{\partial P_k}{\partial \sigma_{ij}}\right)=-\left(\frac{\partial^2 G}{\partial E_k\,\partial \sigma_{ij}}\right)=\left(\frac{\partial \varepsilon_{ij}}{\partial E_k}\right)=d_{kij} \qquad (3.13)$$

$$-\left(\frac{\partial^2 G}{\partial \sigma_{ij}\,\partial H_l}\right)=\left(\frac{\partial M_l}{\partial \sigma_{ij}}\right)=-\left(\frac{\partial^2 G}{\partial H_l\,\partial \sigma_{ij}}\right)=\left(\frac{\partial \varepsilon_{ij}}{\partial H_l}\right)=q_{lij} \qquad (3.14)$$

$$-\left(\frac{\partial^2 G}{\partial E_k\,\partial H_l}\right)=\left(\frac{\partial M_l}{\partial E_k}\right)=-\left(\frac{\partial^2 G}{\partial H_l\,\partial E_k}\right)=\left(\frac{\partial P_k}{\partial H_l}\right)=\lambda_{lk} \qquad (3.15)$$

$$-\left(\frac{\partial^2 G}{\partial \sigma_{ij}\,\partial T}\right)=\left(\frac{\partial S}{\partial \sigma_{ij}}\right)=-\left(\frac{\partial^2 G}{\partial T\,\partial \sigma_{ij}}\right)=\left(\frac{\partial \varepsilon_{ij}}{\partial T}\right)=\alpha_{ij} \qquad (3.16)$$

$$-\left(\frac{\partial^2 G}{\partial T\,\partial E_k}\right)=\left(\frac{\partial P_k}{\partial T}\right)=-\left(\frac{\partial^2 G}{\partial E_k\,\partial T}\right)=\left(\frac{\partial S}{\partial E_k}\right)=p_k \qquad (3.17)$$

$$-\left(\frac{\partial^2 G}{\partial T\,\partial H_l}\right)=\left(\frac{\partial M_l}{\partial T}\right)=-\left(\frac{\partial^2 G}{\partial H_l\,\partial T}\right)=\left(\frac{\partial S}{\partial H_l}\right)=m_l. \qquad (3.18)$$

From the above equations follows that correspondences exist between:

(a) the components of the tensors representing the piezoelectric and reciprocal piezo-electric effect (eq. (3.13)),

(b) the components of the tensors representing the piezo-magnetic and reciprocal piezo-magnetic effect (eq. (3.14)),

(c) the components of the tensors representing the magneto-electric polarization and reciprocal magneto-electric polarization (eq. (3.15)),

(d) the components of the tensors representing the piezo-caloric effect and the thermal dilatation (eq. (3.16)),

(e) the components of the tensors representing the pyroelectric and electrocaloric effect (eq. (3.17)),

(f) the components of the tensors representing the pyromagnetic and magneto-caloric effect (eq. (3.18)).

$$\begin{aligned}
\varepsilon_{ij} &= s_{ijkl}\sigma_{kl} + d_{kij}E_k + q_{lij}H_l + \alpha_{ij}\Delta T \\
P_k &= d_{kij}\sigma_{ij} + \chi_{kl}E_l + \lambda_{lk}H_l + p_k\Delta T \\
M_l &= q_{lij}\sigma_{ij} + \lambda_{lk}E_k + \psi_{lm}H_m + m_l\Delta T \\
\Delta S &= \alpha_{ij}\sigma_{ij} + p_kE_k + m_lH_l + \frac{c}{T}\Delta T \qquad (i, j, k, l = 1, 2, 3).
\end{aligned} \tag{3.19}$$