

5 Thermodynamic Relationships

5.1 Equations of State

The behavior of a crystal under the influence of different external (inducing) quantities can be calculated with knowledge of the given property. We call the existing relationships equations of state. If, for example, the mechanical stress in the form of the stress tensor $\{\sigma_{ij}\}$, an electric field E , a magnetic field H , and the temperature difference ΔT are accepted as independent (inducing) variables, then for the corresponding (dependent) induced quantities such as mechanical deformation $\{\varepsilon_{ij}\}$, electric displacement D , magnetic induction B and entropy difference ΔS per unit volume, one must specify, to a first approximation, the following linear equations:

$$\begin{aligned}\varepsilon_{ij} &= s_{ijkl}^{E,H,T} \sigma_{kl} + c_{ijk}^{H,T} E_k + m_{ijk}^{E,T} H_k + \alpha_{ij}^{E,H} \Delta T \\ \Delta D_i &= d_{ijk}^{H,T} \sigma_{jk} + \epsilon_{ij}^{\sigma,H,T} E_j + q_{ij}^{\sigma,T} H_j + p_i^{\sigma,H} \Delta T \\ \Delta B_i &= n_{ijk}^{E,T} \sigma_{jk} + b_{ij}^{\sigma,T} E_j + \mu_{ij}^{\sigma,E,T} H_j + m_i^{\sigma,E} \Delta T \\ \Delta S &= \beta_{ij}^{E,H} \sigma_{ij} + q_i^{\sigma,H} E_i + n_i^{\sigma,E} H_i + \frac{C^{\sigma,E,H}}{T} \Delta T\end{aligned}$$

The attached symbols σ , E , H , and T mean that each respective quantity is fixed. The relationships are mostly familiar and otherwise easy to interpret. $C^{\sigma,E,H}$ is the specific heat per unit volume. In a following second approximation one has to include the tensor relationships describing the quadratic dependence of the quantities ε_{ij} , D_i , B_i and ΔS on the inducing quantities, hence on the pure quadratic and mixed products, as, for example, $\sigma_{ij} E_k$, $E_i \Delta T$ and so on. The same applies to higher order approximations. Accordingly, the first, second and higher approximation represent nothing else as a Taylor expansion of the dependent quantities with respect to the independent quantities in first, second, and higher orders.

Under suitable experimental arrangements we can also introduce, as independent variables, other combinations, as, for example, mechanical deforma-

tion, the electric and magnetic field and temperature. One then obtains analogous equations of state:

$$\begin{aligned}\sigma_{ij} &= c_{ijkl}^{E,H,T} \varepsilon_{kl} + f_{ijk}^{H,T} E_k + p_{ijk}^{E,T} H_k + \gamma_{ij}^{E,H} \Delta T \\ \Delta D_i &= e_{ijk}^{H,T} \varepsilon_{jk} + \epsilon_{ij}^{\varepsilon,H,T} E_j + q_{ij}^{\varepsilon,T} H_j + p_i^{\varepsilon,H} \Delta T \\ \Delta B_i &= q_{ijk}^{E,T} \varepsilon_{jk} + b_{ij}^{\varepsilon,T} E_j + \mu_{ij}^{\varepsilon,E,T} H_j + m_i^{\varepsilon,E} \Delta T \\ \Delta S &= \delta_{ij}^{E,H} \varepsilon_{ij} + q_i^{\varepsilon,H} E_i + n_i^{\varepsilon,E} H_i + \frac{C^{\varepsilon,E,H}}{T} \Delta T\end{aligned}$$

We inquire as to the relationships existing under the different coefficients. In this case it is convenient to draw upon the so called thermodynamic potential. The density of the internal energy U of a body, measured, for example, in Jm^{-3} , represents the sum of the total energy content. Accordingly, the change ΔU is given by the following expression:

$$\Delta U = \Delta Q + \sigma_{ij} \Delta \varepsilon_{ij} + E_i \Delta D_i + H_i \Delta B_i = \Delta Q + \Delta W,$$

where ΔQ signifies the change of the caloric energy content. In the case of reversible processes $\Delta Q = T \Delta S$. ΔW specifies all noncaloric energy content. A second important function of state is the free enthalpy G , also called the *Gibbs potential* arising from U through the following Legendre transformation:

$$G = U - \sigma_{ij} \varepsilon_{ij} - E_i D_i - H_i B_i - TS.$$

Its differential change is given by

$$\begin{aligned}\Delta G &= \Delta U - \sigma_{ij} \Delta \varepsilon_{ij} - \varepsilon_{ij} \Delta \sigma_{ij} - E_i \Delta D_i - D_i \Delta E_i \\ &\quad - H_i \Delta B_i - B_i \Delta H_i - T \Delta S - S \Delta T \\ &= -\varepsilon_{ij} \Delta \sigma_{ij} - D_i \Delta E_i - B_i \Delta H_i - S \Delta T.\end{aligned}$$

In thermodynamic equilibrium, i.e., here, in a state of constant mechanical stress, constant electric and magnetic field as well as constant temperature, $\Delta G = 0$. This statement plays a fundamental role in the stability of a crystal type under isobaric ($\Delta \sigma_{ij} = 0$), isagriscen ($\Delta E_i = \Delta H_i = 0$) and isothermal ($\Delta T = 0$) conditions. From several arrangements (modifications) of the same chemical constituents existing under the same conditions, the most stable is the one possessing the smallest Gibbs free energy.

We now assume that G is an arbitrarily differentiable function of the variables $(\sigma_{ij}, E_i, H_i, T)$. We can then expand G as a Taylor series:

$$\begin{aligned}\Delta G = & \left(\frac{\partial G}{\partial \sigma_{ij}} \right)_{E,H,T} \Delta \sigma_{ij} + \left(\frac{\partial G}{\partial E_i} \right)_{\sigma,H,T} \Delta E_i + \left(\frac{\partial G}{\partial H_i} \right)_{\sigma,E,T} \Delta H_i \\ & + \left(\frac{\partial G}{\partial T} \right)_{\sigma,E,H} \Delta T + \frac{1}{2} \left(\frac{\partial^2 G}{\partial \sigma_{ij} \partial \sigma_{kl}} \right)_{E,H,T} \Delta \sigma_{ij} \Delta \sigma_{kl} \\ & + \frac{1}{2} \left(\frac{\partial^2 G}{\partial E_i \partial E_j} \right)_{\sigma,H,T} \Delta E_i \Delta E_j + \dots\end{aligned}$$

Comparison with the expression derived from the definition of G gives the following relations:

$$\begin{aligned}\left(\frac{\partial G}{\partial \sigma_{ij}} \right)_{E,H,T} &= -\varepsilon_{ij}, & \left(\frac{\partial G}{\partial E_i} \right)_{\sigma,H,T} &= -D_i, \\ \left(\frac{\partial G}{\partial H_i} \right)_{\sigma,E,T} &= -B_i, & \left(\frac{\partial G}{\partial T} \right)_{\sigma,E,H} &= -S.\end{aligned}$$

Differentiating these expressions again and making use of the permutability of the sequence of differentiation, gives, for example,

$$\left(\frac{\partial^2 G}{\partial \sigma_{ij} \partial E_k} \right)_{H,T} = - \left(\frac{\partial \varepsilon_{ij}}{\partial E_k} \right)_{H,T} = - \left(\frac{\partial D_k}{\partial \sigma_{ij}} \right)_{H,T},$$

hence,

$$c_{ijk}^{H,T} = d_{kij}^{H,T}.$$

In a similar manner we obtain

$$m_{ijk}^{E,T} = n_{kij}^{E,T}, \quad \alpha_{ij}^{E,H} = \beta_{ij}^{E,H}, \quad q_{ij}^{\sigma,T} = b_{ij}^{\sigma,T}, \quad p_i^{\sigma,H} = q_i^{\sigma,H}, \quad m_i^{\sigma,E} = n_i^{\sigma,E}.$$

If one takes into consideration isochore ($\Delta \varepsilon_{ij} = 0$), isagric and isothermal conditions, then analogous relationships can be derived from the *electric-magnetic Gibbs potential* $F = U - E_i D_i - H_i B_i - TS$.

In the corresponding equilibrium state $\Delta F = 0$ because

$$\Delta F = \sigma_{ij} \Delta \varepsilon_{ij} - D_i \Delta E_i - B_i \Delta H_i - S \Delta T.$$

To begin with

$$\begin{aligned}\left(\frac{\partial F}{\partial \varepsilon_{ij}} \right)_{E,H,T} &= \sigma_{ij}, & \left(\frac{\partial F}{\partial E_i} \right)_{\varepsilon,H,T} &= -D_i, \\ \left(\frac{\partial F}{\partial H_i} \right)_{\varepsilon,E,T} &= -B_i, & \left(\frac{\partial F}{\partial T} \right)_{\varepsilon,E,H} &= -S.\end{aligned}$$

From this, we obtain by differentiation, taking into account the permutability of the sequence of differentiation

$$\begin{aligned} e_{ijk}^{H,T} &= -f_{kij}^{H,T}, & p_{ijk}^{E,T} &= -q_{kij}^{E,T}, & \gamma_{ij}^{E,H} &= -\delta_{ij}^{E,H}, \\ q_{ij}^{\varepsilon,T} &= b_{ij}^{\varepsilon,T}, & p_i^{\varepsilon,H} &= q_i^{\varepsilon,H}, & m_i^{\varepsilon,H} &= n_i^{\varepsilon,H}. \end{aligned}$$

We have used some of these relationships, for example, $c_{ijk}^{H,T} = d_{kij}^{H,T}$ and $e_{ijk}^{H,T} = -f_{kij}^{H,T}$, in preceding sections.

Further such relations (*first-order Maxwell relations*) can be calculated in an analogous fashion for all other arbitrary combinations of auxiliary conditions from the associated functions of state F_X , derived from the internal energy U with the help of a Legendre transformation according to $F_X = U - X$. X can be one or even several of the energy terms of type $\sigma_{ij}\varepsilon_{ij}$, $E_i D_i$, $H_i B_i$ or TS . These terms represent products of two conjugate quantities A_k and \tilde{A}_k , also designated as intensive and extensive quantities, respectively (A_k : σ_{ij} , E_i , H_i , ΔT ; \tilde{A}_k : ε_{ij} , D_i , B_i , ΔS).

It is then true that $\partial F_X / \partial A_k = -\tilde{A}_k$ or $\partial F_X / \partial \tilde{A}_k = A_k$, when X contains the product $A_k \tilde{A}_k$ or not respectively. The first-order Maxwell relations then take the form

$$\frac{\partial^2 F_X}{\partial A_k \partial A_l} = -\frac{\partial \tilde{A}_k}{\partial A_l} = -\frac{\partial \tilde{A}_l}{\partial A_k}.$$

Similar results are obtained for $\frac{\partial^2 F_X}{\partial \tilde{A}_k \partial \tilde{A}_l}$.

If one again differentiates these relations with respect to the variables A_i and \tilde{A}_i noting the permutability of the sequence of differentiation, we get the second-order Maxwell relations

$$\frac{\partial^3 F_X}{\partial A_i \partial A_j \partial A_k} = -\frac{\partial^2 \tilde{A}_k}{\partial A_i \partial A_j} = -\frac{\partial^2 \tilde{A}_j}{\partial A_i \partial A_k} = -\frac{\partial^2 \tilde{A}_i}{\partial A_j \partial A_k}$$

and correspondingly

$$\frac{\partial^3 F_X}{\partial \tilde{A}_i \partial \tilde{A}_j \partial \tilde{A}_k} = \frac{\partial^2 A_k}{\partial \tilde{A}_i \partial \tilde{A}_j} = \dots,$$

whereby certain auxiliary conditions must be kept to with respect to the other variables.

From the many relations, we point out here some examples of importance:

Third-rank elasticity tensor $\sigma_{ij} = c_{ijkl}\eta_{kl} + \underline{c_{ijklmn}}\eta_{kl}\eta_{mn}$:

$$\frac{\partial^2 \sigma_{ij}}{\partial \eta_{kl} \partial \eta_{mn}} = \frac{\partial^2 \sigma_{kl}}{\partial \eta_{ij} \partial \eta_{mn}} = \frac{\partial^2 \sigma_{mn}}{\partial \eta_{ij} \partial \eta_{kl}} \rightarrow c_{ijklmn} = c_{klijmn} = c_{mni jkl} = \dots$$

Second-order dielectric tensor $D_i = \epsilon_{ij}E_j + \underline{\epsilon_{ijk}}E_jE_k$:

$$\frac{\partial^2 D_i}{\partial E_j \partial E_k} = \frac{\partial^2 D_j}{\partial E_i \partial E_k} = \frac{\partial^2 D_k}{\partial E_i \partial E_j} \rightarrow \epsilon_{ijk} = \epsilon_{jik} = \epsilon_{kij} = \dots \quad (\text{totally symmetric}).$$

This corresponds to “Kleinmans rule” for nonlinear dielectric susceptibility (see Section 4.4.4).

Second-order piezoelectric effect $D_i = d_{ijk}\sigma_{jk} + \underline{d_{ijklm}}\sigma_{jk}\sigma_{lm}$ and the mecha-noelectric deformation tensor $\epsilon_{jk} = s_{jklm}\sigma_{lm} + \underline{q_{jklmi}}\sigma_{lm}E_i$:

$$\frac{\partial^2 D_i}{\partial \sigma_{jk} \partial \sigma_{lm}} = \frac{\partial^2 \epsilon_{jk}}{\partial \sigma_{lm} \partial E_i} \rightarrow d_{ijklm} = q_{jklmi}.$$

Second-order electrostriction $\epsilon_{ij} = d_{ijk}E_k + \underline{d_{ijkl}}E_kE_l$ and pressure dependence of the dielectric tensor $D_k = \epsilon_{kl}E_l + \underline{e_{klij}}\sigma_{ij}E_l$:

$$\frac{\partial^2 \epsilon_{ij}}{\partial E_k \partial E_l} = \frac{\partial^2 D_k}{\partial \sigma_{ij} \partial E_l} = \frac{\partial^2 D_l}{\partial \sigma_{ij} \partial E_k} \rightarrow d_{ijkl} = e_{klij}.$$

Accordingly, the components of the tensor of quadratic electrostriction are numerically equal to the corresponding components of the tensor describing the dependence of the dielectric constants on external mechanical stress. Hence, we have a simple independent check of these tensors (Preu u. Haussühl, 1983). Substituting the electric quantities by the corresponding magnetic ones results in completely analogous relations.

5.2

Tensor Components Under Different Auxiliary Conditions

The question often arises, whether tensor components differ when measured under different auxiliary conditions, as, for example, at constant electric field and constant electric displacement or at constant temperature (isothermal) and constant entropy (adiabatic). The expected differences are usually very small, often of the order of the measurement accuracy. However, cases exist where substantial differences appear, as we shall now see.

Firstly, we again start from a system of equations of state, for example, from the system of variables σ_{ij} , E_i , H_i and T . Then, for example, $S = \text{const.}$ means that

$$\Delta S = \alpha_{ij}^{E,H} \sigma_{ij} + q_i^{\sigma,H} E_i + m_i^{\sigma,E} H_i + \frac{C^{\sigma,E,H}}{T} \Delta T = 0.$$

Hence, with the absence, for example, of an electric and a magnetic field ($E_i = H_i = 0$) $\Delta T = -\frac{\alpha_{ij}^{E,H} \sigma_{ij}}{C^{\sigma,E,H}} T$. This is the so-called adiabatic temperature increase,

appearing as an effect of an external mechanical stress. We want to calculate the order of magnitude of this effect on a simple example. In a pressure cell, we apply a pressure of 1000 bar (10^8 Pa) on a NaCl crystal, when, for example, investigating some property as a function of pressure. With $\sigma_{ii} = -p = 10^8$ Pa, we expect, with a linear thermal expansion $\alpha_{11}^{E,H} = \alpha_{ii}^{E,H} = 40 \cdot 10^{-6} \text{ K}^{-1}$ and specific heat $C^{\sigma,E,H} = 1,6 \cdot 10^6 \text{ J m}^{-3} \text{ K}^{-1}$, a temperature increase of

$$\Delta T = (\alpha_{11}^{E,H} + \alpha_{22}^{E,H} + \alpha_{33}^{E,H}) p T / C^{\sigma,E,H} \approx 2,5 \text{ K}$$

at around 300 K.

From the equation of state $\varepsilon_{ij} = s_{ijkl}^{E,H,T} \sigma_{kl} + \alpha_{ij}^{E,H} \Delta T$ and with the above expression for ΔT by $E_i = H_i = 0$, we obtain

$$\begin{aligned} \varepsilon_{ij} &= s_{ijkl}^{E,H,T} \sigma_{kl} - \alpha_{ij}^{E,H} \alpha_{kl}^{E,H} \sigma_{kl} T / C^{\sigma,E,H}, \\ &= (s_{ijkl}^{E,H,T} - \alpha_{ij}^{E,H} \alpha_{kl}^{E,H} T / C^{\sigma,E,H}) \sigma_{kl}; \end{aligned}$$

hence,

$$s_{ijkl}^{E,H,S} = s_{ijkl}^{E,H,T} - \alpha_{ij}^{E,H} \alpha_{kl}^{E,H} T / C^{\sigma,E,H}.$$

We obtain a generally valid expression for such differences as follows. Let Y be a function dependent on the variables X_1 and X_2 where X_1 is a function of X_2 and X_3 . Then

$$\Delta Y = \left(\frac{\partial Y}{\partial X_1} \right)_{X_2} \Delta X_1 + \left(\frac{\partial Y}{\partial X_2} \right)_{X_1} \Delta X_2$$

and

$$\Delta X_1 = \left(\frac{\partial X_1}{\partial X_2} \right)_{X_3} \Delta X_2 + \left(\frac{\partial X_1}{\partial X_3} \right)_{X_2} \Delta X_3.$$

Writing the second condition in the first gives

$$\Delta Y = \left(\frac{\partial Y}{\partial X_1} \right)_{X_2} \left(\frac{\partial X_1}{\partial X_2} \right)_{X_3} \Delta X_2 + \left(\frac{\partial Y}{\partial X_1} \right)_{X_2} \left(\frac{\partial X_1}{\partial X_3} \right)_{X_2} \Delta X_3 + \left(\frac{\partial Y}{\partial X_2} \right)_{X_1} \Delta X_2.$$

It follows that

$$\left(\frac{\partial Y}{\partial X_2} \right)_{X_3} - \left(\frac{\partial Y}{\partial X_2} \right)_{X_1} = \left(\frac{\partial Y}{\partial X_1} \right)_{X_2} \left(\frac{\partial X_1}{\partial X_2} \right)_{X_3} \quad \text{with} \quad \Delta X_3 = 0.$$

This formula is valid for arbitrary conditions in all the other variable. These we will only specify below in case of ambiguity.

For example, let $Y = \varepsilon_{ij}$, $X_2 = \sigma_{kl}$, $X_1 = T$ and $X_3 = S$. Then

$$\left(\frac{\partial \varepsilon_{ij}}{\partial \sigma_{kl}}\right)_S - \left(\frac{\partial \varepsilon_{ij}}{\partial \sigma_{kl}}\right)_T = \left(\frac{\partial \varepsilon_{ij}}{\partial T}\right)_{\sigma_{kl}} \left(\frac{\partial T}{\partial \sigma_{kl}}\right)_S = -\alpha_{ij} \alpha_{kl} T / C^\sigma$$

in agreement with the above result for $(s_{ijkl}^S - s_{ijkl}^T)$.

If Y is dependent on several variables X_i ($i = 1, \dots, n$) and if the quantities X may depend on one another as well as on other variables X'_j ($j = 1, \dots, n'$), we have

$$\Delta Y = \sum_{i=1}^{n-1} \left(\frac{\partial Y}{\partial X_i}\right)_{X \neq X_i} \Delta X_i + \left(\frac{\partial Y}{\partial X_n}\right)_{X \neq X_n} \Delta X_n$$

and

$$\Delta X_i = \sum_{\substack{j=1 \\ (j \neq i)}}^n \left(\frac{\partial X_i}{\partial X_j}\right)_{X \neq X_j} \Delta X_j + \sum_{j=1}^{n'} \left(\frac{\partial X_i}{\partial X'_j}\right)_{X \neq X'_j} \Delta X'_j.$$

We now inquire as to the partial differentiation of Y with respect to the variables X_n under the auxiliary condition that all variables X' are kept constant. It is

$$\Delta Y = \sum_{i=1}^{n-1} \left(\frac{\partial Y}{\partial X_i}\right)_{X \neq X_i} \sum_{\substack{j=1 \\ (j \neq i)}}^n \left(\frac{\partial X_i}{\partial X_j}\right)_{X \neq X_j} \Delta X_j + \left(\frac{\partial Y}{\partial X_n}\right)_{X \neq X_n} \Delta X_n$$

and hence,

$$\left(\frac{\partial Y}{\partial X_n}\right)_{X' = \text{const.}} - \left(\frac{\partial Y}{\partial X_n}\right)_{\substack{X = \text{const.} \\ (\text{except } X_n)}} = \sum_{i=1}^{n-1} \left(\frac{\partial Y}{\partial X_i}\right)_{X \neq X_i} \left(\frac{\partial X_i}{\partial X_n}\right)_{X \neq X_n}.$$

Contrary to the notation for tensor components, here we have set the indices, characterizing the auxiliary conditions, as subscripts corresponding to the usage in differential calculus. Finally, it should be pointed out that with a first selection of the independent variables already all material constants of the equation of state are fixed. This means that the material constants appearing with another arbitrary selection of independent variables can be calculated from the constants of the first selection of variables. Already familiar examples are the elastic c and s tensors or the dielectric ϵ and a tensors. As a further example let us look at the tensor γ_{ij} appearing in both equations of state

$$\begin{aligned} \sigma_{ij} &= c_{ijkl}^T \varepsilon_{kl} + \dots + \gamma_{ij} \Delta T \\ \Delta S &= -\gamma_{ij} \varepsilon_{ij} + \dots + \frac{C^\varepsilon}{T} \Delta T. \end{aligned}$$

Under adiabatic conditions we obtain $\Delta T = \gamma_{ij} \varepsilon_{ij} T / C^\varepsilon$, whereby E and H are constant.

Table 5.1 Relations between material constants under various conditions.

	Y	X_i	X_n	X'_j
Specific heat $C^\sigma - C^\epsilon = -\alpha_{ij}\gamma_{ij}T$ with $\gamma_{ij} = -\alpha_{kl}c_{klij}\frac{C^\epsilon}{C^\sigma}$	S	ϵ_{ij}	T	σ_{ij}
Pyroelectric effect $p_i^\sigma - p_i^\epsilon = e_{ijk}^T\alpha_{jk}^\sigma$	D_i	ϵ_{jk}	T	σ_{jk}
Thermal expansion $\alpha_{ij}^D - \alpha_{ij}^E = d_{kij}^T\left(\frac{\partial E_k}{\partial T}\right)_D$	ϵ_{ij}	E_k	T	D_k
Dielectricity tensor $\epsilon_{ij}^S - \epsilon_{ij}^T = -p_i p_j T / C^\sigma$ $\epsilon_{ij}^\sigma - \epsilon_{ij}^\epsilon = e_{ikl}d_{jkl}$	D_i D_i	T ϵ_{kl}	E_j E_j	S σ_{kl}
Piezoelectricity tensor $d_{ijk}^S - d_{ijk}^T = -\alpha_{jk}p_i^\sigma T / C^\sigma$	D_i	T	σ_{jk}	S
Elasticity tensor $s_{ijkl}^S - s_{ijkl}^T = -\alpha_{ij}\alpha_{kl}T / C^\sigma$ $c_{ijkl}^S - c_{ijkl}^T = \alpha_{mn}\alpha_{pq}c_{ijmn}c_{klpq}T\frac{C^\epsilon}{C^{\sigma 2}}$	ϵ_{ij} σ_{ij}	T T	σ_{kl} ϵ_{kl}	S S

With the value for the adiabatic increase in temperature discussed previously

$$\Delta T = -\alpha_{kl}\sigma_{kl}\frac{T}{C^\sigma}$$

one finds, using $\sigma_{kl} = c_{klij}\epsilon_{ij}$, the following relation:

$$\gamma_{ij} = -\alpha_{kl}c_{klij}\frac{C^\epsilon}{C^\sigma}.$$

Further relations are derived in a similar manner.

Table 5.1 presents some important differences which can be derived from the differentiation relation just discussed.

Similar expressions are found for the corresponding case of magnetic auxiliary conditions. Especially large differences, sometimes even a change of sign, can be expected in the case of strong pyroelectric and piezoelectric effects, as, for example, in ferroelectric crystals, when thermal expansion is also large. An influence of mechanical boundary conditions on dielectric constants is only present in piezoelectric crystals.

Phase transitions are often accompanied by a substantial change in certain properties, for example, thermal expansion and pyroelectric effect, which may result in unusually large differences of other coefficients under different auxiliary conditions.

5.3

Time Reversal

Time reversal, that is, a change in the sense of direction of time, acts to change the sense of direction of all quantities possessing a linear time dependence, in particular, velocities, current densities and certain quantities derived from these. The most important types of quantities are the electric current density vector, the magnetic field strength, the magnetization and the magnetic moment which are all coupled to the motion charges. The same applies to all mass current densities. The operation of time reversal, designated by T , effects here a change in sign. Other quantities, conserved in the static case under time reversal are, for example the electric field, the electric moment, the mechanical state of stress, the mechanical deformation and the temperature. We now want to take a closer look at the effects of time reversal for magnetic interactions.

In the linear equations of state with the magnetic field strength \mathbf{H} as the independent variable, we have the following magnetic terms:

$$\varepsilon_{ij} = \dots m_{ijk} H_k \dots$$

$$\Delta D_i = \dots q_{ij} H_j \dots$$

$$\Delta B_i = \dots \mu_{ij} H_j \dots$$

$$\Delta S = \dots m_i H_i \dots$$

Under time reversal, the induced quantities on the left-hand side do not change except B_i . On the right-hand side \mathbf{H} changes its sign. The question arises whether the quantities m_{ijk} , q_{ij} , μ_{ij} and m_i are invariant or not under time reversal. In crystals, where the magnetic moments of the lattice particles are statistically distributed, thus producing no total moment, as in diamagnetic and paramagnetic materials, time reversal cannot effect a change in the properties. This means that the tensors $\{m_{ijk}\}$, $\{q_{ij}\}$ and $\{m_i\}$ must vanish. If higher powers of H_i are included in the equations of state, then the following is true: The magnetomechanical, magnetoelectrical, and magnetothermal tensors vanish for all odd powers or products of the components of the magnetic field strength, respectively. On the other hand, terms with even powers are not forbidden.

Other relationships prevail in crystals in which the magnetic moments are aligned (ferromagnetic: all magnetic moments are aligned; ferrimagnetic: different types of magnetic moments exist which can assume various ordered orientations, however, one nonvanishing total moment remains; antiferromagnetic: ordered magnetic moments compensate to zero). In these, time reversal effects a change in sign of the magnetic moment and hence in the material properties. The combination of spacial symmetry and time reversal leads to a classification of the "magnetic" crystals in the form of so-called *point sym-*

metry groups, magnetic, identical to the black–white point symmetry groups (see, for example, Taschentext *Kristallgeometrie*). There exists a total of 58 real black–white groups aside from the familiar 32 crystallographic point symmetry groups. An analysis of the tensor properties of the “magnetic” crystals requires a consideration of the combined space-time symmetry.

As an example, we consider the magnetoelectrical effect in a rhombic crystal of the magnetic point symmetry group $m'm'2$. The symbol m' or n' specifies a mirror plane or n -fold rotation axis respectively, combined with a change in sign under time reversal. Hence, we examine the effect described by $D_i = q_{ij}H_j$. $\{q_{ij}\}$ is an axial tensor, because \mathbf{H} is axial and \mathbf{D} not. The negative sign of time reversal then compensates the negative sign factor when the axial tensor is transformed by a rotation-inversion. Symmetry reduction thus leads to the same result as with a second-rank polar tensor. It is $q_{12} = q_{13} = q_{21} = q_{31} = q_{23} = q_{32} = 0$. In contrast, q_{11} , q_{22} and q_{33} remain without restrictions. Consequently, the magnetoelectrical tensor here possesses the three components q_{11} , q_{22} and q_{33} .

As a further example for the effect of time reversal we consider the magnetostriction $\varepsilon_{ij} = m_{ijk}H_k$ in cubic crystals of the magnetic point symmetry group $m3m'$ (complete $4'/m\bar{3}2'/m'$). It is enough to draw on the generating symmetry operations. Since 23 is a subgroup of the PSG at hand, it is first of all true, as with all third-rank polar tensors that

$$m_{123} = m_{231} = m_{312},$$

and furthermore, due to the symmetry of the deformation tensor $m_{ijk} = m_{jik}$. With

$$R_{\bar{2}||(\mathbf{e}_1+\mathbf{e}_2)} = \begin{pmatrix} 0 & \bar{1} & 0 \\ \bar{1} & 0 & 0 \\ 0 & 0 & 1 \end{pmatrix}$$

we obtain, taking into account time reversal and axiality $m'_{123} = m_{123}$. The same results from the symmetry plane

$$R_{\bar{2}||\mathbf{e}_1} = \begin{pmatrix} \bar{1} & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix}.$$

An inspection of the symmetry elements $4'$, $\bar{3}$ and $2'$ leads to no further condition. This means, the first-order magnetostriction tensor exists in the PSG $m3m'$. The only independent component is m_{123} . One can see straight away (subgroup relationships to $m3m'$!), that the following PSGs 23, $m3$, $\bar{4}'3m$ and $4'32'$ can also exhibit such an effect. All other cubic PSGs exhibit no first-order magnetostriction.

The effect of time reversal in transport processes requires special consideration. In the case of magnetic interactions we must again distinguish between “nonmagnetic” crystals (*diamagnetic* and *paramagnetic*) and “magnetic” crystals (*ferromagnetic* and so on). For example, let a second-rank tensor, the tensor of electric or thermal conductivity, be dependent on the magnetic field, thus $s_{ij}(\mathbf{H})$. A time reversal effects a reversal of the direction of \mathbf{H} . This also means that an interaction, initially described in a right-handed system, given, for example, by e_i, e_j and \mathbf{H} , is to be represented, after time reversal, in a left-handed system $e_i, e_j, \mathbf{H}' (= -\mathbf{H})$ with the same tensor. The Onsager relation $s_{ij} = s_{ji}$ valid for transport processes considered in the magnetic interaction above for “nonmagnetic” crystals takes on the form $s_{ij}(\mathbf{H}) = s_{ji}(-\mathbf{H})$.

A dependence of the magnetic field, expanded according to powers of the components of the magnetic field strength, then demands the following:

$$\begin{aligned} s_{ij}(\mathbf{H}) &= s_{ij}^0 + s_{ijk}H_k + s_{ijkl}H_kH_l + \cdots \\ s_{ji}(-\mathbf{H}) &= s_{ji}^0 - s_{jik}H_k + s_{jikl}H_kH_l + \cdots \end{aligned}$$

This means that $s_{ijk\dots} = -s_{jik\dots}$ is true for the odd-rank s -tensors and $s_{ijk\dots} = s_{jik\dots}$ is true for those of even rank. We encounter such conditions with the Hall effect, with the magnetic resistance tensor, with the Righi–Leduc effect as well as with the thermomagnetic resistance tensor.

In “magnetic” crystals one must also take into consideration the change in direction of ordered magnetic moments under time reversal. Hence, if a transport property is also dependent on the position of the magnetic moment then the general Onsager relation takes the form $s_{ij}(\mathcal{M}, \mathbf{H}) = s_{ji}(-\mathcal{M}, -\mathbf{H})$, where \mathcal{M} designates the magnetic moment. This can lead to a modification of magnetic interactions in transport processes. For example, a quasi Hall effect, i.e., the build-up of an electric field perpendicular to the current, is conceivable in “magnetic” crystals, even without an external magnetic field, when the corresponding symmetry properties are present.

5.4

Thermoelectrical Effect

The driving force for electrical charge transport or caloric energy transport are the corresponding gradients of the electric potential and temperature respectively. The Joule heat generated in each volume element traversed by an electric current influences the temperature distribution and hence the heat current. This suggests the use of a general approach of the type

$$\begin{aligned} I_i &= -s_{ij}(\text{grad } \varphi)_j - k_{ij}(\text{grad } T)_j \\ Q_i &= -t_{ij}(\text{grad } \varphi)_j - l_{ij}(\text{grad } T)_j \end{aligned}$$

for the description of the simultaneous existence of transport processes of electric charge and caloric energy.

Consequently, the tensors $\{s_{ij}\}$, $\{k_{ij}\}$, $\{t_{ij}\}$ and $\{l_{ij}\}$ represent generalized conductivities. If one interchanges the inducing quantities with the currents, which, at least is formally conceivable, then the corresponding basic equations are

$$-(\text{grad } \phi)_i = \sigma_{ij} I_j + \kappa_{ij} Q_j$$

$$-(\text{grad } T)_i = \tau_{ij} I_j + \lambda_{ij} Q_j.$$

The tensors emerging here have the property of general resistors. In all these processes we must note that ϕ , T , I and Q are functions of position. This means, the basic equations are only valid for correspondingly small volume elements. Thus, the equations here have the character of differential equations. Moreover, one must keep in mind that the material constants must be specified as functions dependent on position. This is especially true for the temperature dependence of the electrical conductivity. In this sense, the above equations can be drawn upon as basic equations for transport processes under inhomogeneous conditions. The tensors $\{\sigma_{ij}\}$, $\{\kappa_{ij}\}$, $\{\tau_{ij}\}$, and $\{\lambda_{ij}\}$ appearing in the first-order approximation of the interaction are not only linked to electrical and thermal conductivity discussed in Sections 4.3.7 and 4.3.8 but, moreover, describe the appearance of certain additional phenomena. For example, they describe the onset of an electric field in a heat current or a temperature gradient with the passage of an electric current even in directions normal to the current vector. Such phenomena are designated as thermoelectrical effects.

If one introduces an additional magnetic field, whereby the material tensors are to be represented as a Taylor series of the components of the magnetic field, in a manner similar to that discussed in the preceding section, one expects further interesting effects. At present, however, little is known concerning the experimental clarification of these effects.