

Thermoelectric effects

$$f(\vec{k}) \approx f_0(\vec{k}) + \frac{\tau(\vec{k})e(\vec{v} \times \vec{B} + \vec{E}) \cdot \nabla_{\vec{k}} f_0}{\hbar} + \tau(\vec{k})\vec{v} \cdot \left(\frac{\partial f_0}{\partial T} \nabla T + \frac{\partial f_0}{\partial \mu} \nabla \mu \right)$$

Electrical current: $\vec{j}_{elec} = \frac{-e}{4\pi^3} \int \vec{v}(\vec{k}) f(\vec{k}) d^3k$

Particle current: $\vec{j}_n = \frac{1}{4\pi^3} \int \vec{v}(\vec{k}) f(\vec{k}) d^3k$

Energy current: $\vec{j}_E = \frac{1}{4\pi^3} \int \vec{v}(\vec{k}) E(\vec{k}) f(\vec{k}) d^3k$

Heat current: $\vec{j}_Q = \frac{1}{4\pi^3} \int \vec{v}(\vec{k}) (E(\vec{k}) - \mu) f(\vec{k}) d^3k$

Thermal conductivity

$$\vec{j}_Q = \frac{1}{4\pi^3} \int \vec{v}_{\vec{k}} \left(E(\vec{k}) - \mu \right) \left(\tau(\vec{k}) \frac{\partial f_0}{\partial \mu} \left(-\frac{e}{\hbar} (\vec{v}(\vec{k}) \times \vec{B} + \vec{E}) \cdot \nabla_{\vec{k}} E(\vec{k}) + \vec{v}(\vec{k}) \cdot \left(\frac{E(\vec{k}) - \mu}{T} \nabla T + \nabla \mu \right) \right) \right) d^3 k$$

$$\vec{B} = 0, \quad \vec{E} = 0, \quad \nabla \mu = 0$$

$$\vec{j}_Q = \frac{1}{4\pi^3} \int \vec{v}_{\vec{k}} \left(E(\vec{k}) - \mu \right) \tau(\vec{k}) \frac{\partial f_0}{\partial \mu} \vec{v}(\vec{k}) \cdot \frac{E(\vec{k}) - \mu}{T} \nabla T d^3 k$$

$$\kappa_{mn} = \frac{-j_{Qm}}{\nabla T_n}$$

Thermoelectric effects

$$f(\vec{k}) \approx f_0(\vec{k}) + \frac{\tau e (\vec{v} \times \vec{B} + \vec{E}) \cdot \nabla_{\vec{k}} f_0}{\hbar} - \tau \frac{\partial f_0}{\partial T} \vec{v} \cdot \nabla T$$

Electrical conductivity: $\sigma_{mn} = \frac{j_{em}}{E_n} \quad \nabla T = 0, \vec{B} = 0$

Thermal conductivity: $\kappa_{mn} = \frac{-j_{Qm}}{\nabla T_n} \quad \vec{j}_e = 0, \vec{B} = 0$

Peltier coefficient: $\Pi_{mn} = \frac{j_{Qm}}{j_{en}} \quad \nabla T = 0, \vec{B} = 0$

Thermopower (Seebeck effect): $Q_{mn} = \frac{E_m}{\nabla T_n} \quad \vec{j}_e = 0, \vec{B} = 0$

Thermoelectric effects

$$f(\vec{k}) \approx f_0(\vec{k}) + \frac{\tau e (\vec{v} \times \vec{B} + \vec{E}) \cdot \nabla_{\vec{k}} f_0}{\hbar} - \tau \frac{\partial f_0}{\partial T} \vec{v} \cdot \nabla T$$

Hall effect: $R_{lmn} = \frac{E_l}{j_{em} B_n} \quad \nabla T = 0, j_{el} = 0$

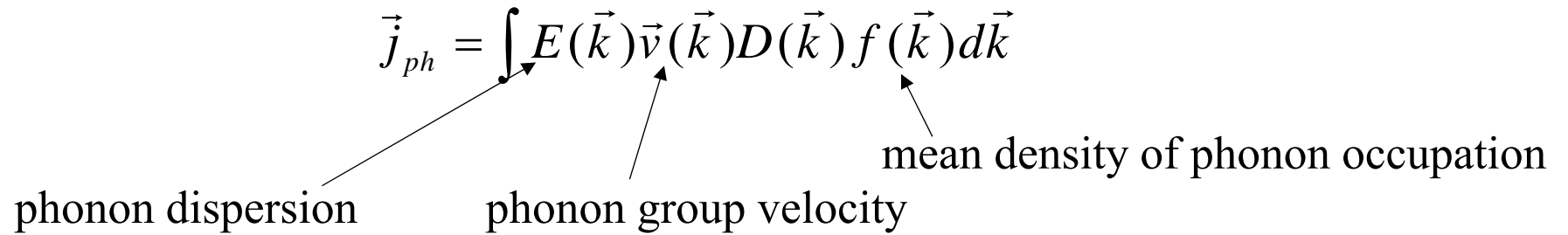
Nerst effect: $N_{lmn} = \frac{E_l}{B_m \nabla T_n} \quad j_{el} = 0$

Ettingshausen effect: $P_{lmn} = \frac{-1}{j_{el} B_m \nabla T_n}$

Boltzmann equation for phonons

$$\vec{j}_{ph} = \int E(\vec{k}) \vec{v}(\vec{k}) D(\vec{k}) f(\vec{k}) d\vec{k}$$

phonon dispersion phonon group velocity mean density of phonon occupation

The diagram shows the Boltzmann equation for phonons: $\vec{j}_{ph} = \int E(\vec{k}) \vec{v}(\vec{k}) D(\vec{k}) f(\vec{k}) d\vec{k}$. Three arrows point from labels below to terms in the equation: 'phonon dispersion' points to $E(\vec{k})$, 'phonon group velocity' points to $\vec{v}(\vec{k})$, and 'mean density of phonon occupation' points to $f(\vec{k})$.

For phonons, there is no external force term.

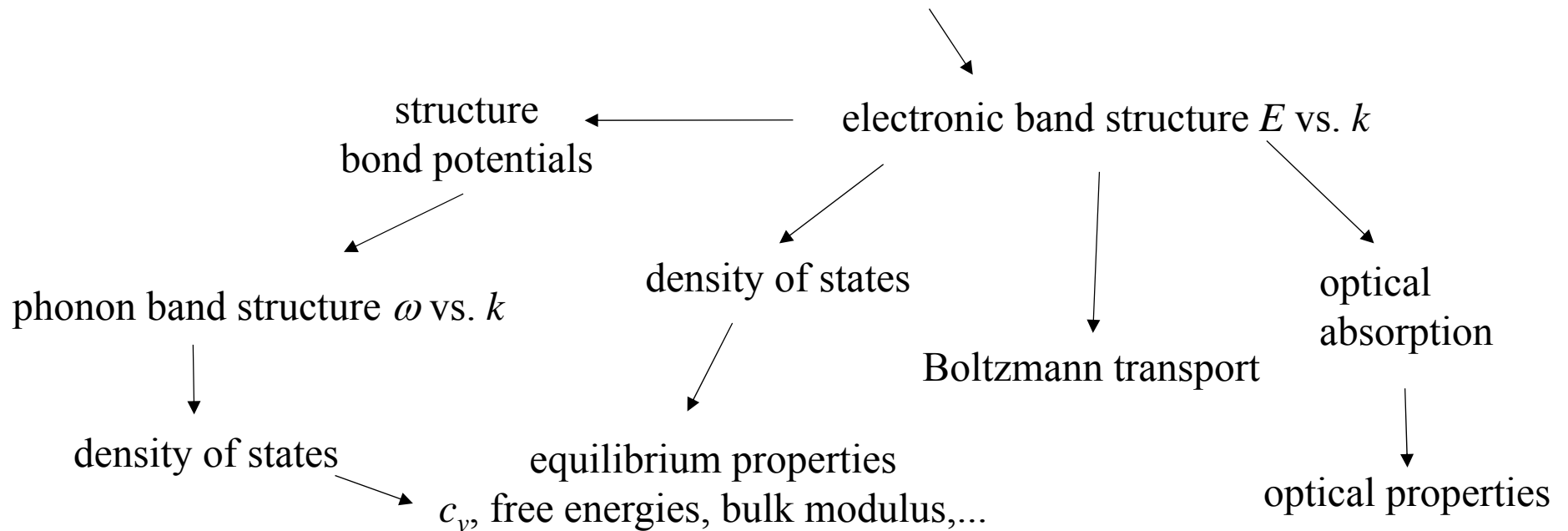
Student project

Assume that the dispersion relation is $\frac{\hbar^2 k^2}{2m^*}$

and that a single relaxation time can be used for all k .
Calculate the some transport property.

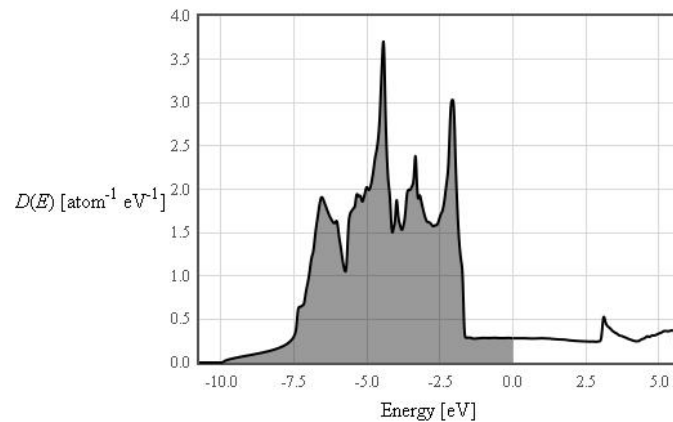
The properties of solids

$$H = -\sum_i \frac{\hbar^2}{2m_e} \nabla_i^2 - \sum_A \frac{\hbar^2}{2m_A} \nabla_A^2 - \sum_{i,A} \frac{Z_A e^2}{4\pi\epsilon_0 r_{iA}} + \sum_{i<j} \frac{e^2}{4\pi\epsilon_0 r_{ij}} + \sum_{A<B} \frac{Z_A Z_B e^2}{4\pi\epsilon_0 r_{AB}}$$



Calculating free energies

Electronic component

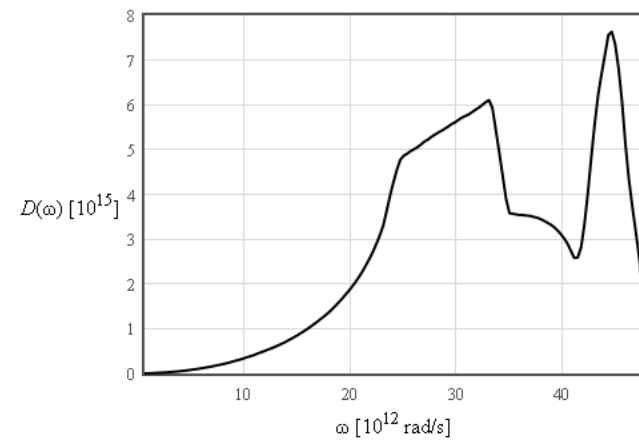


$$n = \int_{-\infty}^{\infty} \frac{D(E)}{1 + \exp\left(\frac{E - \mu}{k_B T}\right)} dE$$

$$f = \phi + \mu n = \int_{-\infty}^{\infty} D(E) \left[\frac{\mu}{1 + \exp\left(\frac{E - \mu}{k_B T}\right)} - k_B T \ln \left(\exp\left(-\frac{(E - \mu)}{k_B T}\right) + 1 \right) \right] dE$$

Phonon component

$$f(T) = k_B T \int_0^{\infty} D(\omega) \ln \left(1 - \exp\left(\frac{-\hbar\omega}{k_B T}\right) \right) d\omega$$



Helmholtz free energy

Canonical ensemble: At constant temperature, make a Legendre transformation to the Helmholtz free energy.

$$F = U - TS$$

$$F(T, N, M, P, \varepsilon)$$

$$dF = dU - TdS - SdT$$

$$dF = -SdT + \mu_i dN_i + \sigma_{ij} d\varepsilon_{ij} + E_k dP_k + H_l dM_l$$

$$S = -\left(\frac{\partial F}{\partial T}\right)_{N, M, P, \varepsilon} \quad \mu_i = \left(\frac{\partial F}{\partial N_i}\right)_{T, M, P, \varepsilon, N_{j \neq i}} \quad \sigma_{ij} = \left(\frac{\partial F}{\partial \varepsilon_{ij}}\right)_{N, M, P, T}$$

$$E_k = \left(\frac{\partial F}{\partial P_k}\right)_{N, M, T, \varepsilon} \quad H_l = \left(\frac{\partial F}{\partial M_l}\right)_{N, T, P, \varepsilon}$$

Gibbs free energy

$$G(T, \mu, H, E, \sigma)$$

$$G = U - TS - \mu_i N_i - \sigma_{ij} \varepsilon_{ij} - E_k P_k - H_l M_l$$

$$dU = TdS + \mu_i dN_i + \sigma_{ij} d\varepsilon_{ij} + E_k dP_k + H_l dM_l$$

$$dG = -SdT - N_i d\mu_i - \varepsilon_{ij} d\sigma_{ij} - P_k dE_k - M_l dH_l$$

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

$$S = - \left(\frac{\partial G}{\partial T} \right)_{\sigma, E, H, \mu} \quad N_i = - \left(\frac{\partial G}{\partial \mu_i} \right)_{T, E, H, \sigma} \quad \varepsilon_{ij} = - \left(\frac{\partial G}{\partial \sigma_{ij}} \right)_{T, E, H, \mu}$$

$$P_k = - \left(\frac{\partial G}{\partial E_k} \right)_{T, \mu, H, \sigma} \quad M_l = - \left(\frac{\partial G}{\partial H_l} \right)_{T, \mu, E, \sigma}$$

$$\begin{aligned}
d\epsilon_{ij} &= \left(\frac{\partial \epsilon_{ij}}{\partial \sigma_{kl}}\right) d\sigma_{kl} + \left(\frac{\partial \epsilon_{ij}}{\partial E_k}\right) dE_k + \left(\frac{\partial \epsilon_{ij}}{\partial H_l}\right) dH_l + \left(\frac{\partial \epsilon_{ij}}{\partial T}\right) dT \\
dP_i &= \left(\frac{\partial P_i}{\partial \sigma_{kl}}\right) d\sigma_{kl} + \left(\frac{\partial P_i}{\partial E_k}\right) dE_k + \left(\frac{\partial P_i}{\partial H_l}\right) dH_l + \left(\frac{\partial P_i}{\partial T}\right) dT \\
dM_i &= \left(\frac{\partial M_i}{\partial \sigma_{kl}}\right) d\sigma_{kl} + \left(\frac{\partial M_i}{\partial E_k}\right) dE_k + \left(\frac{\partial M_i}{\partial H_l}\right) dH_l + \left(\frac{\partial M_i}{\partial T}\right) dT \\
dS &= \left(\frac{\partial S}{\partial \sigma_{kl}}\right) d\sigma_{kl} + \left(\frac{\partial S}{\partial E_k}\right) dE_k + \left(\frac{\partial S}{\partial H_l}\right) dH_l + \left(\frac{\partial S}{\partial T}\right) dT
\end{aligned}$$

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.

<http://it.iucr.org>

INTERNATIONAL TABLES
for CRYSTALLOGRAPHY
WILEY



2006 edition available through
TU Graz library

[| home](#) | [resources](#) | [purchase](#) | [contact us](#) | [help](#) |

INTERNATIONAL TABLES Physical properties of crystals

[| A](#) | [A1](#) | [B](#) | [C](#) | [D](#) | [E](#) | [F](#) | [G](#) |

[Home](#) > [Volume D](#) > [Contents](#)

International Tables for Crystallography Volume D: Physical properties of crystals

Second online edition (2013) ISBN: 978-1-118-76229-5 doi: 10.1107/97809553602060000113

Edited by **A. Authier**

Contents

Part 1. Tensorial aspects of physical properties

1.1. Introduction to the properties of tensors (pp. 3-33) | [html](#) | [pdf](#) | [chapter contents](#) |

A. Authier

1.1.1. The matrix of physical properties (pp. 3-5) | [html](#) | [pdf](#) |

1.1.2. Basic properties of vector spaces (pp. 5-7) | [html](#) | [pdf](#) |

1.1.3. Mathematical notion of tensor (pp. 7-10) | [html](#) | [pdf](#) |

1.1.4. Symmetry properties (pp. 10-31) | [html](#) | [pdf](#) |

1.1.5. Thermodynamic functions and physical property tensors (pp. 31-32) | [html](#) | [pdf](#) |

1.1.6. Glossary (pp. 32-33) | [html](#) | [pdf](#) |

References | [html](#) | [pdf](#) |

1.2. Representations of crystallographic groups (pp. 34-71) | [html](#) | [pdf](#) | [chapter contents](#) |

T. Janssen

1.2.1. Introduction (pp. 34-35) | [html](#) | [pdf](#) |

1.2.2. Point groups (pp. 35-46) | [html](#) | [pdf](#) |

1.2.3. Space groups (pp. 46-51) | [html](#) | [pdf](#) |

1.2.4. Tensors (pp. 51-53) | [html](#) | [pdf](#) |

1.2.5. Magnetic symmetry (pp. 53-56) | [html](#) | [pdf](#) |

1.2.6. Tables (pp. 56-62) | [html](#) | [pdf](#) |

1.2.7. Introduction to the accompanying software *Tenχar* (pp. 62-70) | [html](#) | [pdf](#) |

M. Ephraïm, T. Janssen, A. Janner and A. Thiers

1.2.8. Glossary (pp. 70-71) | [html](#) | [pdf](#) |

References | [html](#) | [pdf](#) |

1.3. Elastic properties (pp. 72-99) | [html](#) | [pdf](#) | [chapter contents](#) |

A. Authier and A. Zarembowitch

1.3.1. Strain tensor (pp. 72-76) | [html](#) | [pdf](#) |

1.3.2. Stress tensor (pp. 76-80) | [html](#) | [pdf](#) |

Groups

Crystals can have symmetries: translation, rotation, reflection, inversion,...

$$\begin{pmatrix} x' \\ y' \\ z' \end{pmatrix} = \begin{pmatrix} 1 & 0 & 0 \\ 0 & \cos \alpha & \sin \alpha \\ 0 & -\sin \alpha & \cos \alpha \end{pmatrix} \begin{pmatrix} x \\ y \\ z \end{pmatrix}$$

Symmetries can be represented by matrices.

All such matrices that bring the crystal into itself form the group of the crystal.

$$AB \in G \text{ for } A, B \in G$$

32 point groups (one point remains fixed during transformation)

230 space groups

Strain

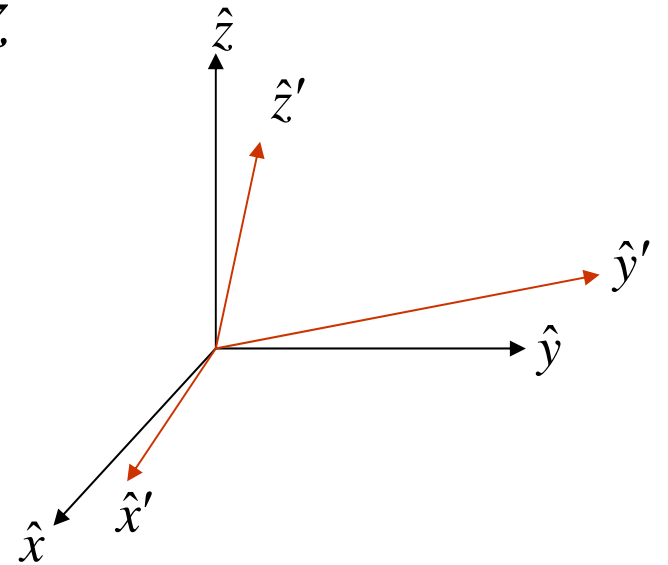
A distortion of a material is described by the strain matrix

$$x' = (1 + \varepsilon_{xx}) \hat{x} + \varepsilon_{xy} \hat{y} + \varepsilon_{xz} \hat{z}$$

$$y' = \varepsilon_{yx} \hat{x} + (1 + \varepsilon_{yy}) \hat{y} + \varepsilon_{yz} \hat{z}$$

$$z' = \varepsilon_{zx} \hat{x} + \varepsilon_{zy} \hat{y} + (1 + \varepsilon_{zz}) \hat{z}$$

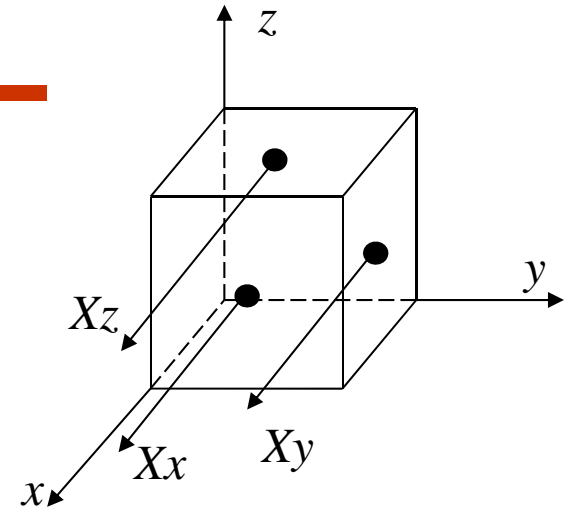
Strain is dimensionless $\Delta L/L$



Stress

9 forces describe the stress

$X_x, X_y, X_z, Y_x, Y_y, Y_z, Z_x, Z_y, Z_z$



X_x is a force applied in the x -direction to the plane normal to x

X_y is a shear force applied in the x -direction to the plane normal to y

stress tensor:

$$\sigma = \begin{bmatrix} \frac{X_x}{A_x} & \frac{X_y}{A_y} & \frac{X_z}{A_z} \\ \frac{Y_x}{A_x} & \frac{Y_y}{A_y} & \frac{Y_z}{A_z} \\ \frac{Z_x}{A_x} & \frac{Z_y}{A_y} & \frac{Z_z}{A_z} \end{bmatrix}$$

Stress is force/m²

Stress and Strain

$$\epsilon_{ij} = S_{ijkl} \sigma_{kl}$$

The stress - strain relationship is described by a rank 4 stiffness tensor. The inverse of the stiffness tensor is the compliance tensor.

$$\sigma_{ij} = C_{ijkl} \epsilon_{kl}$$

Einstein convention: sum over repeated indices.

$$\begin{aligned} \epsilon_{xx} = & S_{xxxx} \sigma_{xx} + S_{xxxy} \sigma_{xy} + S_{xxxz} \sigma_{xz} + S_{xxyx} \sigma_{yx} + S_{xxyy} \sigma_{yy} \\ & + S_{xxyz} \sigma_{yz} + S_{xxzx} \sigma_{zx} + S_{xxzy} \sigma_{zy} + S_{xxzz} \sigma_{zz} \end{aligned}$$

Pyroelectricity

Pyroelectricity is described by a rank 1 tensor

$$\pi_i = \frac{\partial P_i}{\partial T}$$

$$\begin{bmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & -1 \end{bmatrix} \begin{bmatrix} \pi_x \\ \pi_y \\ \pi_z \end{bmatrix} = \begin{bmatrix} \pi_x \\ \pi_y \\ -\pi_z \end{bmatrix} \Rightarrow \begin{bmatrix} \pi_x \\ \pi_y \\ 0 \end{bmatrix}$$

rank 1: pyroelectric effect, pyromagnetic effect, electrocaloric effect, magnetocaloric effect