

# Lecture 9 (week 9: 14 April 2025)

## Transport properties of solids

- Electrical conductivity
- Thermal conductivity
- Thermoelectric effects

# Exercises – Series 9, cross-coupled effects, thermoelectromechanics

## Use of constitutive equations: tips and recommendations

$$D_i = \varepsilon_0 K_{ij} E_j + d_{in} \sigma_n + p_i \delta T$$

$$\varepsilon_n = d_{in} E_i + s_{nm} \sigma_m + \alpha_n \delta T$$

$$\delta S = p_i E_i + \alpha_m \sigma_m + \frac{C}{T} \delta T$$

- What do you need to find?
- What are the boundary conditions?
- Maybe, some input data are redundant? (some effects are not permitted because of symmetry...)

**This reasoning helps selecting right equations**

# Exercises – Series 9, cross-coupled effects, thermoelectromechanics

## Use of constitutive equations

$$D_i = \varepsilon_0 K_{ij} E_j + d_{in} \sigma_n + p_i \delta T$$

$$\varepsilon_n = d_{in} E_i + s_{nm} \sigma_m + \alpha_n \delta T$$

$$\delta S = p_i E_i + \alpha_m \sigma_m + \frac{C}{T} \delta T$$

- Choose a suitable set of equations (previous slide)
- Identify the tensor structure, use symmetry, boundary conditions and input data to simplify equations as much as possible
- check about the coordinate system of your problem, rotate the tensors if needed
- combine equations, get the answer

# Exercises – Series 9, cross-coupled effects, thermoelectromechanics: solutions and comments

In all the exercises, the material used is BaTiO<sub>3</sub> in its tetragonal phase *4mm*. The 4-fold axis is always directed along the  $x_3$  axis. You may use the table of values for BaTiO<sub>3</sub> given below if needed.

$s_{11}$	$8.05 \times 10^{-12} \text{ m}^2/\text{N}$	$d_{15}$	$392 \times 10^{-12} \text{ C/N}$
$s_{12}$	$-2.35 \times 10^{-12} \text{ m}^2/\text{N}$	$d_{31}$	$-35 \times 10^{-12} \text{ C/N}$
$s_{13}$	$-5.24 \times 10^{-12} \text{ m}^2/\text{N}$	$d_{33}$	$86 \times 10^{-12} \text{ C/N}$
$s_{33}$	$15.7 \times 10^{-12} \text{ m}^2/\text{N}$	$K_{33}$	150
$C$	$2.42 \times 10^6 \text{ J}/(\text{m}^3 \cdot \text{K})$	$p_3$	$-5 \times 10^{-4} \text{ C}/(\text{m}^2 \cdot \text{K})$
$\alpha_3$	$3.5 \times 10^{-5} \text{ 1/K}$		

Some data are usable, others maybe redundant or irrelevant...

# Exercises from Week 8

- 9.1. The effect of mechanical conditions on the pyroelectric response is measured
- 9.2 The effect of mechanical conditions on the capacitance is investigated
  - For both exercises one needs to check mechanical boundary conditions (clamped/free - what components of  $\varepsilon$  and  $\sigma$  are zero/nonzero)

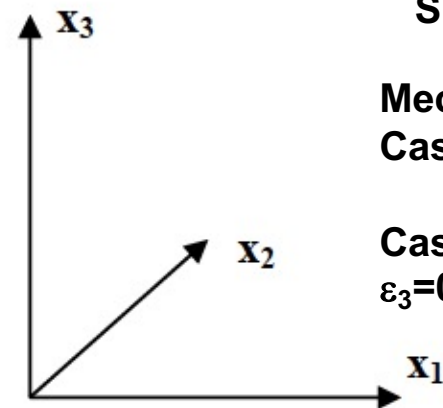
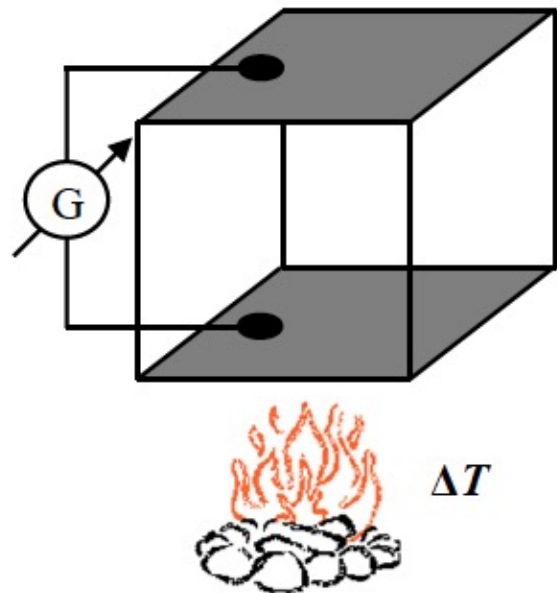
# Exercise 8.1

**9.1.** The effect of mechanical conditions on the pyroelectric response is measured. To do it, the (001) surfaces of the parallelepiped  $\text{BaTiO}_3$  sample are covered with electrodes, and the change of the surface charge, driven by the temperature change, is measured (**Fig.1**).

In measurement **(a)**, the sample is kept mechanically free.

In measurement **(b)**, the sample is kept mechanically free in the  $x_1$  and  $x_2$  directions, while the motion in the  $x_3$  direction is blocked.

Find the difference between the pyroelectric coefficients  $p_{(a)}$  and  $p_{(b)}$  measured these two ways (provide the answer in the analytical form)



**Electric boundary conditions:**  
Short circuit,  $E_3=0$

**Mechanical boundary conditions:**  
Case(a):  $\sigma_i = 0$

Case (b) only  $\sigma_3 \neq 0$   
 $\epsilon_3=0$

# Exercise 8.1

$$D_i = \varepsilon_0 K_{ij} E_j + d_{ij} \sigma_j + p_i \Delta T,$$

$$\varepsilon_i = d_{ji} E_j + s_{ij} \sigma_j + \alpha_i \Delta T.$$

In both cases, the electric field  $E_3 = 0$  since the (001) electrodes are electrically connected. In order to simplify the equation for  $D_3$ , we use the  $4mm$  symmetry restrictions for tensor  $K_{ij}$  ( $K_{31} = K_{32} = 0$ ), thus  $K_{31}E_1 = K_{32}E_2 = 0$ . The equation for  $D_3$  attains the following form:

$$D_3 = d_{3j} \sigma_j + p_3 \Delta T$$

In case **(a)**, the sample is mechanically free, implying all  $\sigma_j = 0$ . Then,  $D_3 = p_3 \Delta T$ , and

$$p_{(a)} = \frac{D_3}{\Delta T} = p_3.$$

In case **(b)**, the sample is kept mechanically free in  $x_1$  and  $x_2$  directions, implying  $\sigma_1 = \sigma_2 = \sigma_4 = \sigma_5 = \sigma_6 = 0$ , and  $\sigma_3 \neq 0$ . Then, equation for  $D_3$  rewrites as

$$D_3 = d_{33} \sigma_3 + p_3 \Delta T$$

To find  $\sigma_3$ , we use the constitutive equation for  $\varepsilon_3 = 0$ , which must not change during the measurement (note that  $E_3 = 0$ ):

$$\varepsilon_3 = d_{j3} E_j + s_{33} \sigma_3 + \alpha_3 \Delta T = d_{13} E_1 + d_{23} E_2 + s_{33} \sigma_3 + \alpha_3 \Delta T$$

**Result:**

$$D_3 = \left( p_3 - \frac{d_{33} \alpha_3}{s_{33}} \right) \Delta T,$$

$$p_{(b)} = \frac{D_3}{\Delta T} = p_3 - \frac{d_{33} \alpha_3}{s_{33}}.$$

Thus, in **(a)** and **(b)** the measured pyroelectric responses are different. Specifically,

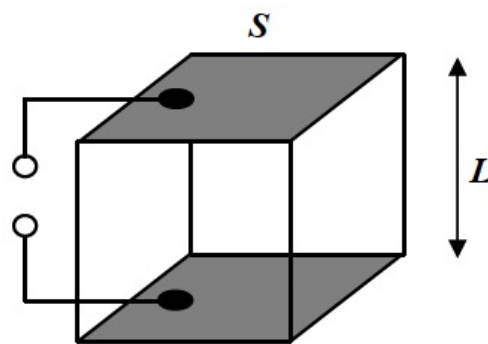
$$p_{(a)} - p_{(b)} = \frac{d_{33} \alpha_3}{s_{33}}$$

## Exercise 8.2

The effect of mechanical conditions on the capacitance is investigated. To do it, the (001) surfaces of the parallelepiped  $\text{BaTiO}_3$  sample (distance between the (001) faces is  $L$ , the area of each (001) face is  $S$ ) are covered with electrodes (**fig.2**), and the capacitance of the sample is measured.

In measurement (**a**), the sample is kept mechanically free.

In measurement (**b**), the sample is kept mechanically free in the  $x_1$  and  $x_2$  directions (i.e., in plane of capacitor), while the distance between electrodes  $L$  is forced to not change.



**electrical boundary conditions are not determined!**

**But, you do not need them to define  $C$**

$$C = \frac{\Delta Q}{\Delta V} = \frac{\Delta D_3 \cdot S}{\Delta E_3 \cdot L}$$

Show that the two measured capacitances  $C_{(a)}$  and  $C_{(b)}$  have different values. Calculate the relative difference between them  $\frac{C_{(a)} - C_{(b)}}{C_{(a)}}$ . All measurements are done at constant temperature.



## Exercise 8.2

$$D_i = \varepsilon_0 K_{ij} E_j + d_{ij} \sigma_j,$$

$$\varepsilon_i = d_{ji} E_j + s_{ij} \sigma_j.$$

$$(K_{31} = K_{32} = 0)$$

$$D_3 = \varepsilon_0 K_{33} E_3 + d_{3j} \sigma_j.$$

(a), the sample is mechanically free, implying all  $\sigma_j = 0$ . Then,  $D_3 = \varepsilon_0 K_{33} E_3$ , and

$$C_{(a)} = \frac{D_3 \cdot S}{E_3 \cdot L} = \varepsilon_0 K_{33} \frac{S}{L}.$$

In case (b), the sample is kept mechanically free in  $x_1$  and  $x_2$  directions, implying  $\sigma_1 = \sigma_2 = \sigma_4 = \sigma_5 = \sigma_6 = 0$ , and  $\sigma_3 \neq 0$ . Then, equation for  $D_3$  rewrites as

$$D_3 = \varepsilon_0 K_{33} E_3 + d_{33} \sigma_3.$$

$$\varepsilon_3 = d_{j3} E_j + s_{33} \sigma_3 = d_{13} E_1 + d_{23} E_2 + d_{33} E_3 + s_{33} \sigma_3$$

$$\varepsilon_3 = d_{33} E_3 + s_{33} \sigma_3 = 0 \Rightarrow \sigma_3 = -\frac{d_{33}}{s_{33}} E_3,$$

$$D_3 = \left( \varepsilon_0 K_{33} - \frac{d_{33}^2}{s_{33}} \right) E_3,$$

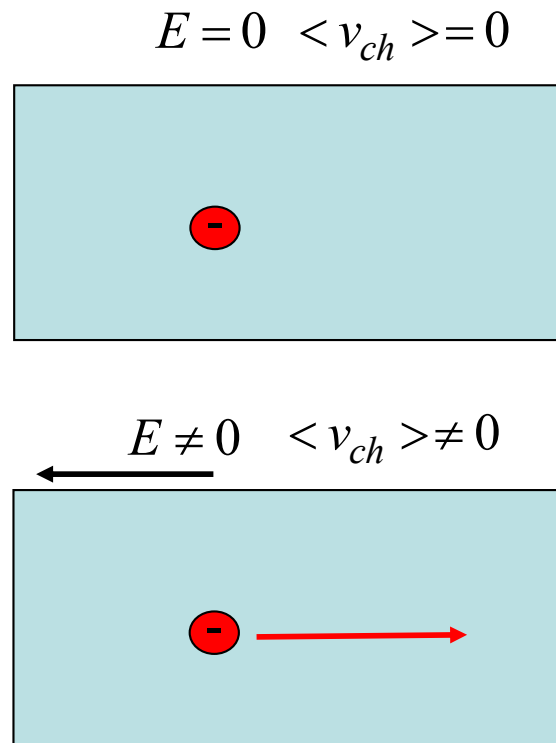
$$C_{(b)} = \frac{D_3 \cdot S}{E_3 \cdot L} = \left( \varepsilon_0 K_{33} - \frac{d_{33}^2}{s_{33}} \right) \frac{S}{L}.$$

Thus, in (a) and (b) the measured capacitances are different. Specifically,

$$\frac{C_{(a)} - C_{(b)}}{C_{(a)}} = \frac{d_{33}^2 / s_{33}}{\varepsilon_0 K_{33}} = 0.35$$

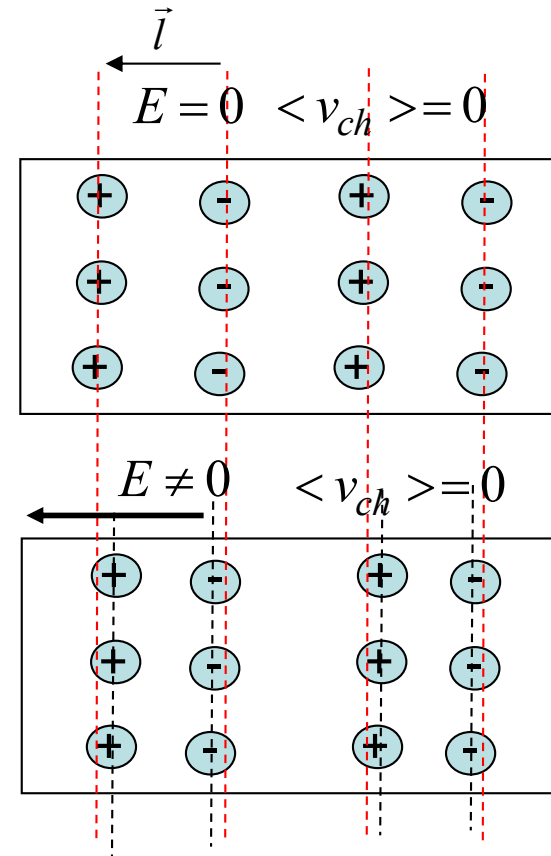
# Electric response of solids: transport vs. dielectric response

## Conductivity



Displacements of the charges are much *larger* than the interatomic distance

## Polarization



Displacements of the charges are much *smaller* than the interatomic distance

Both described by 2<sup>nd</sup> rank tensor, but there are differences!

# Electric response of solids, formal description

## Conductivity

$$\vec{J} = \frac{\sum_i q_i \vec{v}_i}{V}$$

## Polarization

$$\vec{P} = \frac{\sum_i q_i \delta \vec{x}_i}{V}$$

## Linear response

$$J_i = \tau_{ij} E_j$$

$$P_i = \chi_{ij} E_j$$

## Conductivity tensor

## Dielectric susceptibility tensor

$$\tau_{ij}$$

$$\chi_{ij}$$

can be shown

$$\tau_{ij} = \tau_{ji}$$

$$\chi_{ij} = \chi_{ji}$$

# Transport property vs. equilibrium property

## Dielectric response - equilibrium property

$$D_i = \varepsilon_o K_{ij} E_j$$

$$K_{ij} = K_{ji}$$

## Energy at fixed $E$

$$dW = E_i dD_i \quad W = \frac{1}{2} E_j D_j$$

## Electrical Conductivity - transport property















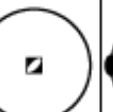
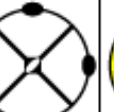

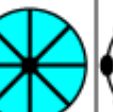





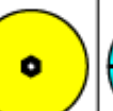








$$J_i = \tau_{ij} E_j$$

$$\tau_{ij} = \tau_{ji}$$

## Energy loss at fixed $E$

$$\frac{dW}{dt} = -E_j J_j$$

# Conductivity : Effect of Neumann in conventional axes

 1 (C <sub>1</sub> )			 $\bar{1}$ (C <sub>1</sub> )			
 2 (C <sub>2</sub> )				 m (C <sub>s</sub> )		 2/m (C <sub>2h</sub> )
				 mm2 (C <sub>2v</sub> )	 222 (D <sub>2</sub> )	 mmm (D <sub>2h</sub> )
 3 (C <sub>3</sub> )			 $\bar{3}$ (S <sub>6</sub> )	 3m (C <sub>3h</sub> )	 32 (D <sub>3</sub> )	 $\bar{3}m$ (D <sub>3d</sub> )
 4 (C <sub>4</sub> )	 $\bar{4}$ (S <sub>8</sub> )	 $\bar{4}2m$ (D <sub>2d</sub> )	 4/m (C <sub>4h</sub> )	 4mm (C <sub>4v</sub> )	 422 (D <sub>4</sub> )	 4/mmm (D <sub>4h</sub> )
 6 (C <sub>6</sub> )	 $\bar{6}$ (C <sub>3h</sub> )	 $\bar{6}2m$ (D <sub>3h</sub> )	 6/m (C <sub>6h</sub> )	 6mm (C <sub>6v</sub> )	 622 (D <sub>6</sub> )	 6/mmm (D <sub>6h</sub> )
 23 (T)			 $m\bar{3}$ (T <sub>h</sub> )	 $\bar{4}3m$ (T <sub>d</sub> )	 432 (O)	 $m\bar{3}m$ (O <sub>h</sub> )

$$\begin{matrix} \longrightarrow & \begin{pmatrix} \tau_{11} & \tau_{12} & \tau_{13} \\ & \tau_{22} & \tau_{23} \\ & & \tau_{33} \end{pmatrix} \end{matrix}$$

$$\begin{matrix} \longrightarrow & \begin{pmatrix} \tau_{11} & 0 & \tau_{13} \\ & \tau_{22} & 0 \\ & & \tau_{33} \end{pmatrix} \end{matrix}$$

$$\begin{matrix} \longrightarrow & \begin{pmatrix} \tau_{11} & 0 & 0 \\ & \tau_{22} & 0 \\ & & \tau_{33} \end{pmatrix} \end{matrix}$$

$$\begin{matrix} \longrightarrow & \begin{pmatrix} \tau_1 & 0 & 0 \\ & \tau_1 & 0 \\ & & \tau_3 \end{pmatrix} \end{matrix}$$

$$\begin{matrix} \infty & \infty m & \infty 2 \\ \infty / m & \infty / mm \end{matrix}$$

$$\begin{matrix} \longrightarrow & \begin{pmatrix} \tau & 0 & 0 \\ & \tau & 0 \\ & & \tau \end{pmatrix} \end{matrix}$$

$$\infty \infty \infty \infty m$$


# Anisotropy of conductivity

$$J_i = \tau_{ij} E_j$$

**Current is always parallel to the field only if**


$$\tau_{ij} = \tau \delta_{ij}$$

**In anisotropic materials current is NOT ALWAYS parallel to the field !**



*mm2*

$$\begin{pmatrix} \tau_{11} & 0 & 0 \\ & \tau_{22} & 0 \\ & & \tau_{33} \end{pmatrix}$$



**2**

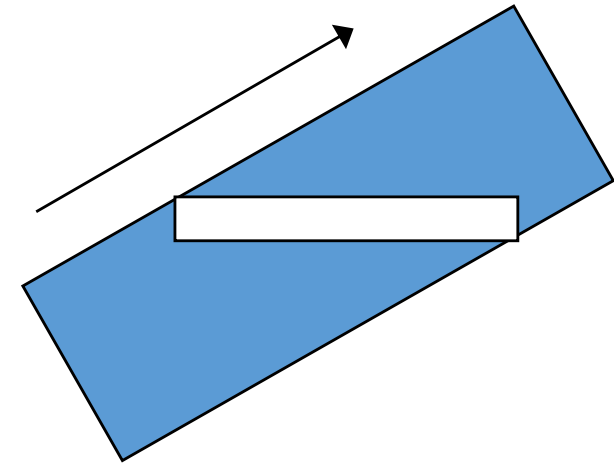
$$\begin{pmatrix} \tau_{11} & 0 & \tau_{13} \\ & \tau_{22} & 0 \\ & & \tau_{33} \end{pmatrix}$$

# Transversal voltage

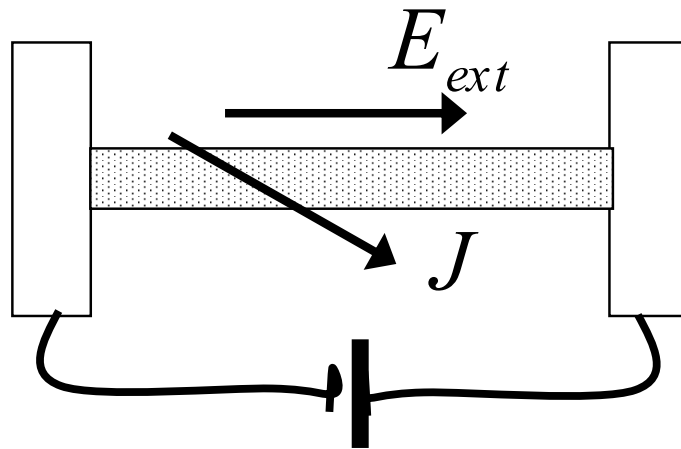
4 /  $mmm$

$\text{Bi}_4\text{Ti}_3\text{O}_{12}$

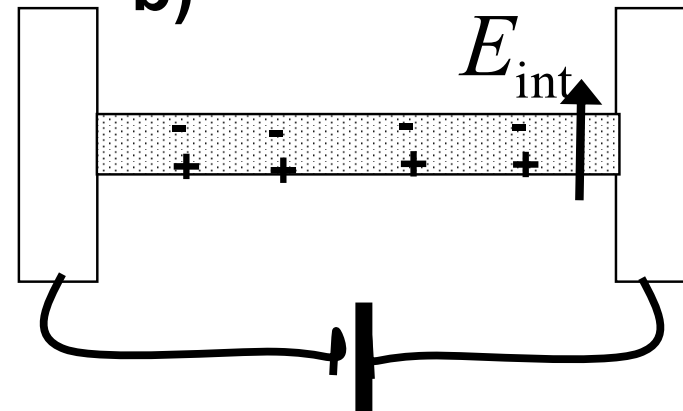
4



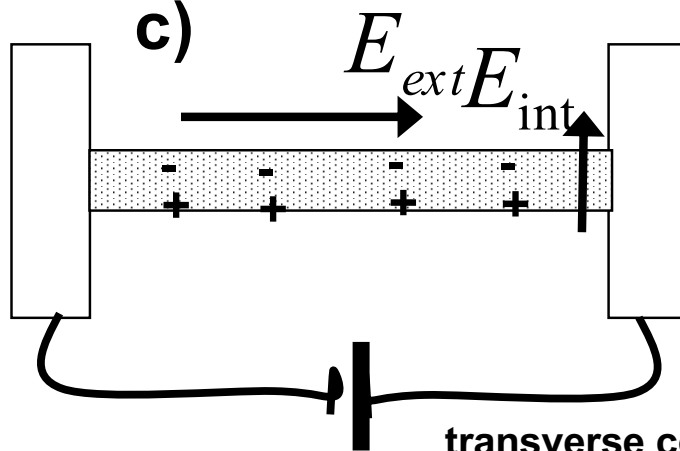
**a)** (first moment, transient response)



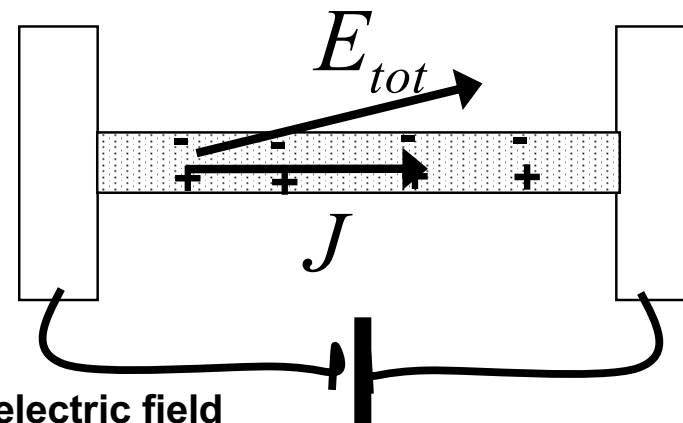
**b)**



**c)**



**d)** (steady-state current response)



transverse component of the electric field

# Transversal voltage

**Example  $\text{Bi}_4\text{Ti}_3\text{O}_{12}$**

**Made of less conductive layers  $\text{TiO}_2$   
and more conductive layers  $\text{Bi}_2\text{O}_3$**

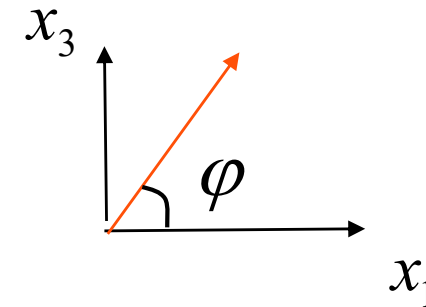
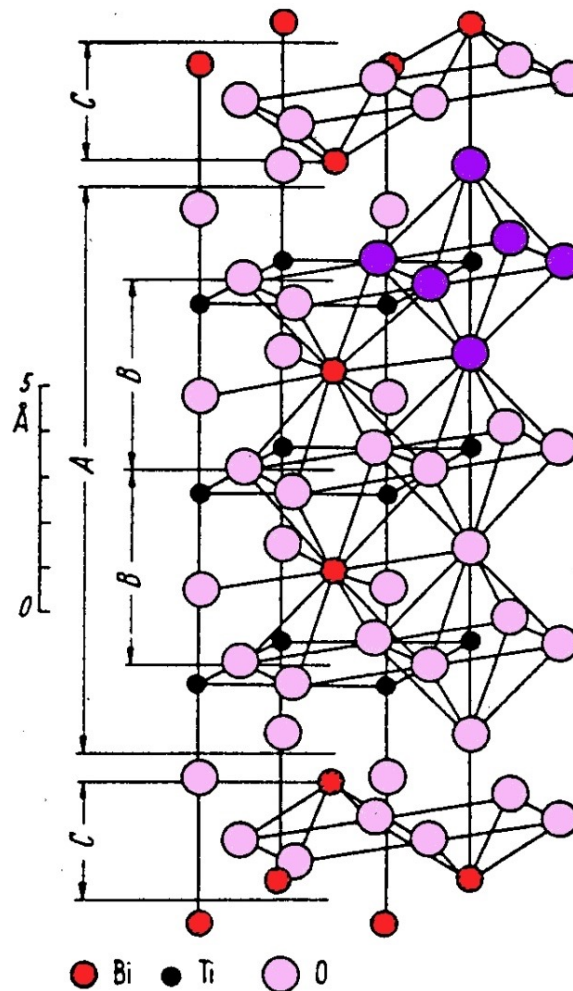
**$4/mmm$**

$$T = 800^\circ\text{C}$$

$$a = 0.25 (\Omega\text{m})^{-1}$$

$$b = 0.016 (\Omega\text{m})^{-1}$$

$$\underline{\tau} = \begin{pmatrix} a & 0 & 0 \\ 0 & a & 0 \\ 0 & 0 & b \end{pmatrix}$$

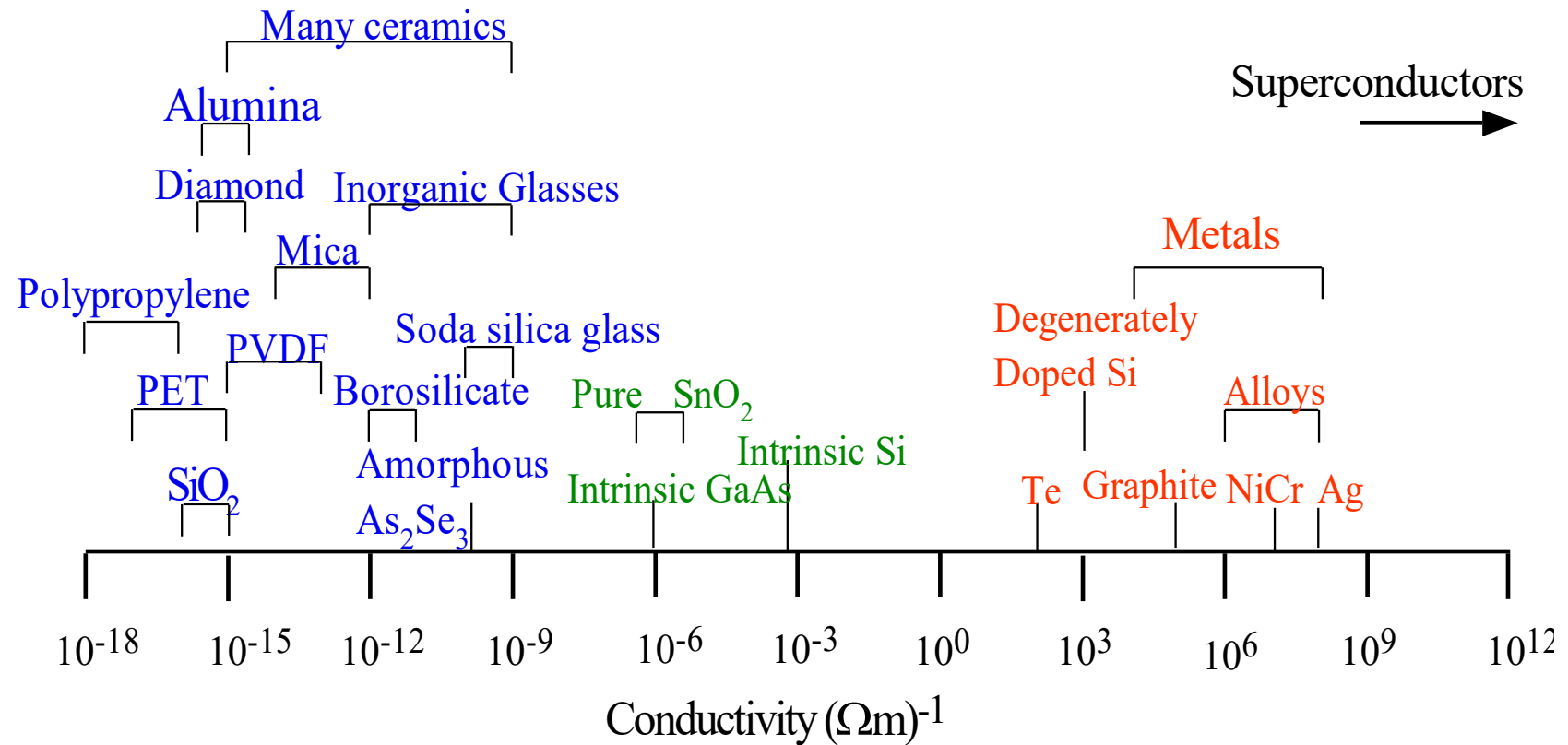


$$\left. \frac{E_{\perp}}{E_{\uparrow\uparrow}} \right|_{\text{max}} \approx 2$$

$$\varphi|_{\text{max}} \approx 4^\circ$$



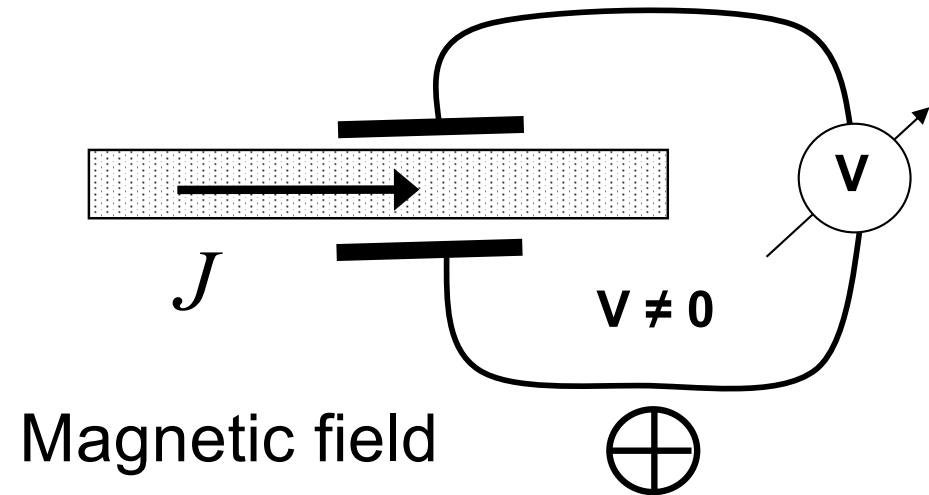
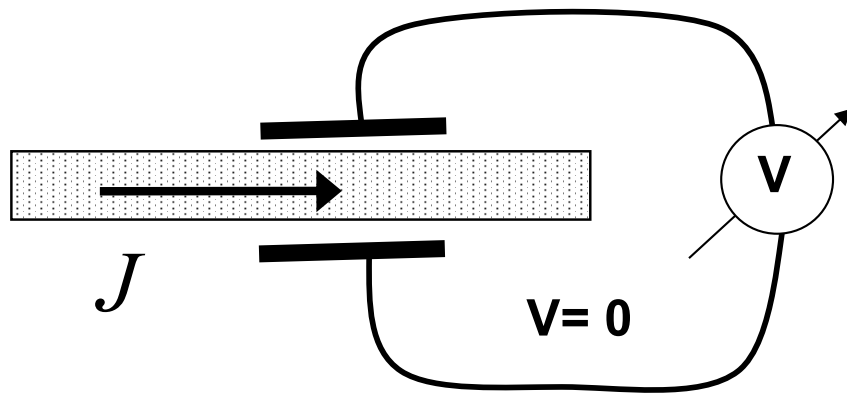
# Spread of conduction



# Transversal voltage and Hall effect

$m\bar{3}m$

**Cu** isotropic conductor



**Lorentz force:**

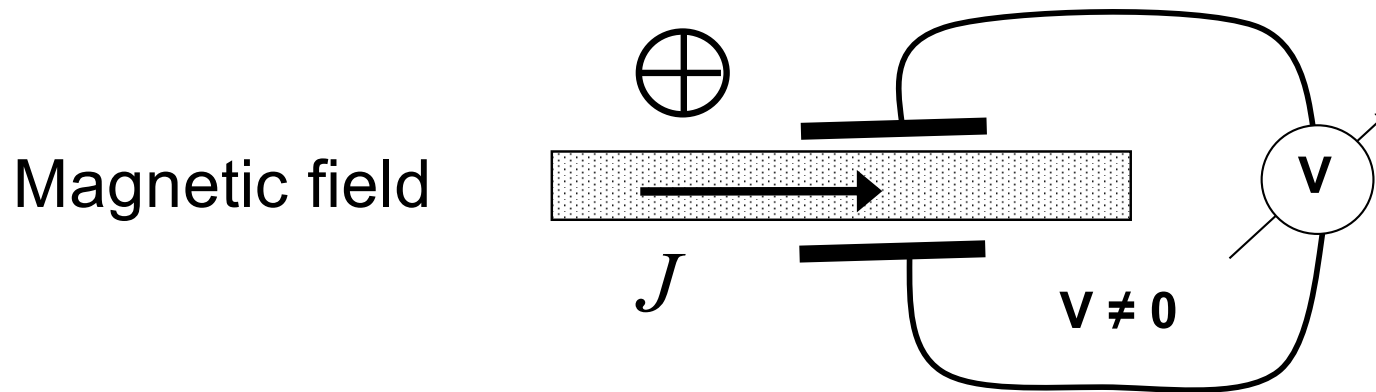
$$F = q (\mathbf{v} \times \mathbf{B})$$

**Hall voltage:**

$V_H = (I_x B_z) / (ntq)$ , where  $n$ -charge density,  $t$ -thickness,  $q$ -charge

# Hall effect

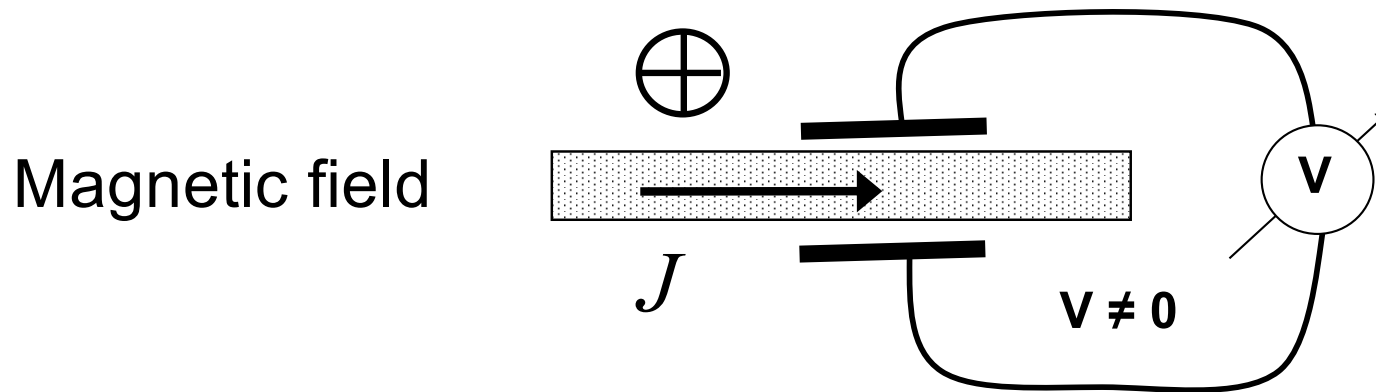
## Isotropic conductor



1. Magnetic field modify the symmetry of the system allowing the transverse voltage in isotropic conductor
2. Transport effect  $\rightarrow$  current

# Hall effect: tensor aspect

## Isotropic conductor



**Hall effects is controlled by a 3rd rank pseudo-tensor**

$$E_i = R_{ijk} B_j J_k$$

# Thermoelectric transport effects

# Thermal conductivity

## Energy dissipation

$$h_i = -k_{ij} \frac{\partial T}{\partial x_j}$$

$$k_{ji} = k_{ij}$$

$$\frac{dW}{dt} = \frac{h_i}{T} \frac{\partial T}{\partial x_j}$$

$k_{ij}$  (kappa) – thermal conductivity tensor,  $h_i$  – heat flux

## Analogy to electrical conductivity

$$E_i = -\frac{\partial \varphi}{\partial x_j}$$

$$J_i = -\tau_{ij} \frac{\partial \varphi}{\partial x_j}$$

$$\frac{dW}{dt} = J_j \frac{\partial \varphi}{\partial x_j}$$

$$\frac{\partial \varphi}{\partial x_j} \Rightarrow \frac{\partial T}{\partial x_j}$$

$$J_i \Rightarrow \frac{h_i}{T}$$

# Thermoelectricity

## Electrical Conductivity

$$J_i = \tau_{ij} E_j$$

## Thermal Conductivity

$$h_i = -k_{ij} \frac{\partial T}{\partial x_j}$$

## Thermoelectricity

$$J_i = \tau_{ij} E_j + a_{ij} \frac{\partial T}{\partial x_j}$$

$$h_i = b_{ij} E_j - k_{ij} \frac{\partial T}{\partial x_j}$$

**Cross effects:**

**There should be a component of current proportional to the temperature gradient!**

# Thermoelectricity vs. piezoelectricity

## Piezoelectricity

$$D_i = \varepsilon_0 K_{ij} E_j + d_{ijk} \sigma_{jk}$$

$$\varepsilon_{ij} = d_{kij} E_k + s_{ijkl} \sigma_{kl}$$

**Maxwell relations**

## Thermoelectricity

$$J_i = \tau_{ij} E_j + a_{ij} \frac{\partial T}{\partial x_j}$$

$$h_i = b_{ij} E_j - k_{ij} \frac{\partial T}{\partial x_j}$$

**??????????**



# Onsager relations for thermo-electric transport phenomena

$$\tau_{ij} = \tau_{ji}$$

$$k_{ji} = k_{ij}$$

$$b_{ij} = -Ta_{ji}$$

**Maxwell relations cannot be applied because the energy does not characterize the state of the material in a transport phenomenon**

**Onsager relations can be obtained from considerations in terms of the energy dissipation in a process**

# Thermoelectricity vs. piezoelectricity

## Piezoelectricity

$$D_i = \varepsilon_0 K_{ij} E_j + d_{ijk} \sigma_{jk}$$

$$\varepsilon_{ij} = d_{kij} E_k + s_{ijkl} \sigma_{kl}$$

**Maxwell relations**

## Thermoelectricity

$$J_i = \tau_{ij} E_j + a_{ij} \frac{\partial T}{\partial x_j}$$

$$h_i = -T a_{ji} E_j - k_{ij} \frac{\partial T}{\partial x_j}$$

**Onsager relations**

# Standard description of thermoelectricity

**Changing variables:**

**Instead of field use current and temperature**

$$J_i = \tau_{ij} E_j + a_{ij} \frac{\partial T}{\partial x_j}$$

$$h_i = -T a_{ji} E_j - k_{ij} \frac{\partial T}{\partial x_j}$$

$$E_i = \rho_{ij} J_j + \Sigma_{ij} \frac{\partial T}{\partial x_j}$$

$$h_i = T \Sigma_{ji} J_j - \tilde{k}_{ij} \frac{\partial T}{\partial x_j}$$

$$\rho_{ij} = \tau^{-1}_{ij}$$

$$\Sigma_{ij} = -\rho_{il} a_{lj}$$

$$\tilde{k}_{ij} = k_{ij} - T a_{si} \rho_{sl} a_{lj}$$

$\Sigma_{ij}$

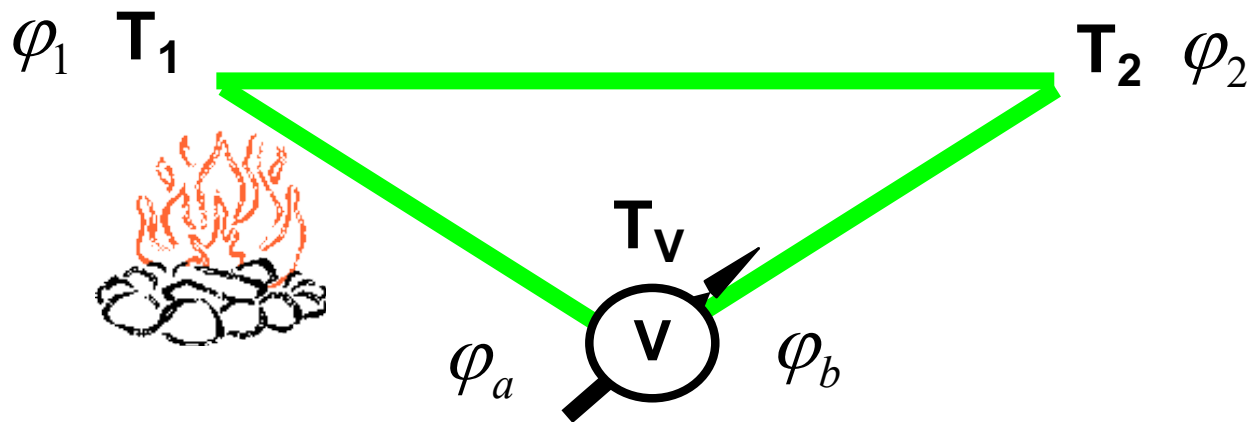
**Thermoelectric tensor  
(Seebeck coefficients)**

**In general**

$$\Sigma_{ij} \neq \Sigma_{ji}$$

# Thermoelectric effect - example

## Seebeck effect



$$\varphi_b - \varphi_a \quad ?$$

$$E = \rho J + \Sigma \frac{\partial T}{\partial x}$$

$$J = 0 \quad E = -\frac{\partial \varphi}{\partial x}$$

$$\frac{\partial}{\partial x} (\varphi + \Sigma T) = 0$$

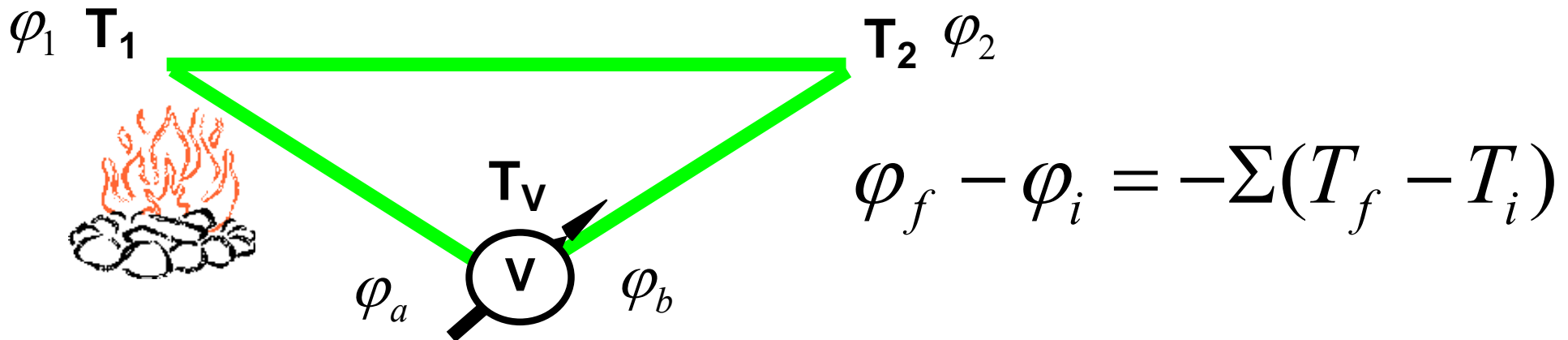
$$\varphi + \Sigma T = \text{const}$$

$$\varphi_f - \varphi_i = -\Sigma (T_f - T_i)$$

For simplicity Seebeck coefficients are considered T-independent

# Thermoelectric effect - example

## Seebeck effect



$$\varphi_b - \varphi_2 = -\Sigma(T_V - T_2)$$

$$\varphi_b - \varphi_1 = -\Sigma(T_V - T_2) - \Sigma(T_2 - T_1)$$

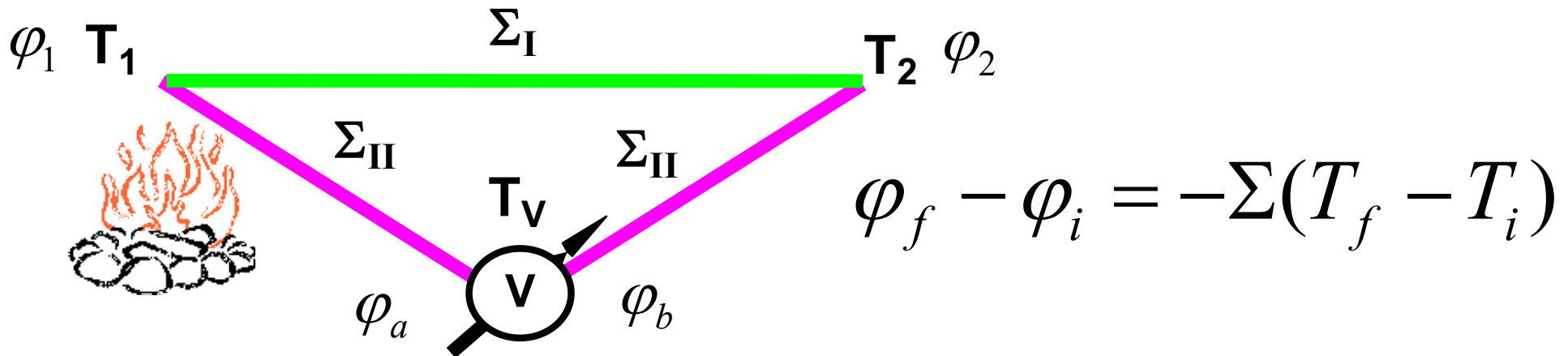
$$\varphi_b - \varphi_a = -\Sigma(T_V - T_2) - \Sigma(T_2 - T_1) - \Sigma(T_1 - T_V) = 0$$

$\Sigma$  cannot be measured this way

**This is rigorous for small  $T_1 - T_2$ , since  $\Sigma$  is temperature dependent.**

# Thermoelectric effect - example

## Seebeck effect



$$\varphi_b - \varphi_2 = -\Sigma_{II}(T_V - T_2) \qquad \varphi_b - \varphi_1 = -\Sigma_{II}(T_V - T_2) - \Sigma_I(T_2 - T_1)$$

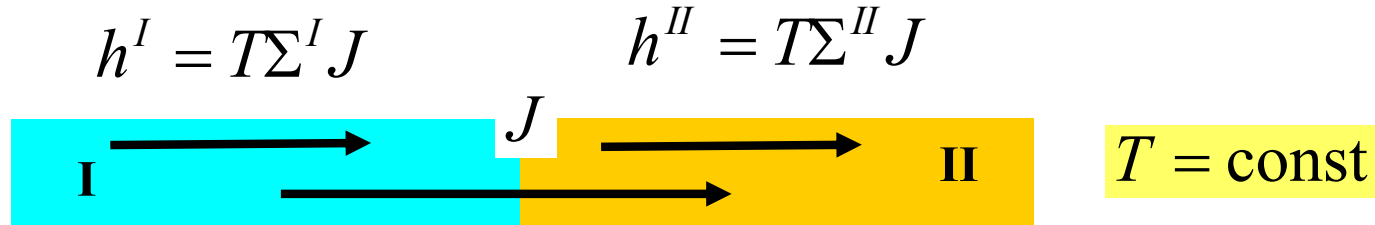
$$\varphi_b - \varphi_a = -\Sigma_{II}(T_V - T_2) - \Sigma_I(T_2 - T_1) - \Sigma_{II}(T_1 - T_V) = (\Sigma_{II} - \Sigma_I)(T_2 - T_1)$$

**This is rigorous for small  $T_1 - T_2$ , since  $\Sigma$  is temperature dependent.**

# Thermoelectric effect - example

## Peltier effect

$$h = T\Sigma J - \tilde{k} \frac{\partial T}{\partial x}$$



$$\frac{dQ}{dt} = S(h^I - h^{II}) = STJ(\Sigma^I - \Sigma^{II}) = T(\Sigma^I - \Sigma^{II})I$$

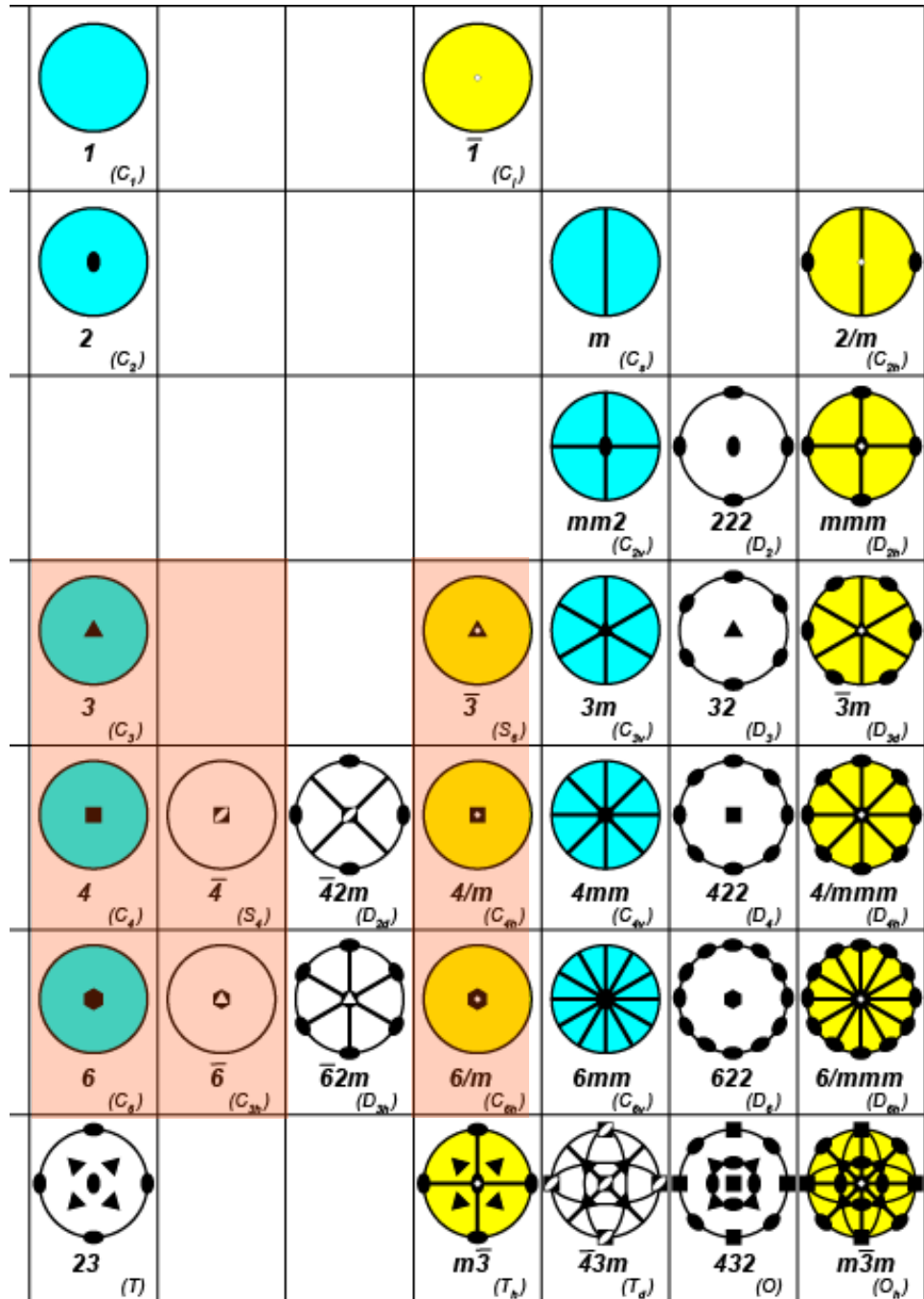
# Thermoelectric Peltier and Seebeck effects

- We can regard the Peltier effect as the back-action counterpart to the Seebeck effect :
  - if a thermoelectric circuit is closed then the Seebeck effect will drive a current
    - this current in turn will always transfer heat from the hot to the cold junction (via the Peltier effect)
    - relationship between Peltier and Seebeck effects is seen in the connection between their coefficients
- Applications:
  - small refrigerators /coolers (Peltier effect) –compact, no fluids
  - temperature sensors (Seebeck effects ) - thermocouples



# All symmetries

There is no physical reason to expect Seebeck tensor to be symmetrical



$$\begin{pmatrix} \Sigma_{11} & \Sigma_{12} & \Sigma_{13} \\ \Sigma_{21} & \Sigma_{22} & \Sigma_{23} \\ \Sigma_{31} & \Sigma_{32} & \Sigma_{33} \end{pmatrix}$$

$$\begin{pmatrix} \Sigma_{11} & \Sigma_{12} & 0 \\ \Sigma_{21} & \Sigma_{22} & 0 \\ 0 & 0 & \Sigma_{33} \end{pmatrix}$$

$$\begin{pmatrix} \Sigma_{11} & 0 & 0 \\ 0 & \Sigma_{22} & 0 \\ 0 & 0 & \Sigma_{33} \end{pmatrix}$$

$$\begin{pmatrix} \Sigma_{11} & 0 & 0 \\ 0 & \Sigma_{11} & 0 \\ 0 & 0 & \Sigma_{33} \end{pmatrix}$$

$\infty / mm \quad \infty 2 \quad \infty m$

$$\begin{pmatrix} \Sigma_{11} & \Sigma_{12} & 0 \\ -\Sigma_{12} & \Sigma_{11} & 0 \\ 0 & 0 & \Sigma_{33} \end{pmatrix}$$

$\infty \quad \infty / m$

$$\begin{pmatrix} \Sigma & 0 & 0 \\ 0 & \Sigma & 0 \\ 0 & 0 & \Sigma \end{pmatrix}$$

$\infty \infty \quad \infty \infty m$

# Seebeck coefficients of selected metals

$m\bar{3}m$	$\Sigma$ at 0 °C ( $\mu\text{V K}^{-1}$ )	$\Sigma$ at 27 °C ( $\mu\text{V K}^{-1}$ )
Al	1.6	1.8
Au	-1.79	-1.94
Cu	-1.70	-1.84
Na		5
Pd	9.00	9.99
Pt	4.45	

at room temperature

$$\Delta T = 100 \text{ K}$$

$$\Delta\varphi \cong 10^{-1} - 10^{-3} \text{ V}$$

Bi <sub>2</sub> Te <sub>3</sub> n-type	$\Sigma$ at 54 °C
rhombohedral	287 $\mu\text{V K}^{-1}$

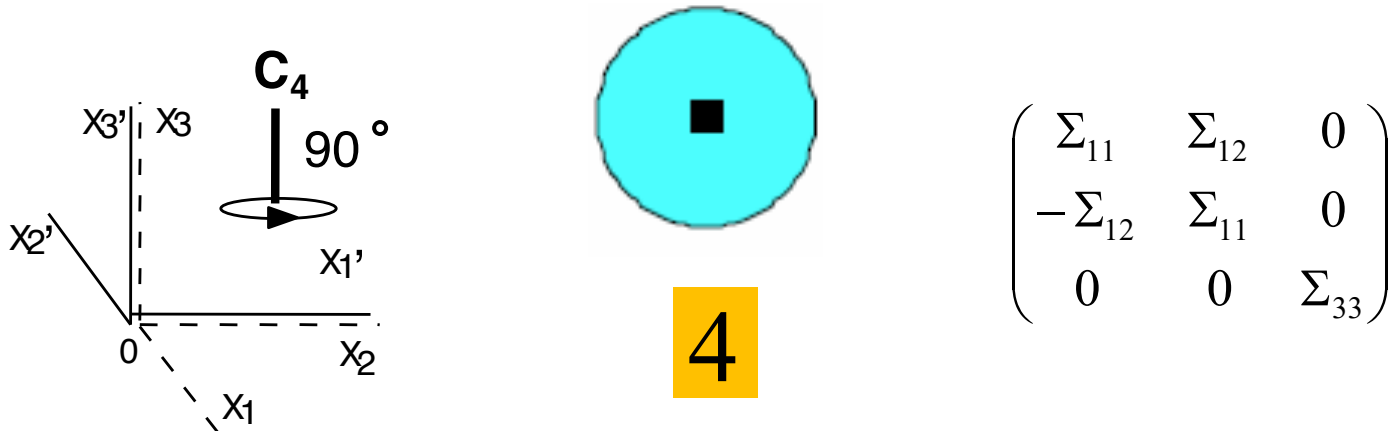
Useful numbers, temperature ranges:

<https://www.omega.com/en-us/colorcodes>

Convention in engineering: Seebeck coefficient  $S = - \Sigma$

# Applications of Neumann equation

Example:  $\Sigma_{12}$ ?



rotation  $4_z(90^\circ)$

$$p'_1 p'_2 = -p_2 p_1 \Rightarrow \Sigma'_{12} = -\Sigma_{21}$$

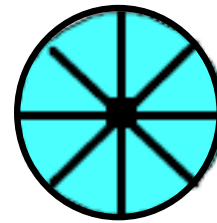
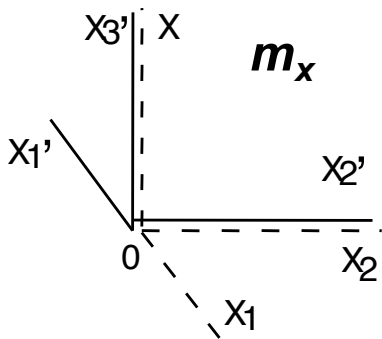
$$\begin{aligned} p'_1 &= p_2 \\ p'_2 &= -p_1 \\ p'_3 &= p_3 \end{aligned}$$

**Neumann equation**

$$\Sigma_{12} = -\Sigma_{21}$$

# Applications of Neumann equation

Example:  $\Sigma_{12}$ -?



$$\begin{pmatrix} \Sigma_{11} & 0 & 0 \\ 0 & \Sigma_{11} & 0 \\ 0 & 0 & \Sigma_{33} \end{pmatrix}$$

**4mm**

**plane  $m_x$**

$$p'_1 = -p_1$$

$$p'_2 = p_2$$

















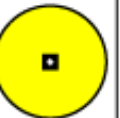
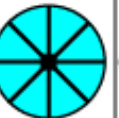



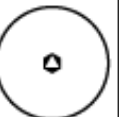


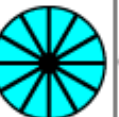







$$p'_3 = p_3$$

$$p'_1 p'_2 = -p_1 p_2 \Rightarrow \Sigma'_{12} = -\Sigma_{12}$$

**Neumann equation**

$$\Sigma_{12} = -\Sigma_{12} = 0$$

# Thermoelectric anisotropy and axis choice

 1 (C <sub>1</sub> )			 $\bar{1}$ (C <sub>1</sub> )			
 2 (C <sub>2</sub> )				 m (C <sub>s</sub> )		 2/m (C <sub>2h</sub> )
				 mm2 (C <sub>2v</sub> )	 222 (D <sub>2</sub> )	 mmm (D <sub>2h</sub> )
 3 (C <sub>3</sub> )			 $\bar{3}$ (S <sub>6</sub> )	 3m (C <sub>3h</sub> )	 32 (D <sub>3</sub> )	 $\bar{3}m$ (D <sub>3d</sub> )
 4 (C <sub>4</sub> )	 $\bar{4}$ (S <sub>8</sub> )	 $\bar{4}2m$ (D <sub>2d</sub> )	 4/m (C <sub>4h</sub> )	 4mm (C <sub>4v</sub> )	 422 (D <sub>4</sub> )	 4/mmm (D <sub>4h</sub> )
 6 (C <sub>6</sub> )	 $\bar{6}$ (C <sub>3h</sub> )	 $\bar{6}2m$ (D <sub>3h</sub> )	 6/m (C <sub>6h</sub> )	 6mm (C <sub>6v</sub> )	 622 (D <sub>6</sub> )	 6/mmm (D <sub>6h</sub> )
 23 (T)			 $m\bar{3}$ (T <sub>h</sub> )	 $\bar{4}3m$ (T <sub>d</sub> )	 432 (O)	 $m\bar{3}m$ (O <sub>h</sub> )

9  $\Rightarrow$  6

5  $\Rightarrow$  4

3

2-3

$$\Sigma_{ij} \neq \Sigma_{ji}$$

1

# Equilibrium and transport properties

## Equilibrium

Dielectric response  $K_{ij}$

Elasticity  $C_{ijkl}$   $S_{ijkl}$

Heat capacity  $C$

Piezoelectricity and  
converse piezoelectricity  $d_{ijk}$

Pyroelectricity and  
electrocaloric  $p_i$

Thermal expansion and  
piezocaloric  $\alpha_{ji}$

## Maxwell relations

## Transport

Electrical conductivity  $\tau_{ij}$

Thermal conductivity  $k_{ij}$

Seebeck and Peltier  
effect  $\Sigma_{ij}$

Hall effect  $R_{ijk}$

## Onsager relations

# Essential

1. The symmetry of a material can be translated into the symmetry of its transport properties.
2. Thermoelectric effects: Peltier and Seebeck effects
3. Transport properties give an examples of a non-symmetric second rank tensor - Thermoelectric tensor (Seebeck coefficients)