

# 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  $\epsilon$  and  $\sigma$  are zero/nonzero)

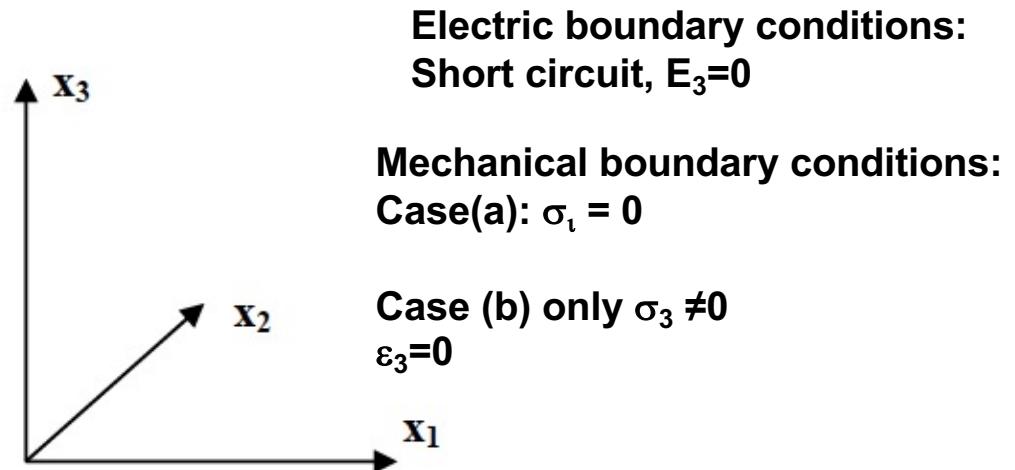
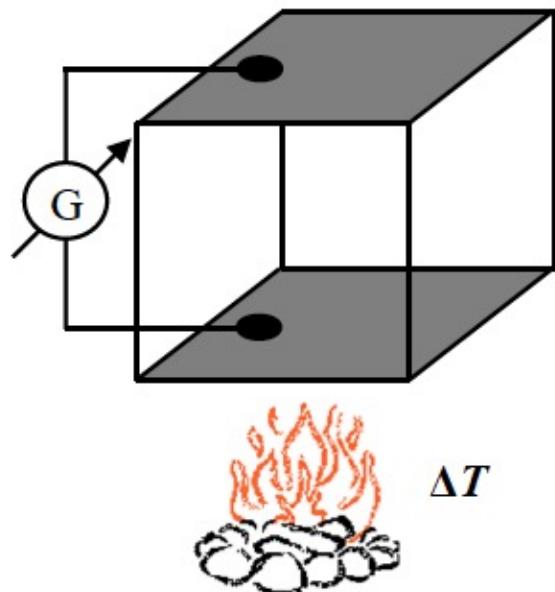
# Exercise 8.1

**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)



# 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,

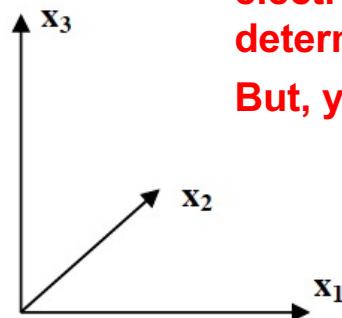
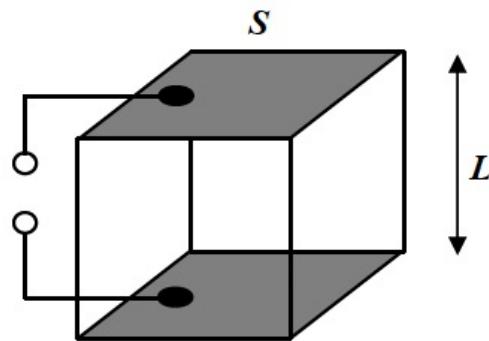
$$p_{(a)} - p_{(b)} = \frac{d_{33} \alpha_3}{s_{33}}$$

# 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

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

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

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

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

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

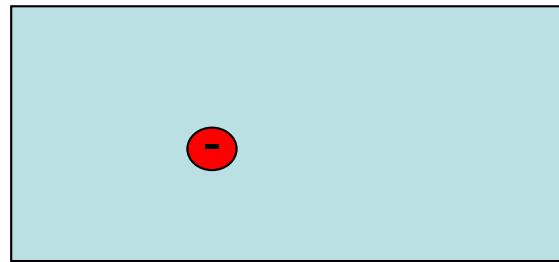
Thus, in (a) and (b) the measured capacitances are different. Specifically,

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

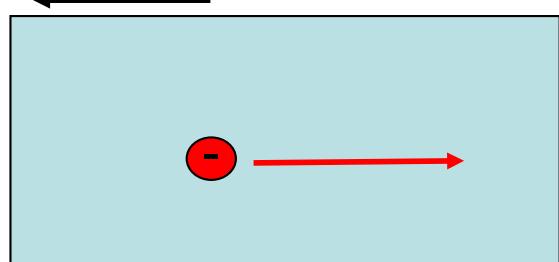
# Electric response of solids: transport vs. dielectric response

## Conductivity

$$E = 0 \quad \langle v_{ch} \rangle = 0$$



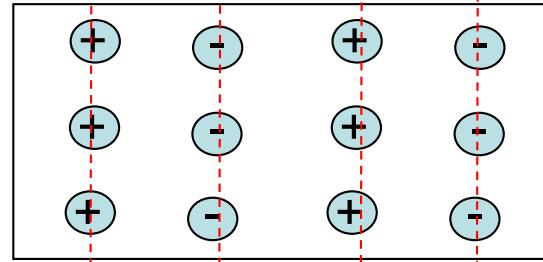
$$E \neq 0 \quad \langle v_{ch} \rangle \neq 0$$



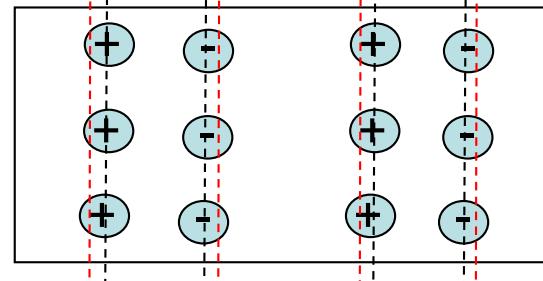
Displacements of the charges are much  
*larger* than the interatomic distance

## Polarization

$$\vec{l} \quad E = 0 \quad \langle v_{ch} \rangle = 0$$



$$\vec{l} \quad E \neq 0 \quad \langle v_{ch} \rangle = 0$$



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

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

## Linear response

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

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

## Conductivity tensor

$$\tau_{ij}$$

can be shown

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

## Dielectric susceptibility tensor

$$\chi_{ij}$$

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

# Transport property vs. equilibrium property

**Dielectric response**  
- equilibrium property

$$D_i = \epsilon_0 K_{ij} E_j$$

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

**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> )			 1-bar (C <sub>1</sub> )			
 2 (C <sub>2</sub> )			 m (C <sub>2</sub> )		 2/m (C <sub>2n</sub> )	
 3 (C <sub>3</sub> )			 mm2 (C <sub>2v</sub> )	 222 (D <sub>2</sub> )	 mmm (D <sub>3n</sub> )	
 4 (C <sub>4</sub> )	 4-bar (S <sub>4</sub> )	 42m (D <sub>2d</sub> )	 4/m (C <sub>4v</sub> )	 4mm (C <sub>4v</sub> )	 422 (D <sub>4</sub> )	 4/mmm (D <sub>4h</sub> )
 6 (C <sub>6</sub> )	 6-bar (C <sub>3h</sub> )	 62m (D <sub>3d</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)			 m3-bar (T <sub>2h</sub> )	 43m (T <sub>d</sub> )	 432 (O)	 m3m (O <sub>h</sub> )

$$\begin{array}{c}
 \xrightarrow{\hspace{2cm}} \begin{pmatrix} \tau_{11} & \tau_{12} & \tau_{13} \\ \tau_{22} & \tau_{23} & \\ \tau_{33} & & \end{pmatrix} \\
 \xleftarrow{\hspace{2cm}} \begin{pmatrix} \tau_{11} & 0 & \tau_{13} \\ \tau_{22} & 0 & \\ \tau_{33} & & \end{pmatrix} \\
 \xrightarrow{\hspace{2cm}} \begin{pmatrix} \tau_{11} & 0 & 0 \\ \tau_{22} & 0 & \\ \tau_{33} & & \end{pmatrix} \\
 \xleftarrow{\hspace{2cm}} \left\{ \begin{pmatrix} \tau_1 & 0 & 0 \\ \tau_1 & 0 & \\ \tau_3 & & \end{pmatrix} \right. \\
 \xleftarrow{\hspace{2cm}} \left. \begin{pmatrix} \infty & \infty m & \infty 2 \\ \infty / m & \infty / mm & \end{pmatrix} \right. \\
 \xleftarrow{\hspace{2cm}} \left\{ \begin{pmatrix} \tau & 0 & 0 \\ \tau & 0 & \\ \tau & & \end{pmatrix} \right. \\
 \xleftarrow{\hspace{2cm}} \left. \begin{pmatrix} \infty \infty \infty & \infty \infty m & \end{pmatrix} \right.
 \end{array}$$

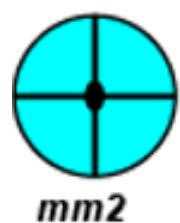
# Anisotropy of conductivity

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

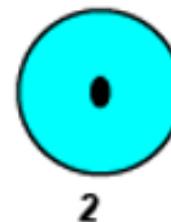
**Current is always parallel to the field only if**

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

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



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



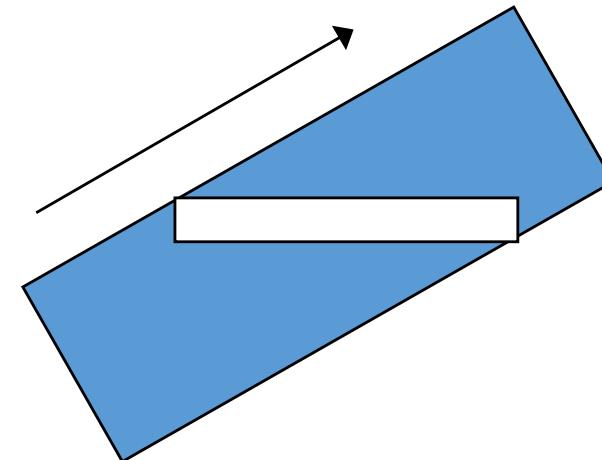
$$\begin{pmatrix} \tau_{11} & 0 & \tau_{13} \\ & \tau_{22} & 0 \\ & & \tau_{33} \end{pmatrix}$$

# Transversal voltage

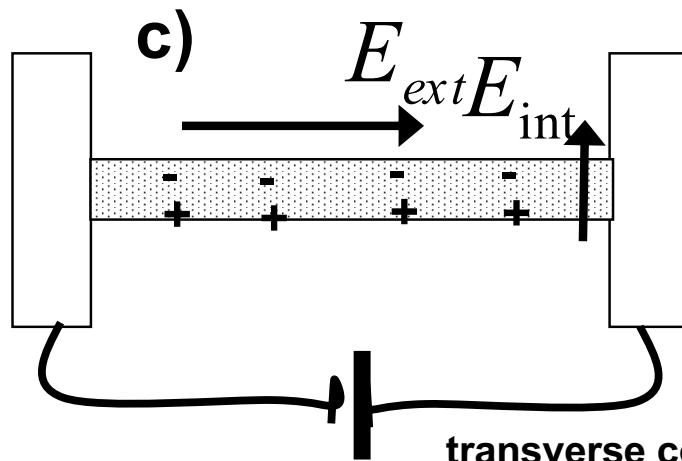
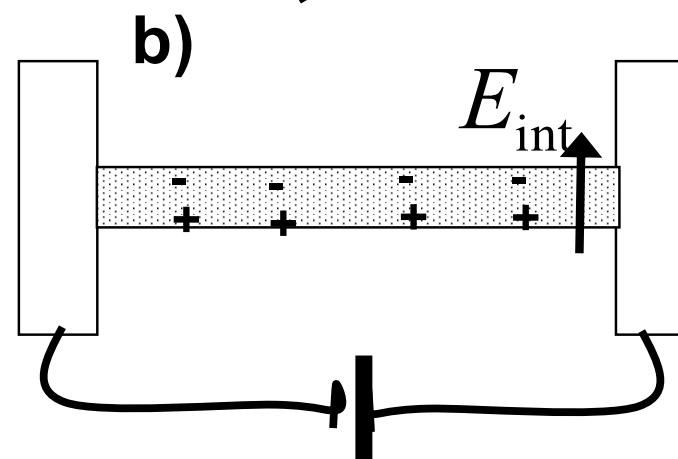
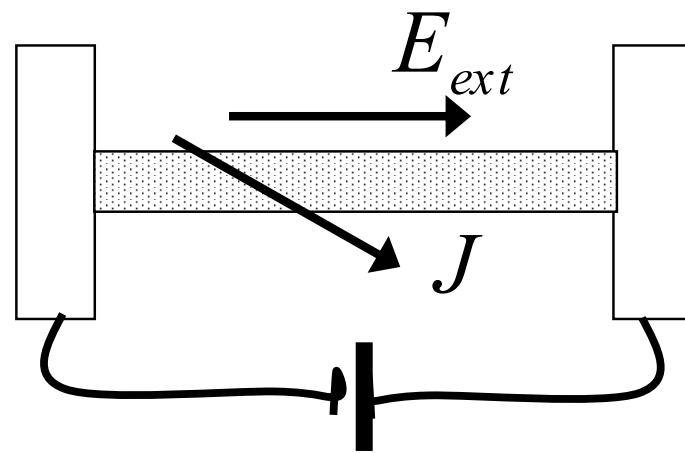
4 / *mmm*

**Bi<sub>4</sub>Ti<sub>3</sub>O<sub>12</sub>**

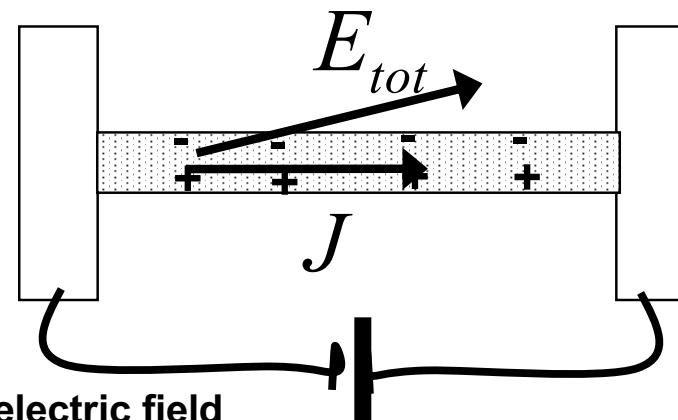
4



a) (first moment, transient response)



d) (steady-state current response)



# Transversal voltage

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

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

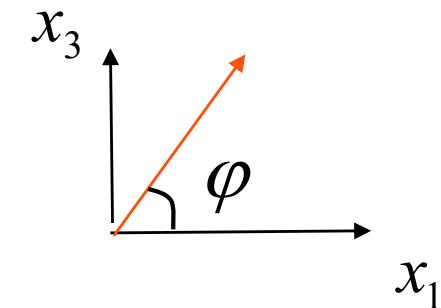
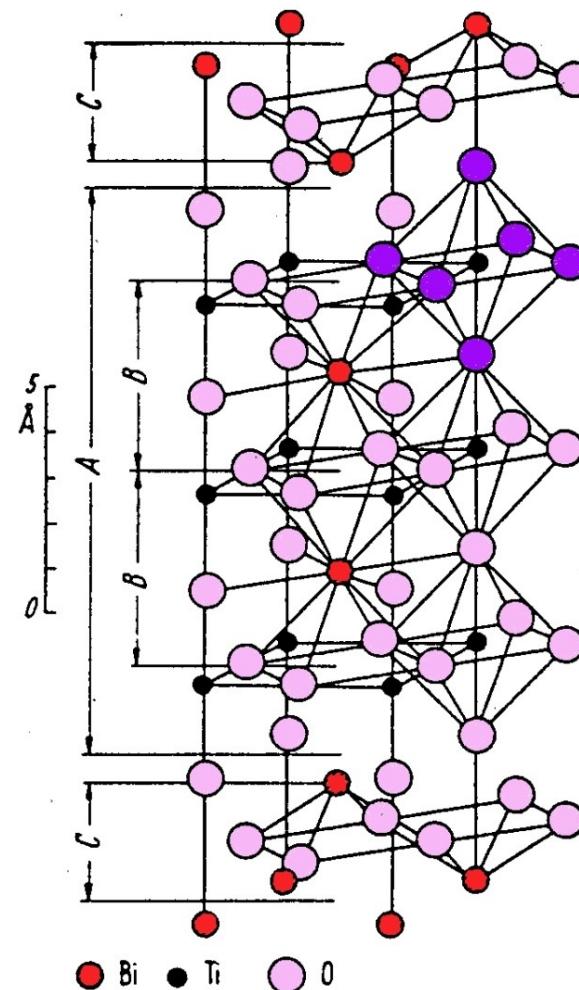
**4/mmm**

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

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

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

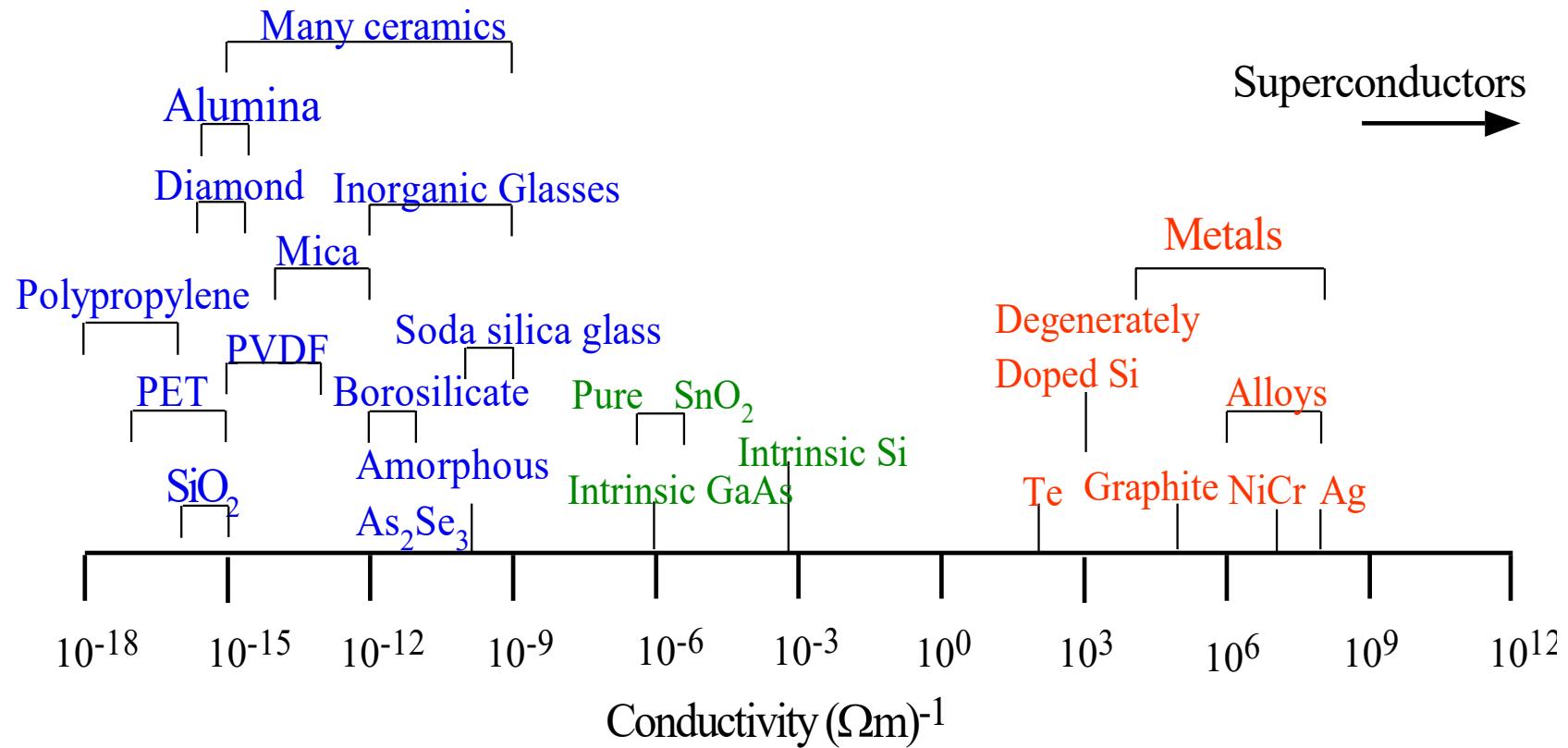
$$\underline{\tau} = \begin{pmatrix} a & 0 & 0 \\ 0 & a & 0 \\ 0 & 0 & b \end{pmatrix}$$



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

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

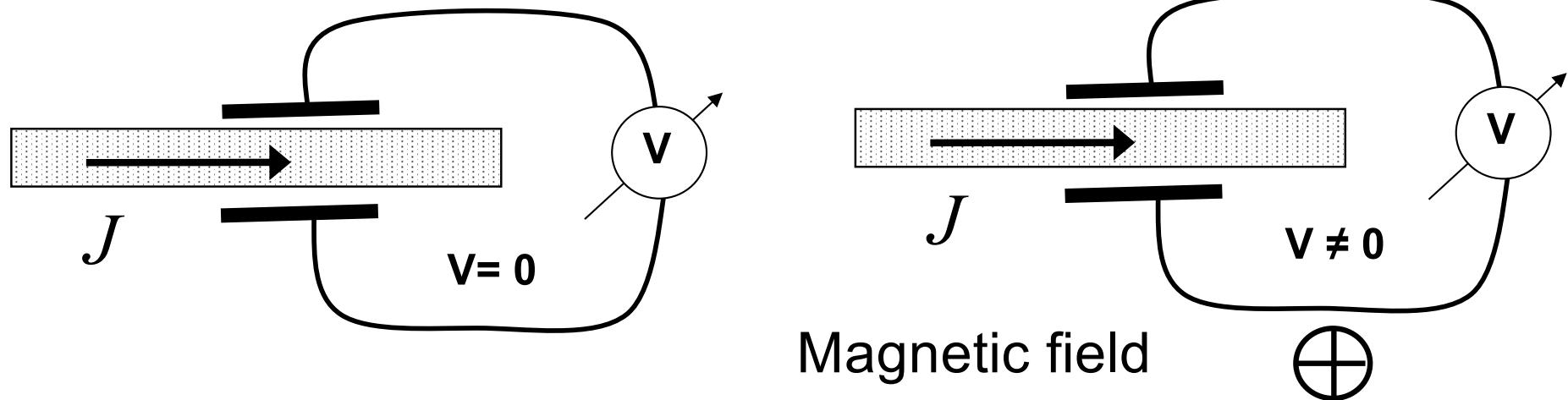
# Spread of conduction



# Transversal voltage and Hall effect

$m\bar{3}m$

**Cu isotropic conductor**



**Lorentz force:**

$$F = q (v \times B)$$

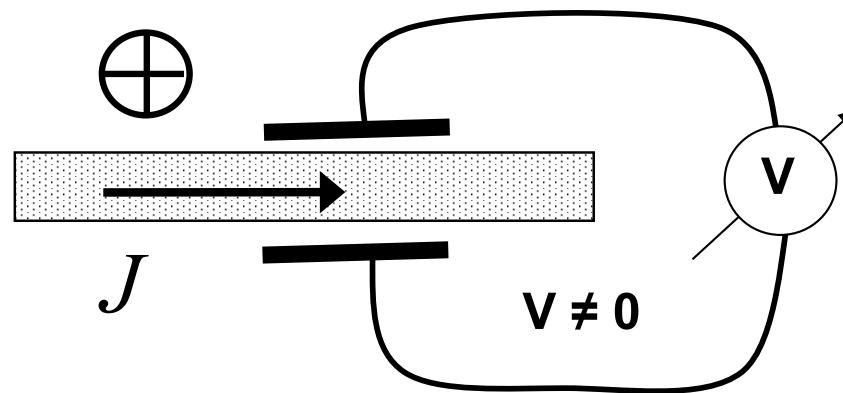
**Hall voltage:**

$$V_H = (I_x B_z) / (n t q), \text{ where } n - \text{charge density, } t - \text{thickness, } q - \text{charge}$$

# Hall effect

## Isotropic conductor

Magnetic field

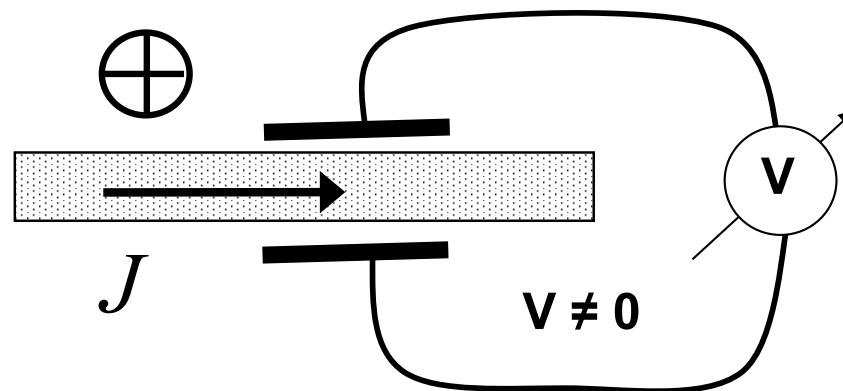


- 1. Magnetic field modify the symmetry of the system allowing the transverse voltage in isotropic conductor**
- 2. Transport effect → current**

# Hall effect: tensor aspect

## Isotropic conductor

Magnetic field



**Hall effect 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

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

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

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

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

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

# 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

$$D_i = \epsilon_0 K_{ij} E_j + d_{ijk} \sigma_{jk}$$

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

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

$$D_i = \epsilon_0 K_{ij} E_j + d_{ijk} \sigma_{jk}$$

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

**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**

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

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

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

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

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

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

$$\Sigma_{ij}$$

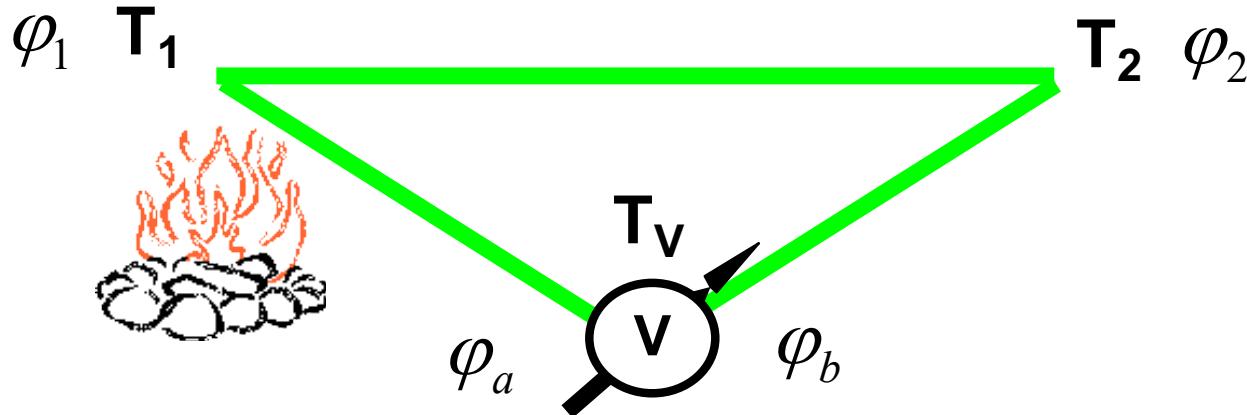
**Thermoelectric tensor  
(Seebeck coefficients)**

**In general**

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

# Thermoelectric effect - example

## Seebeck effect



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

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

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

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

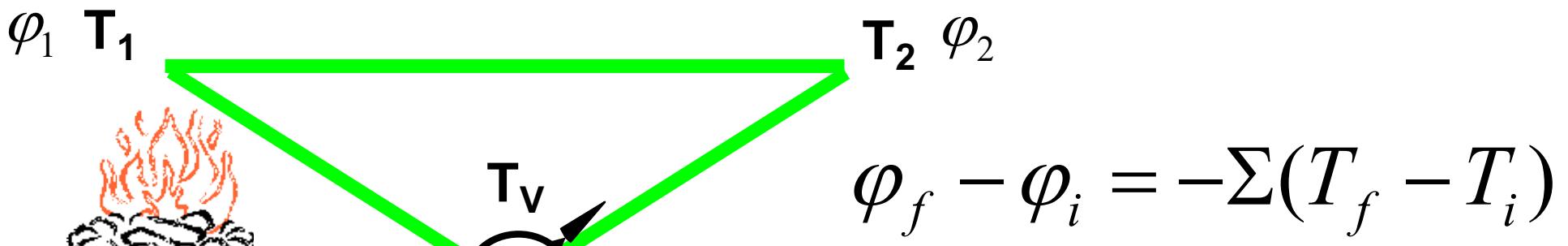
$$\frac{\partial}{\partial x}(\varphi + \sum T) = 0$$

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

For simplicity Seebeck koefficients are considered T-independent

# Thermoelectric effect - example

## Seebeck effect



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

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

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

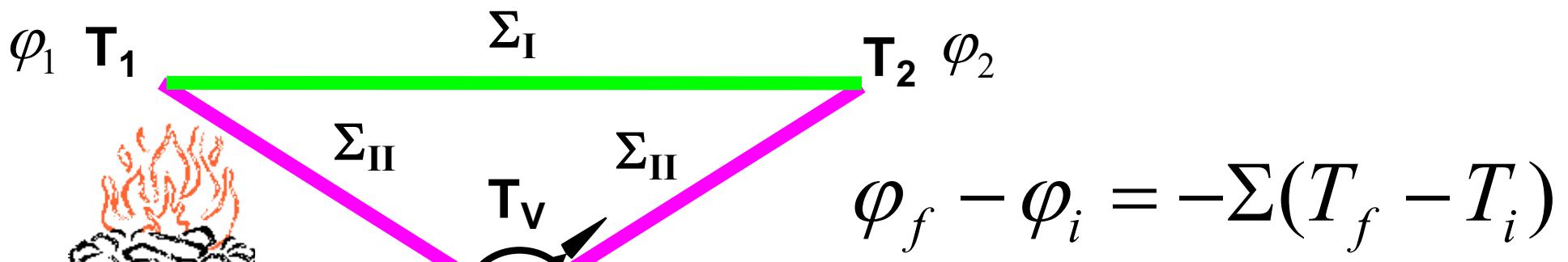
$$\varphi_b - \varphi_a = -\sum(T_V - T_2) - \sum(T_2 - T_1) - \sum(T_1 - T_V) = 0$$

$\Sigma$  cannot be measured this way

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

# Thermoelectric effect - example

## Seebeck effect



$$\varphi_b - \varphi_2 = -\Sigma_{\text{II}}(T_V - T_2)$$

$$\varphi_b - \varphi_1 = -\Sigma_{\text{II}}(T_V - T_2) - \Sigma_{\text{I}}(T_2 - T_1)$$

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

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

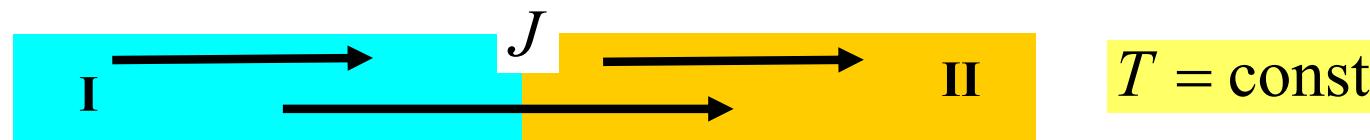
# Thermoelectric effect - example

## Peltier effect

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

$$h^I = T \Sigma^I J$$

$$h^{II} = T \Sigma^{II} J$$



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

# 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


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

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

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

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

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

$\infty$     $\infty/m$

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

$\infty\infty$     $\infty\infty m$

# Seebeck coefficients of selected metals

$m\bar{3}m$	$\Sigma$ at 0 °C ( $\mu\text{V K}^{-1}$ )	$\Sigma$ at 27 °C ( $\mu\text{V K}^{-1}$ )	at room temperature
Al	1.6	1.8	
Au	-1.79	-1.94	$\Delta T = 100 \text{ K}$
Cu	-1.70	-1.84	
Na		5	$\Delta\varphi \cong 10^{-1} - 10^{-3} \text{ V}$
Pd	9.00	9.99	
Pt	4.45		

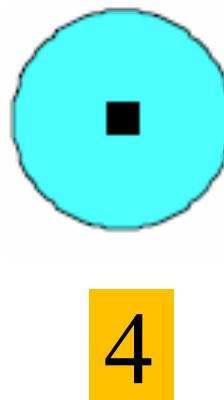
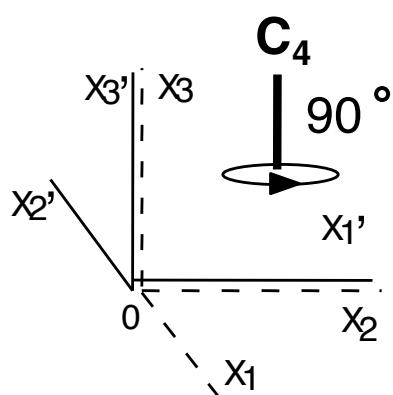
  

Bi <sub>2</sub> Te <sub>3</sub> n-type rhombohedral	$\Sigma$ at 54 °C 287 $\mu\text{V K}^{-1}$	Useful numbers, temperature ranges: <a href="https://www.omega.com/en-us/colorcodes">https://www.omega.com/en-us/colorcodes</a>
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Convention in engineering: Seebeck coefficient  $S = -\Sigma$

# Applications of Neumann equation

Example:  $\Sigma_{12}$ ?



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

rotation  $4_z(90^\circ)$

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

$$p'_1 = p_2$$

$$p'_2 = -p_1$$

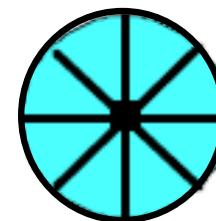
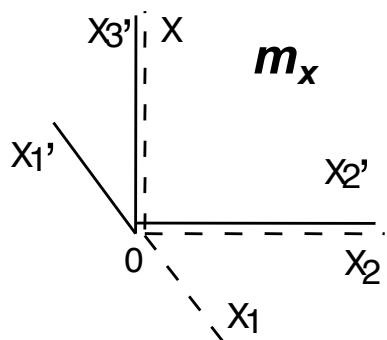
$$p'_3 = p_3$$

**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  $m_x$

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

$$p'_1 = -p_1$$

$$p'_2 = p_2$$

$$p'_3 = p_3$$

Neumann equation

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

# Thermoelectric anisotropy and axis choice

 1 (C <sub>1</sub> )			 1-bar (C <sub>1</sub> )			
 2 (C <sub>2</sub> )				 m (C <sub>3</sub> )		 2/m (C <sub>2m</sub> )
				 mm2 (C <sub>2v</sub> )	 222 (D <sub>2</sub> )	 mmm (D <sub>2m</sub> )
 3 (C <sub>3</sub> )			 3-bar (S <sub>4</sub> )	 3m (C <sub>3v</sub> )	 32 (D <sub>3</sub> )	 3-bar m (D <sub>3d</sub> )
 4 (C <sub>4</sub> )	 4-bar (S <sub>4</sub> )	 4-bar 2m (D <sub>2d</sub> )	 4/m (C <sub>4v</sub> )	 4mm (C <sub>4v</sub> )	 422 (D <sub>4</sub> )	 4/mmm (D <sub>4h</sub> )
 6 (C <sub>6</sub> )	 6-bar (C <sub>3h</sub> )	 6-bar 2m (D <sub>3d</sub> )	 6/m (C <sub>6v</sub> )	 6mm (C <sub>6v</sub> )	 622 (D <sub>6</sub> )	 6/mmm (D <sub>6h</sub> )
 23 (T)			 m-bar 3 (T <sub>4</sub> )	 43m (T <sub>4</sub> )	 432 (O)	 m-bar 3m (O <sub>4h</sub> )

$$9 \rightarrow 6$$

$$5 \rightarrow 4$$

$$3$$

$$2-3$$

$$1$$

$$\sum_{ij} \neq \sum_{ji}$$

# 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**  $\sum_{ij}$

**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)