Test of 15.04.2025: Solutions

1. As a result of a phase transition, a crystal of the 422 symmetry loses all elements of point symmetry except for the 2-fold axis marked with 'A' in Fig.1. Find the variation in the dielectric constant tensor caused by this phase transition. For the presentation of this tensor, use the crystallographic reference frame corresponding to symmetry 422 (shown in the Fig. 1). The information from the table of K-tensors can be used without additional justification.

What change of the symmetry of the dielectric response is induced by this transition?

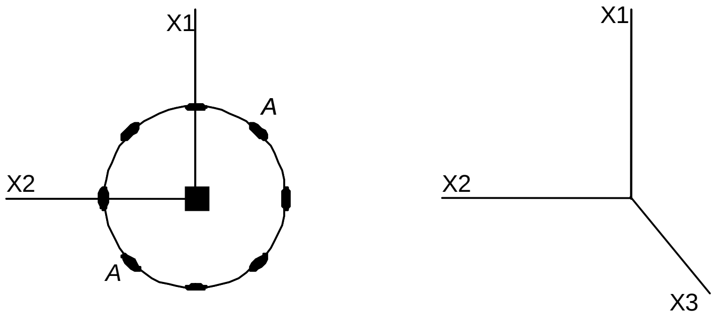

Fig.1. Symmetry elements of the 422 point group and corresponding reference frame

We will use the Neumann's principle.

In general, the dielectric tensor has the following form:

$$K_{ij} = \begin{pmatrix} K_{11} & K_{12} & K_{13} \\ K_{12} & K_{22} & K_{23} \\ K_{13} & K_{23} & K_{33} \end{pmatrix}$$

We will apply the element of symmetry in point group 2 in order to obtain all symmetry restrictions on the tensor.

Two-fold axis: directed along $[\bar{1}10]$

During this transformation, the reference frame changes as: $x_1' = -x_2,\ x_2' = -x_1,\ x_3' = -x_3$.

$$K_{11}' \sim p_1' p_1' = (-p_2)(-p_2) = p_2 p_2 \sim K_{22}$$
$$K_{22}' \sim p_2' p_2' = (-p_1)(-p_1) = p_1 p_1 \sim K_{11}$$
$$K_{33}' \sim p_3' p_3' = (-p_3)(-p_3) = p_3 p_3 \sim K_{33}$$
$$K_{12}' \sim p_1' p_2' = (-p_2)(-p_1) = p_1 p_2 \sim K_{12}$$
$$K_{13}' \sim p_1' p_3' = (-p_2)(-p_3) = p_2 p_3 \sim K_{23}$$
$$K_{23}' \sim p_2' p_3' = (-p_1)(-p_3) = p_1 p_3 \sim K_{13}$$

According to Neumann principle, the tensor must not change during this transform:

$$K_{ij}' = K_{ij}$$

$$\begin{pmatrix} K_{22} & K_{12} & K_{23} \\ K_{12} & K_{11} & K_{13} \\ K_{23} & K_{13} & K_{33} \end{pmatrix} = \begin{pmatrix} K_{11} & K_{12} & K_{13} \\ K_{12} & K_{22} & K_{23} \\ K_{13} & K_{23} & K_{33} \end{pmatrix}$$

Thus, $K_{11} = K_{22}$, $K_{13} = K_{23}$.

As a result, after applying the two-fold axis $[\bar{1}10]$, the tensor has the following form:

$$K_{ij} = \begin{pmatrix} K_{11} & K_{12} & K_{13} \\ K_{12} & K_{11} & K_{13} \\ K_{13} & K_{13} & K_{33} \end{pmatrix}$$

Finally, it is known (from tables of the course), that in point group 2 the symmetry of the dielectric response, as of any other symmetric second rank tensor, is mmm.

2. The piezoelectric coefficient d_{11} of quartz (symmetry 32) is measured using a setup where the plates of the capacitor are parallel to (100) plane of the crystal (as shown in Fig.2). The sample can freely expand in X2 and X3 directions as shown in Fig.2. The measurements are done twice: under isothermal and under adiabatic conditions. Will be any differences between the results of the measurements?

The information from all tables of the course can be used without additional justification.

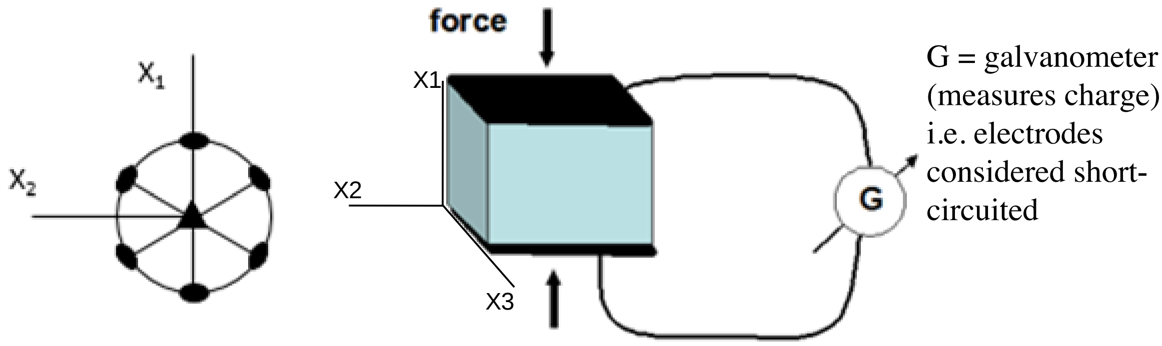

Fig.2. Experimental setup used for piezoelectric coefficient measurements.

Solution:

The piezoelectric response in the system is sought experimentally as:

$$d_{11}^{(\mathrm{exp})} = \frac{Q}{F} = \frac{SD_1}{S\sigma_1} = \frac{D_1}{\sigma_1},$$

where Q is the charge flown through the galvanometer, F is the force applied to the surfaces, S is the surface area. To find the relation between D_1 and σ_1, we will use the constitutive equations at constant temperature:

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

In the investigated problem, the electrodes are short-circuited ($E_1 = 0$), and the sample can freely expand in x_2 and x_3 directions (among all stress components, only $\sigma_1 \neq 0$). Equation for D_1 thus has the following form:

$$D_1 = \varepsilon_0 K_{12} E_2 + \varepsilon_0 K_{13} E_3 + d_{11}\sigma_1 + p_1 \delta T$$

As a next step, we apply symmetry restrictions of group 32. First, tensor of dielectric permittivity has only diagonal components ($K_{12} = K_{13} = 0$). Second, most important, a material of symmetry 32 is **not pyroelectric**, thus $p_1 = 0$. Taking these symmetry restrictions into account, we rewrite the equation for D_1 as follows:

$$D_1 = d_{11}\sigma_1$$

$$d_{11}^{(\mathrm{exp})} = d_{11}$$

The value of piezoelectric response measured experimentally **does not depend** on thermal conditions, whether it is thermostatic or adiabatic. The reason for this – symmetry 32 forbids pyroelectric response of the material.

3. The piezocaloric effect is measured in a sample of $BaTiO_3$ (symmetry $4mm$, the 4-fold axis is directed along x_3 direction). The experimental setup is shown in Fig.3. The surfaces of the sample are under open circuit condition, the sample can freely expand in x_1 and x_2 directions, there is no heat exchange with the environment. Initial temperature of the sample is 300 K.

Determine the change of the temperature at application of pressure 100 MPa in x_3 direction. Use the numerical values for $BaTiO_3$ from the table below (x_3 axis is directed along the 4-fold symmetry axis). The information from all tables of the course can be used without additional justification.

s_{11}	8.05 x 10^{-12} m^2/N	d_{15}	392 x 10^{-12} C/N
s_{12}	-2.35 x 10^{-12} m^2/N	d_{31}	-35 x 10^{-12} C/N
s_{13}	-5.24 x 10^{-12} m^2/N	d_{33}	86 x 10^{-12} C/N
s_{33}	15.7 x 10^{-12} m^2/N	K_{33}	150
C	2.42 x 10^6 $J/(m^3 \cdot K)$	p_3	-5 x 10^{-4} $C/(m^2 \cdot K)$
α_3	3.5 x 10^{-5} 1/K	ε_0	8.85 x 10^{-12} F/m

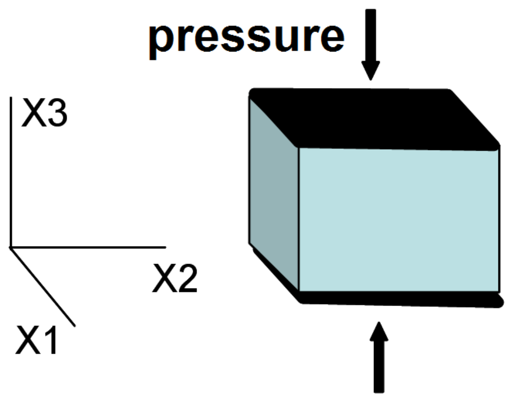

Fig.3. Experimental setup used for piezocaloric effect measurements.

Solution:

In the considered system, the application of pressure σ_3 triggers a change of temperature δT. In order to find relation between these two parameters, we use constitutive equations:

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

$$\frac{\delta Q}{T} = p_i E_i + \alpha_i \sigma_i + \frac{C}{T}\delta T$$

In the investigated problem, all surfaces are open-circuited (all $D_i = 0$), thermally isolated from the environment ($\delta Q = 0$), and the sample can freely expand in x_1 and x_2 directions (among all stress components, only $\sigma_3 \neq 0$). Equations for D_3 and $\delta Q/T$ thus have the following form:

$$D_3 = \varepsilon_0 K_{13} E_1 + \varepsilon_0 K_{23} E_2 + \varepsilon_0 K_{33} E_3 + d_{33}\sigma_3 + p_3 \delta T = 0$$

$$\frac{\delta Q}{T} = p_1 E_1 + p_2 E_2 + p_3 E_3 + \alpha_3 \sigma_3 + \frac{C}{T}\delta T = 0$$

As a next step, we apply symmetry restrictions of group $4mm$. First, tensor of dielectric permittivity has only diagonal components ($K_{13} = K_{23} = 0$). Second, the pyroelectric response is directed along the 4-fold axis, thus $p_1 = p_2 = 0$. Taking these symmetry restrictions into account, we rewrite the equations for D_3 and $\delta Q/T$ as follows:

$$D_3 = \varepsilon_0 K_{33} E_3 + d_{33}\sigma_3 + p_3 \delta T = 0$$

$$\frac{\delta Q}{T} = p_3 E_3 + \alpha_3 \sigma_3 + \frac{C}{T}\delta T = 0$$

From first equation, it is possible to find the dependence of electric field on other parameters:

$$E_3 = -\frac{d_{33}}{\varepsilon_0 K_{33}}\sigma_3 - \frac{p_3}{\varepsilon_0 K_{33}}\delta T$$

Substituting E_3 to the second equation:

$$\frac{\delta Q}{T} = p_3\left(-\frac{d_{33}}{\varepsilon_0 K_{33}}\sigma_3 - \frac{p_3}{\varepsilon_0 K_{33}}\delta T\right) + \alpha_3\sigma_3 + \frac{C}{T}\delta T = 0$$

$$\sigma_3\left(\alpha_3 - \frac{p_3 d_{33}}{\varepsilon_0 K_{33}}\right) + \delta T\left(\frac{C}{T} - \frac{p_3^2}{\varepsilon_0 K_{33}}\right) = 0$$

$$\delta T = -\frac{\alpha_3 - \frac{p_3 d_{33}}{\varepsilon_0 K_{33}}}{\frac{C}{T} - \frac{p_3^2}{\varepsilon_0 K_{33}}}\sigma_3$$

Substituting the numerical values:

$\alpha_3 = 3.5 \times 10^{-5}$ 1/K, $p_3 = -5 \times 10^{-4}$ C/(m$^2 \cdot$ K), $d_{33} = 86 \times 10^{-12}$ C/N, $\varepsilon_0 = 8.85 \times 10^{-12}$ F/m, $K_{33} = 150$, $C = 2.42 \times 10^6$ J/(m$^3 \cdot$ K), $T = 300$ K, σ_3 = -10^8 Pa, we obtain:

$$\delta T = -\frac{3.5 \times 10^{-5} + \frac{5 \times 10^{-4} \cdot 86 \times 10^{-12}}{8.85 \times 10^{-12} \cdot 150}}{\frac{2.42 \times 10^6}{300} - \frac{(5 \times 10^{-4})^2}{8.85 \times 10^{-12} \cdot 150}}(-10^8) = -\frac{3.5 \times 10^{-5} + 3.24 \times 10^{-5}}{8.07 \times 10^3 - 0.188 \times 10^3} \cdot (-10^8)$$

$$= \frac{6.74 \times 10^{-5}}{7.88 \times 10^3} \cdot 10^8 = 0.86 \text{ K}$$

To conclude, application of pressure 100 MPa will lead to 0.86 K change of temperature.

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In the framework of the problem, the voltage applied to (001) electrodes creates electric field with non-zero x_3 component, $E_3 = \frac{V}{L}$, and the temperature change δT is measured. To find the relation between δT and E_3, we will use the constitutive equations for thermally isolated system:

$$\varepsilon_i = d_{ji}E_j + s_{ij}\sigma_j + \alpha_i \delta T,$$
$$\delta Q = Tp_iE_i + T\alpha_i\sigma_i + C\delta T = 0.$$

In case **(a)**, the sample is mechanically free, implying all $\sigma_i = 0$. Then,

$$\delta Q = Tp_1E_1 + Tp_2E_2 + Tp_3E_3 + C\delta T = 0$$

For geometry 4*mm* with 4-fold axis directed along x_3, symmetry restrictions impose $p_1 = p_2 = 0$, $p_3 \neq 0$. Therefore,

$$Tp_3E_3 + C\delta T = 0$$
$$\delta T_{(a)} = -TE_3\frac{p_3}{\mathrm{C}} = -T\frac{V}{L}\frac{p_3}{\mathrm{C}}.$$

To conclude, when the electric field is directed along the pyroelectric response $\vec{p}$ (i.e. antiparallel to the polarization vector $\boldsymbol{P}$) the temperature of the sample decreases. When it is directed in the opposite direction, the temperature increases.

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 $\sigma_3 \neq 0$. The constitutive equation for δQ is then simplified into:

$$\delta Q = Tp_3E_3 + T\alpha_3\sigma_3 + C\delta T = 0.$$

To find σ_3, we use the constitutive equation for $\varepsilon_3 = 0$, which must not change during the measurement:

$$\varepsilon_3 = d_{13}E_1 + d_{23}E_2 + d_{33}E_3 + s_{33}\sigma_3 + \alpha_3\delta T.$$

The symmetry restrictions on a material of 4*mm* point group imply $d_{13} = d_{23} = 0$, and $d_{33} \neq 0$. Then,

$$\varepsilon_3 = d_{33}E_3 + s_{33}\sigma_3 + \alpha_3\delta T = 0 \quad \Rightarrow \quad \sigma_3 = -\frac{d_{33}}{s_{33}}E_3 - \frac{\alpha_3}{s_{33}}\delta T,$$

$$\delta Q = Tp_3E_3 + T\alpha_3\sigma_3 + C\delta T = Tp_3E_3 + T\alpha_3\left(-\frac{d_{33}}{s_{33}}E_3 - \frac{\alpha_3}{s_{33}}\delta T\right) + C\delta T =$$
$$= T\left(p_3 - \frac{\alpha_3 d_{33}}{s_{33}}\right)E_3 + \left(C - T\frac{\alpha_3^2}{s_{33}}\right)\delta T,$$

$$\delta T_{(b)} = -TE_3\frac{p_3 - \frac{\alpha_3 d_{33}}{s_{33}}}{C - T\frac{\alpha_3^2}{s_{33}}} \approx -TE_3\frac{p_3 - \frac{\alpha_3 d_{33}}{s_{33}}}{C} = -T\frac{V}{L}\frac{p_3 - \frac{\alpha_3 d_{33}}{s_{33}}}{C}$$

Since $\frac{\alpha_3 d_{33}}{s_{33}} > 0$, and $p_3 < 0$ the change of temperature is larger in case **(b)**, the difference is:

$$-\frac{\delta T_{(a)} - \delta T_{(b)}}{\delta T_{(a)}} = \frac{\alpha_3 d_{33}}{p_3 s_{33}} = \frac{3.5 \times 10^{-5} \cdot 86 \times 10^{-12}}{5 \times 10^{-4} \cdot 15.7 \times 10^{-12}} = 0.38$$

As in case **(a)**, when the electric field is directed along the pyroelectric response $\vec{p}$, the temperature of the sample decreases. When it is directed in the opposite direction, the temperature increases.