Lecture 6 (week 6: 24-25 March 2025)

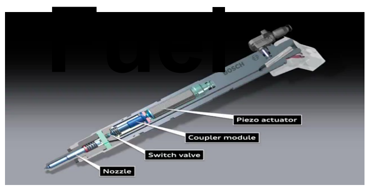
Piezoelectric properties of crystalline materials
- part I: physical principles, symmetry aspects

- introduction to piezoelectricity

- piezoelectricity and symmetry, Neumann principle

- tensor and matrix form for piezoelectric coefficients

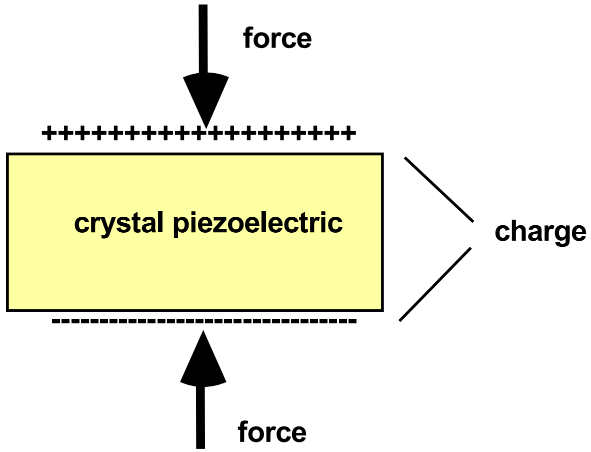
- calculating linear electromechanical response



Piezoelectricity

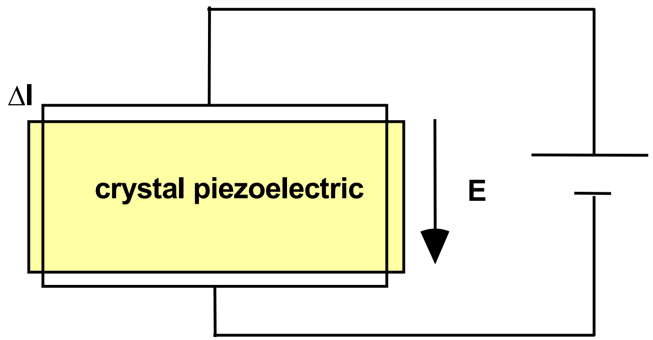
The direct piezoelectric effect:

Electrical charges are generated by mechanical pressure



The converse piezoelectric effect:

Mechanical deformation upon application of electric field



Linear relationships

“piezo” is derived from a Greek word for ”to press"; "piezoelectricity"---> electricity produced by pressure

The direct piezoelectric effect:

$$D = d_{direct}\ P$$

(Coulomb m^{-2}) = (C N^{-1}) (N m^{-2})

P- pressure, D- charge density

Converse effect:

$$x = d_{converse}\ E$$

(m m^{-1}) = (m V^{-1})(V m $^{-1}$)

E – electric field, x – relative deformation

With a help of thermodynamic arguments one can show that:

$$d_{direct} = d_{converse}$$

The direct effect is used for sensors.

The converse effect is used for actuators.

Piezoelectric response

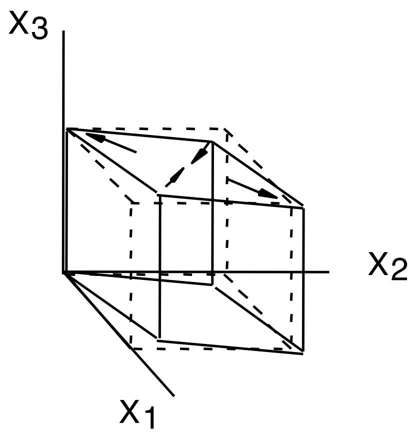
$$P_i = d_{ijk}\sigma_{jk} \quad \text{or} \quad D_i = d_{ijk}\sigma_{jk} \quad \text{at} \quad E_i = 0$$

Piezoelectric tensor
3rd rank, symmetric with respect to the last two suffixes

$$\boxed{d_{ijk} = d_{ikj}}$$

Electromechanical response

Strained crystal



strain → displacements of the charges of the material

Question:" Do these displacements lead to the appearance of polarization?"

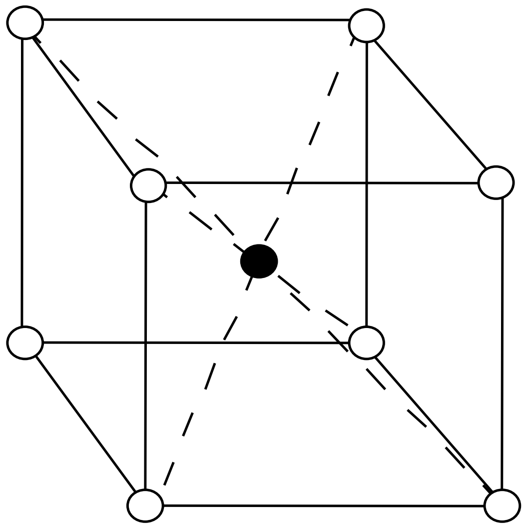
$$\vec{P} = \frac{\sum_i q_i \delta \vec{x}_i}{V}$$

"Is this sum not zero?""

Electromechanical response

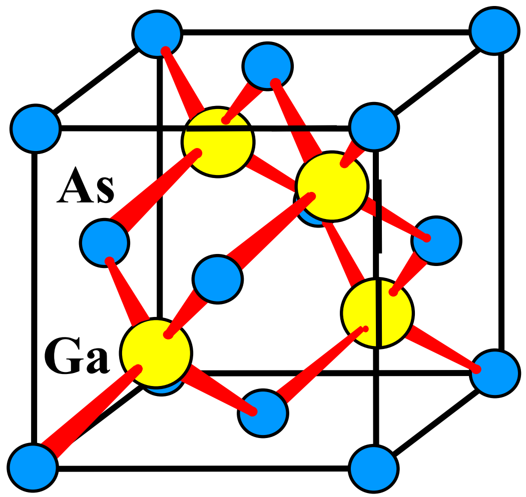
The answer depends on the structure of the material

The essential difference between these two structures: inversion center



$m\bar{3}m$

$$\vec{P} = \frac{\sum_i q_i \delta\vec{x}_i}{V} = 0$$



$\bar{4}3m$

$$\vec{P} = \frac{\sum_i q_i \delta\vec{x}_i}{V} \neq 0$$

Piezoelectric response: impact of symmetry

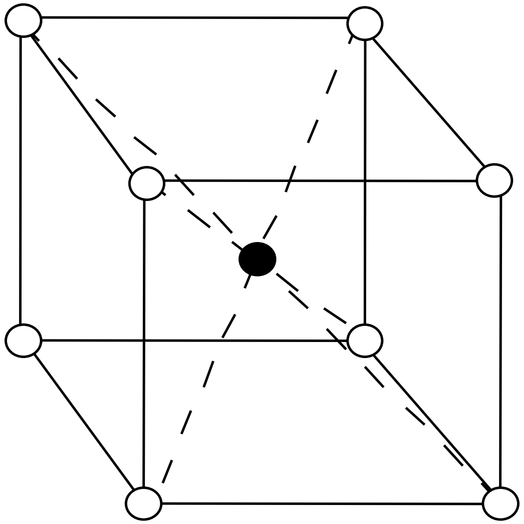
$$\boxed{d_{ijk} = d_{ikj}}$$

Neumann equations

$$d_{i'j'k'} = a_{i'i}(t_1)a_{j'j}(t_1)a_{k'k}(t_1)d_{ijk}$$
$$d_{i'j'k'} = a_{i'i}(t_2)a_{j'j}(t_2)a_{k'k}(t_2)d_{ijk}$$

and so on

Piezoelectric response – Neumann principle



$$m\bar{3}m$$

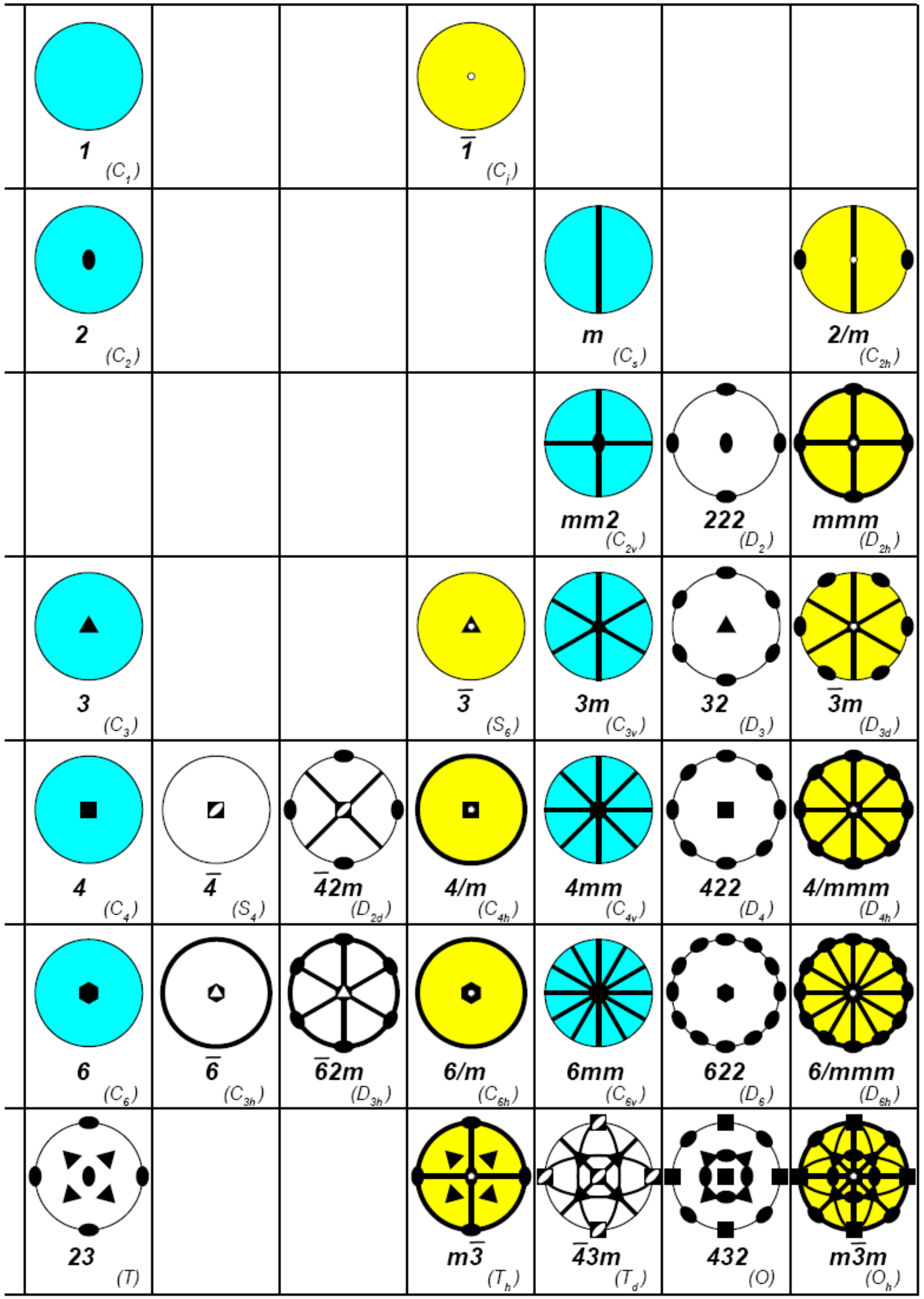
$$d_{i'j'k'} = a_{i'i}(t_1)a_{j'j}(t_1)a_{k'k}(t_1)d_{ijk}$$

t_1 - inversion

$$a_{ij}(t_1) = -\delta_{ij}$$

$$d_{i'j'k'} = -\delta_{i'i}\delta_{j'j}\delta_{k'k}d_{ijk} = -d_{i'j'k'} = 0$$

No piezoelectric effect!



Symmetry restrictions on piezoelectric effect

1. Forbidden for centrosymmetric structures:

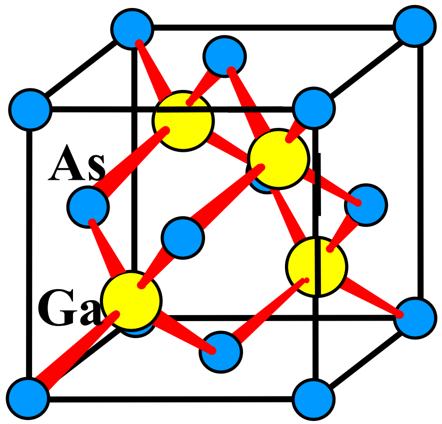
$$d_{ijk} \xrightarrow{\text{inversion}} -d_{ijk}$$

These two Curie groups are also centrosymmetric:

$$\infty\infty m \qquad \infty / mm$$

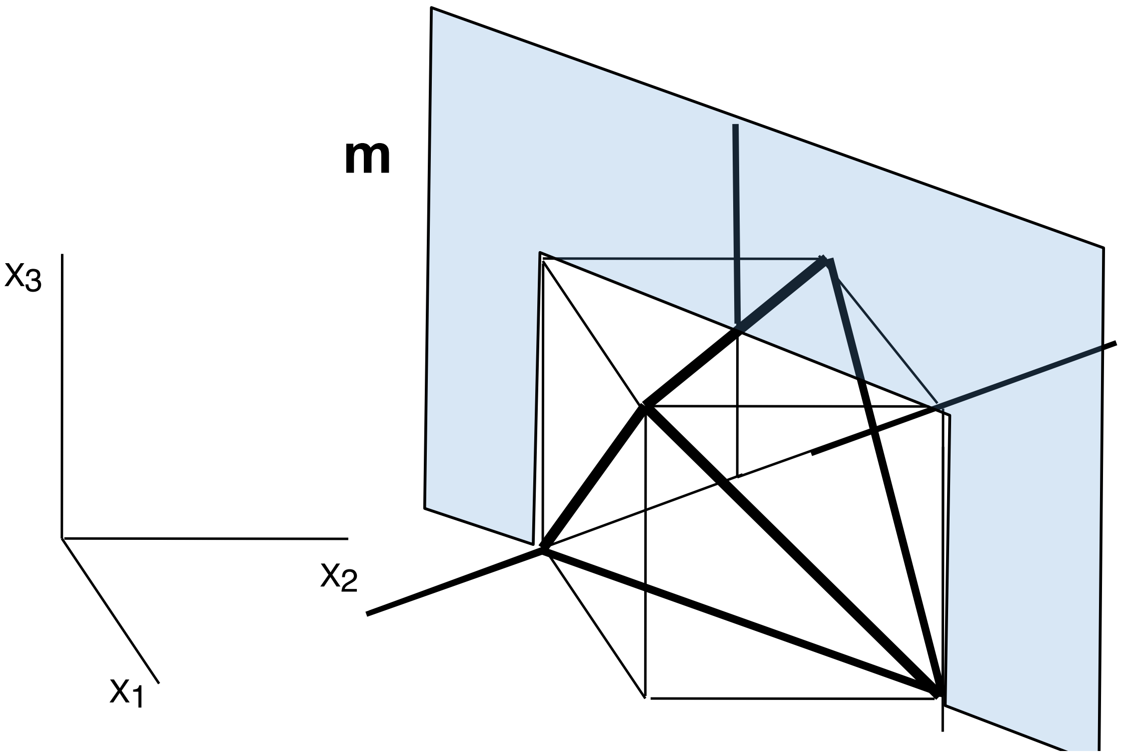
2. Allowed for non-centrosymmetric structures
except for 1 point group
and one Curie group (exercises)

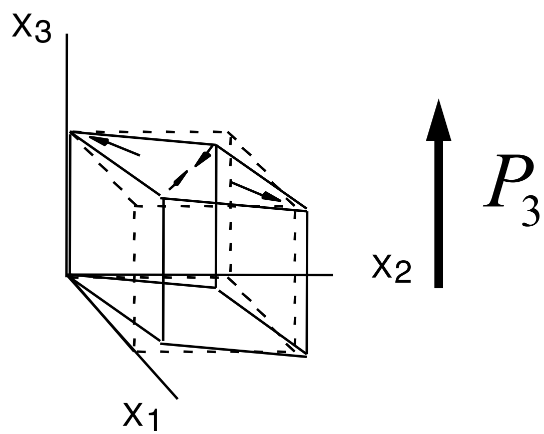
Piezoelectric response – Neumann principle



$\bar{4}3m$ symmetry of tetrahedron

$$d_{312} \qquad \sigma_{12} \Rightarrow P_3$$



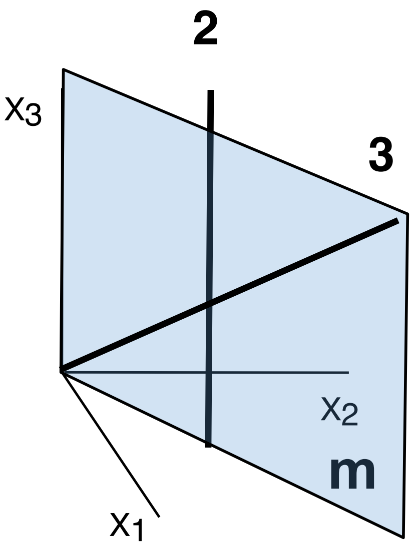


Show for this symmetry that the components $d_{xyz} = d$ if x,y,z are all different, and zero otherwise

- Check 3_{xyz}, 2_z, m_{xy} (others are obtained automatically)

$\bar{4}3m$

Piezoelectric response – Neumann principle



2

$$q_3' = q_3 \qquad 3 \to 3$$
$$q_2' = -q_2 \qquad 2 \to -2$$
$$q_1' = -q_1 \qquad 1 \to -1$$

3

$$q_3' = q_1 \qquad 1 \to 3$$
$$q_2' = q_3 \qquad 3 \to 2$$
$$q_1' = q_2 \qquad 2 \to 1$$

m

$$q_3' = q_3 \qquad 3 \to 3$$
$$q_2' = q_1 \qquad 1 \to 2$$
$$q_1' = q_2 \qquad 2 \to 1$$

$\bar{4}3m$

Piezoelectric response – Neumann principle

Test for d_{312}

2

$$3 \to 3$$
$$2 \to -2$$
$$1 \to -1$$

$$d_{312} \to d_{312}$$

m

$$3 \to 3$$
$$1 \to 2$$
$$2 \to 1$$

$$d_{312} \to d_{321}$$

Works for: $d_{ijk} = d_{ikj}$

Piezoelectric response – Neumann principle

$\bar{4}3m$

Test d_{312}

3

$$3 \rightarrow 2$$
$$1 \rightarrow 3$$
$$2 \rightarrow 1$$

$$d_{312} \rightarrow d_{231}$$

3

$$3 \rightarrow 2$$
$$1 \rightarrow 3$$
$$2 \rightarrow 1$$

$$d_{231} \rightarrow d_{123}$$

3

$$3 \rightarrow 2$$
$$1 \rightarrow 3$$
$$2 \rightarrow 1$$

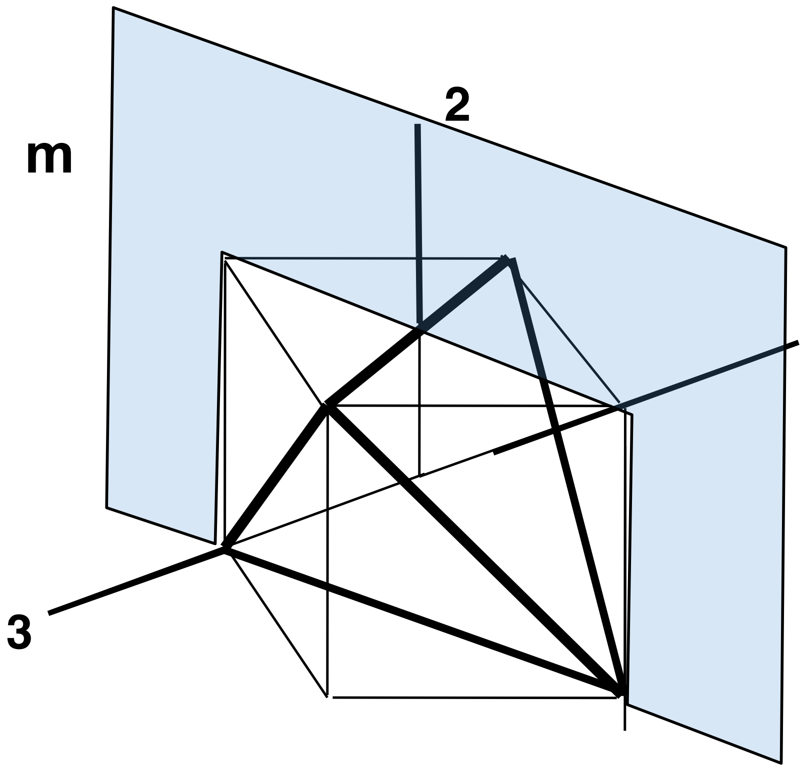
$$d_{123} \rightarrow d_{321} = d_{312}$$

Works for

$d_{312} = d_{231} = d_{123}$

Piezoelectric response – Neumann principle

$\bar{4}3m$

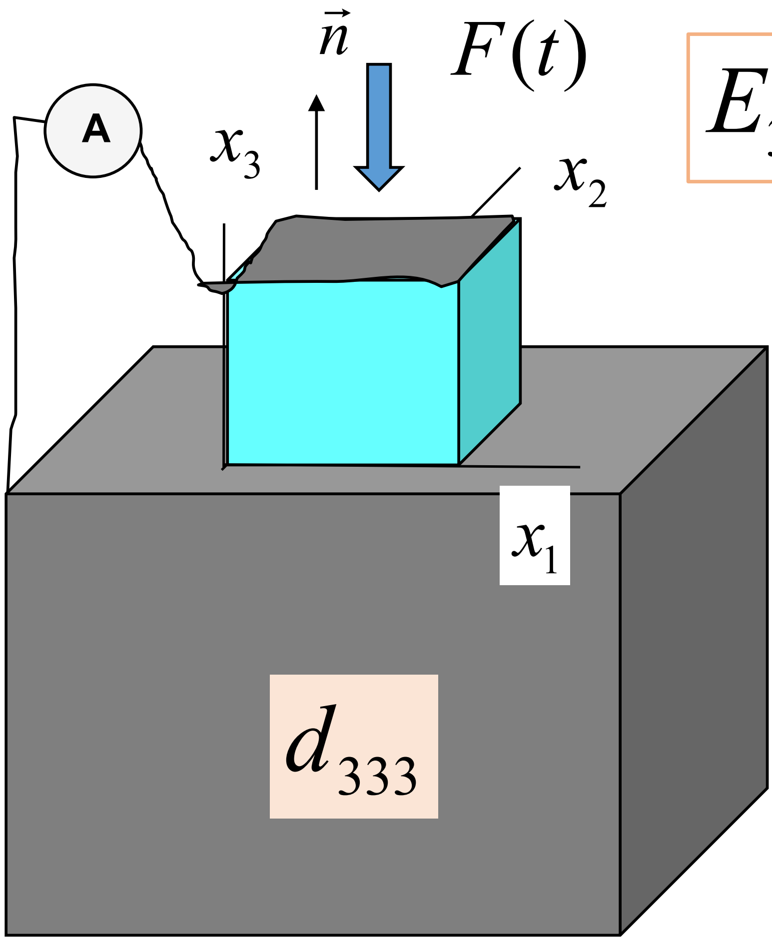


$d_{312} = d_{231} = d_{123}$

2

$d_{112} = d_{221} = \ldots\ldots = 0$

Measurement of piezoelectric tensor components



$$\boxed{E_3 = 0}$$

$$F(t) = F_0 \sin \omega t$$

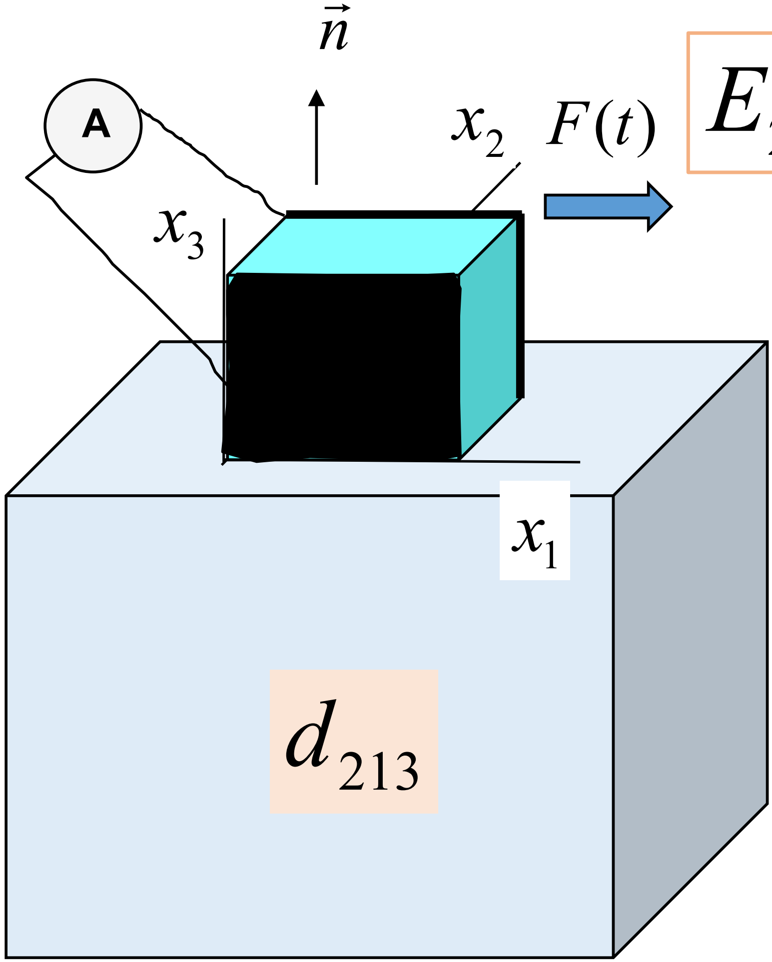
$$\vec{n} = \begin{pmatrix} 0 & 0 & 1 \end{pmatrix} \qquad \vec{F} = \begin{pmatrix} 0 & 0 & F \end{pmatrix}$$

$$\frac{F_i}{S} = \sigma_{ij} n_j \qquad \sigma_{33} = \frac{F}{S}$$

$$D_i = d_{ijk} \sigma_{jk}$$

$$I(t) = \frac{dQ}{dt} = S \frac{dD_3(t)}{dt} = S d_{333} \frac{d\sigma_{33}(t)}{dt} = d_{333} \frac{dF(t)}{dt}$$

Measurement of piezoelectric tensor components: d_{213}



$$\boxed{E_2 = 0}$$

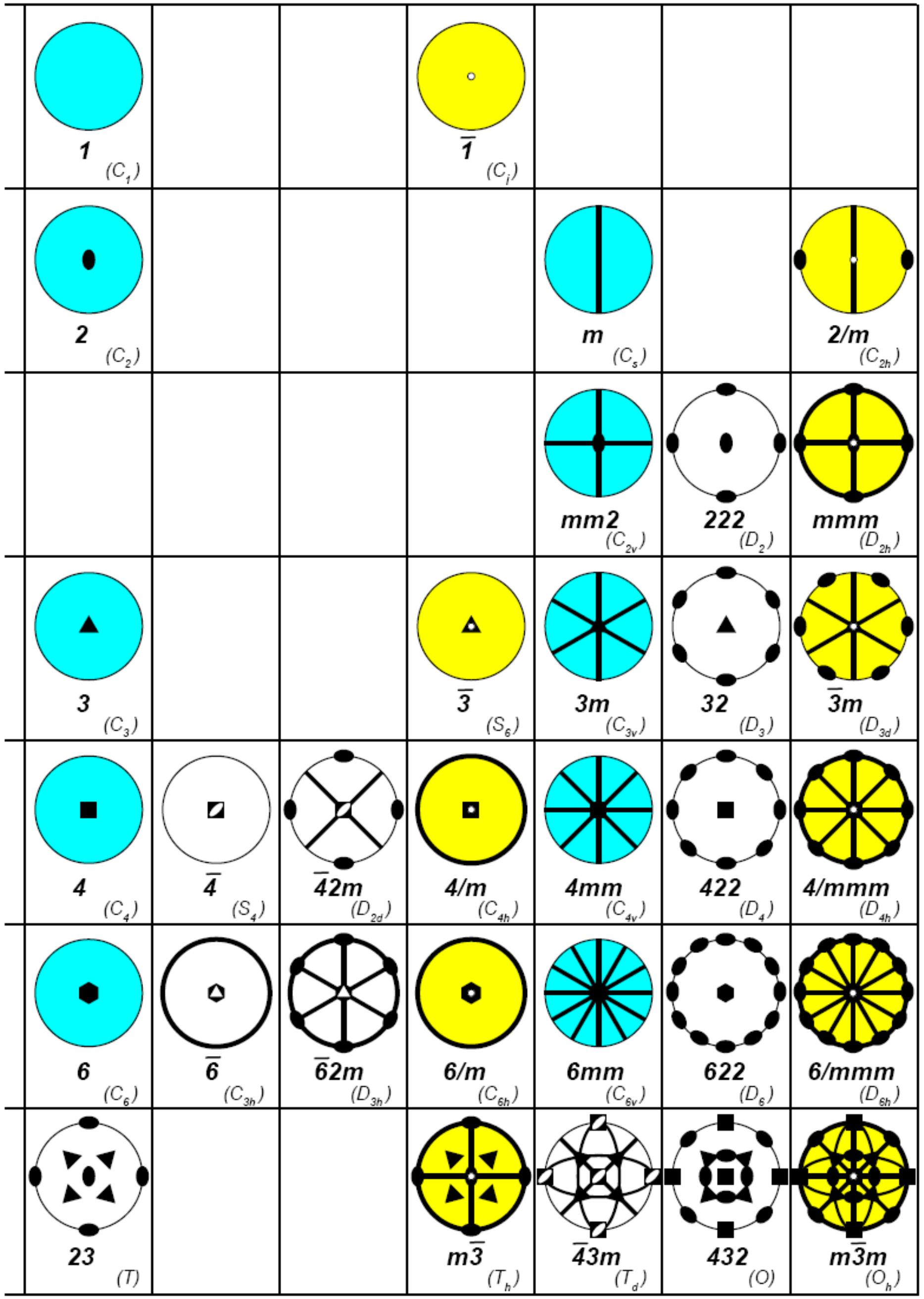
$$F(t) = F_0 \sin \omega t$$

$$\vec{n} = \begin{pmatrix} 0 & 0 & 1 \end{pmatrix} \qquad \vec{F} = \begin{pmatrix} F & 0 & 0 \end{pmatrix}$$

$$\frac{F_i}{S} = \sigma_{ij} n_j \qquad \sigma_{13} = \frac{F}{S}$$

$$D_i = d_{ijk} \sigma_{jk}$$

$$I(t) = \frac{dQ}{dt} = S \frac{dD_2(t)}{dt} = S d_{213} \frac{d\sigma_{13}(t)}{dt} = d_{213} \frac{dF(t)}{dt}$$



Symmetry restrictions on piezoelectric effect

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These two Curie groups are also centrosymmetric:

$$\infty\infty m \qquad \infty/mm$$

2. Allowed for non-centrosymmetric structures except for

$$432 \quad \text{and} \quad \infty\infty$$

Matrix description (Voigt notations) for elasticity

Stress tensor

$$\begin{pmatrix} \sigma_{11} & \sigma_{12} & \sigma_{13} \\ & \sigma_{22} & \sigma_{23} \\ & & \sigma_{33} \end{pmatrix} \Rightarrow \begin{pmatrix} \sigma_1 \\ \sigma_2 \\ \sigma_3 \\ \sigma_4 \\ \sigma_5 \\ \sigma_6 \end{pmatrix}$$

Strain tensor

$$\begin{pmatrix} \varepsilon_{11} & \varepsilon_{12} & \varepsilon_{13} \\ & \varepsilon_{22} & \varepsilon_{23} \\ & & \varepsilon_{33} \end{pmatrix} \Rightarrow \begin{pmatrix} \varepsilon_1 \\ \varepsilon_2 \\ \varepsilon_3 \\ \varepsilon_4 = 2\varepsilon_{23} \\ \varepsilon_5 = 2\varepsilon_{13} \\ \varepsilon_6 = 2\varepsilon_{12} \end{pmatrix}$$

$$\sigma_{ij} = c_{ijkl}\varepsilon_{kl}$$

$$\varepsilon_{ij} = s_{ijkl}\sigma_{kl}$$

$$\sigma_n = c_{nm}\varepsilon_m$$

$$\varepsilon_n = s_{nm}\sigma_m$$

Matrix description: piezoelectricity

$$P_i = d_{ijk}\sigma_{jk}$$

Stress tensor

$$\begin{pmatrix} \sigma_{11} & \sigma_{12} & \sigma_{13} \\ & \sigma_{22} & \sigma_{23} \\ & & \sigma_{33} \end{pmatrix} \Rightarrow \begin{pmatrix} \sigma_1 \\ \sigma_2 \\ \sigma_3 \\ \sigma_4 \\ \sigma_5 \\ \sigma_6 \end{pmatrix}$$

Polarization

$$\begin{pmatrix} P_1 \\ P_2 \\ P_3 \end{pmatrix}$$

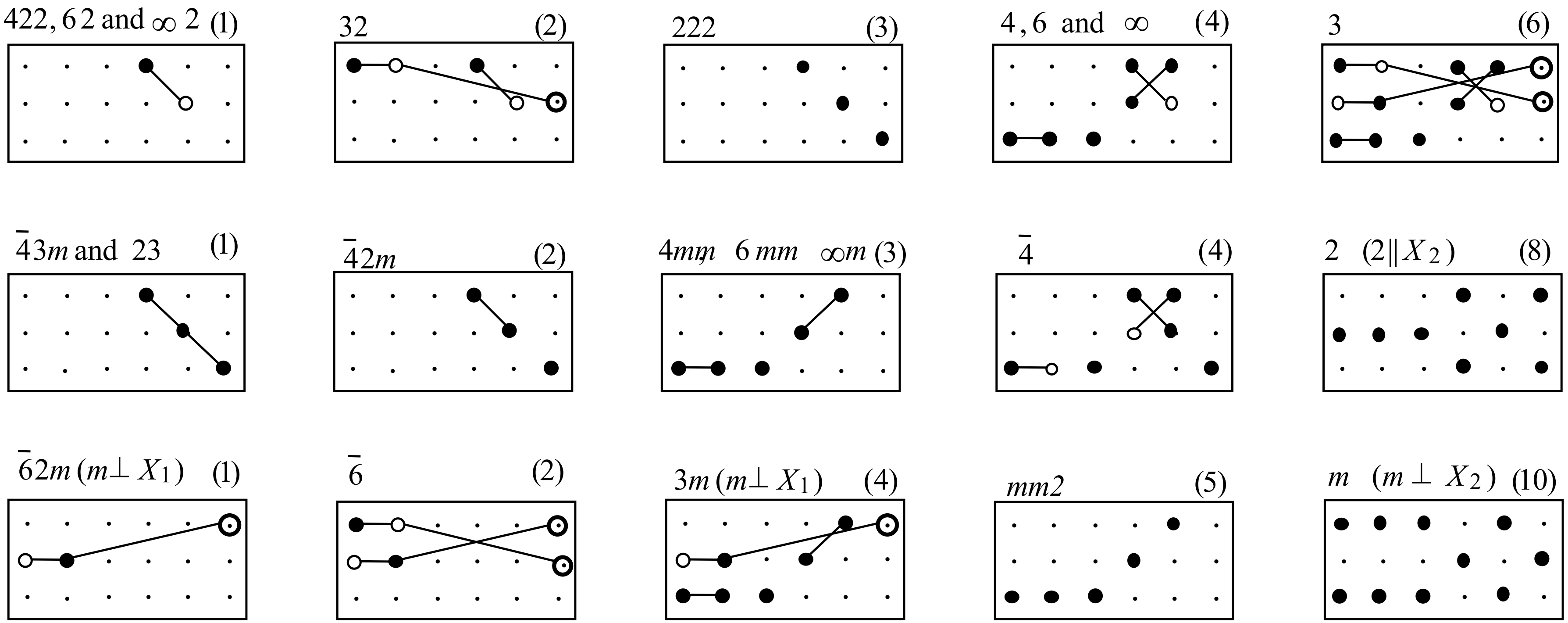
$$\begin{pmatrix} P_1 \\ P_2 \\ P_3 \end{pmatrix} = \begin{pmatrix} d_{11} & d_{12} & d_{13} & d_{14} & d_{15} & d_{16} \\ d_{21} & d_{22} & d_{23} & d_{24} & d_{25} & d_{26} \\ d_{31} & d_{32} & d_{33} & d_{34} & d_{35} & d_{36} \end{pmatrix} \begin{pmatrix} \sigma_1 \\ \sigma_2 \\ \sigma_3 \\ \sigma_4 \\ \sigma_5 \\ \sigma_6 \end{pmatrix}$$

Matrix description

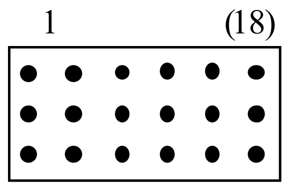
$$
\begin{pmatrix}
d_{11} & d_{12} & d_{13} & d_{14} & d_{15} & d_{16} \\
d_{21} & d_{22} & d_{23} & d_{24} & d_{25} & d_{26} \\
d_{31} & d_{32} & d_{33} & d_{34} & d_{35} & d_{36}
\end{pmatrix}
$$

$$
= \begin{pmatrix}
d_{111} & d_{122} & d_{133} & 2d_{123} & 2d_{113} & 2d_{112} \\
d_{211} & d_{222} & d_{233} & 2d_{223} & 2d_{213} & 2d_{212} \\
d_{311} & d_{322} & d_{333} & 2d_{323} & 2d_{313} & 2d_{312}
\end{pmatrix}
$$

d tensor for all symmetries



centrosymmetric, 432, and ∞∞ $d_{ijk} = 0$

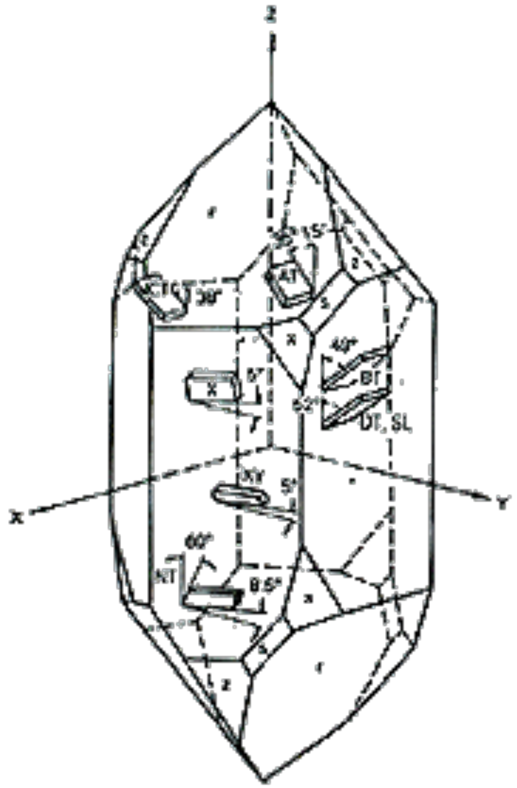


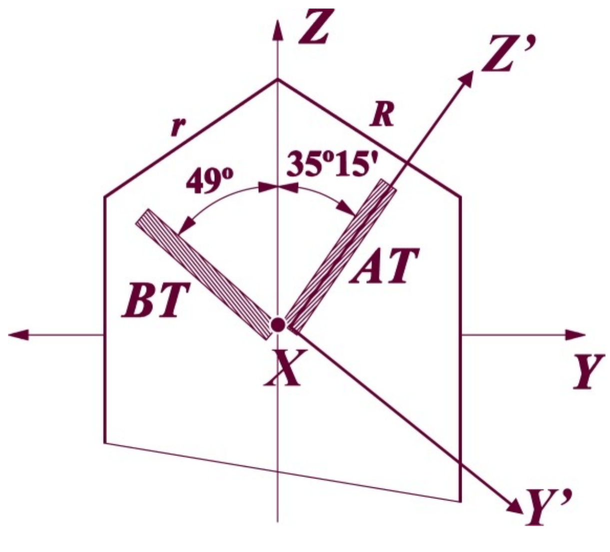
zero component, non-zero component, components numerically equal

a component equal to <u>minus</u> 2 times the heavy dot component to which it is joined

components numerically equal, but opposite in sign

Example- Quartz





Quartz is used for frequency and time standards

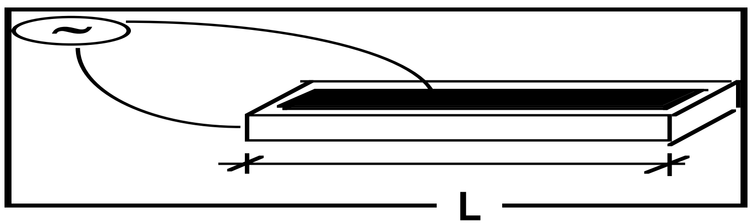
- **There are nearly zero temperature coefficient cuts**
- **High quality factor (low loss)**
- **inexpensive**

The piezoelectric resonance

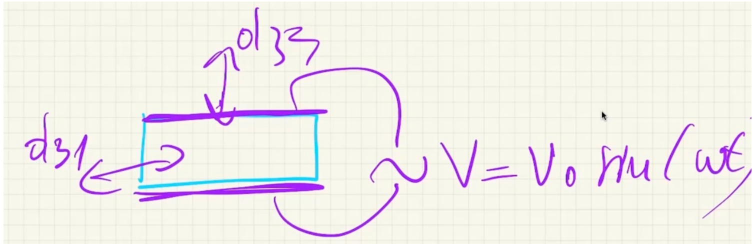
- If a piezoelectric samples is covered with electrodes and connected to an alternating voltage, the sample will vibrate

- If the frequency of oscillation of the field is equal to the frequency of the mechanical resonance of the sample, the elastic vibrations become very large.

- Thus, a mechanical resonance is induced in a piezoelectric sample by the converse piezoelectric effect.



Piezoelectric resonance

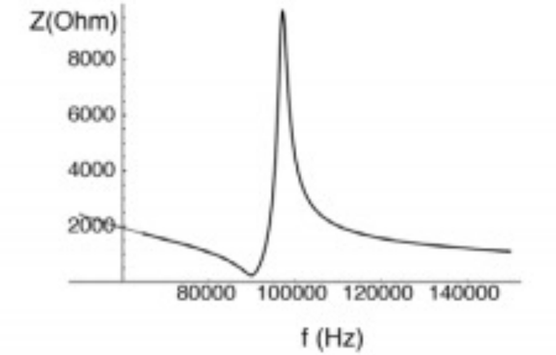


- The frequency of the longitudinal mode of vibration

$$f = \frac{1}{2L\sqrt{\rho/E}}$$

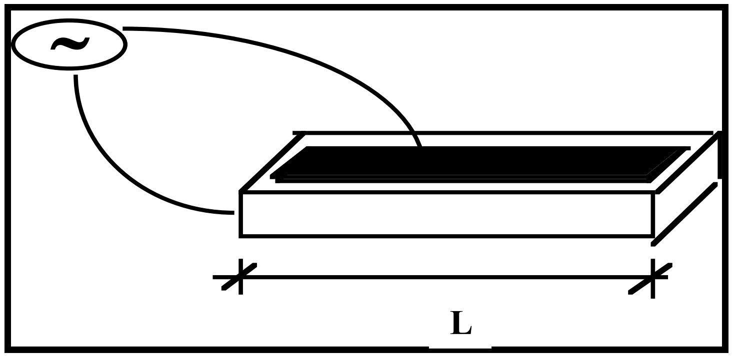
where E is Young modulus and ρ is the density of the material**,** L- dimension

- **d31 – f $\propto$ 1/L (lenth)**
- **d33 – f $\propto$ 1/t (thickness)**



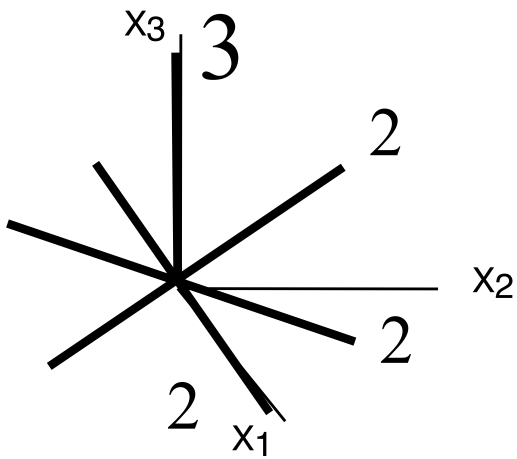
PZT coefficients:
ρ= 7.6 g/cm^3
S_{11}=1/E=1.5E-11 ms^2/kg

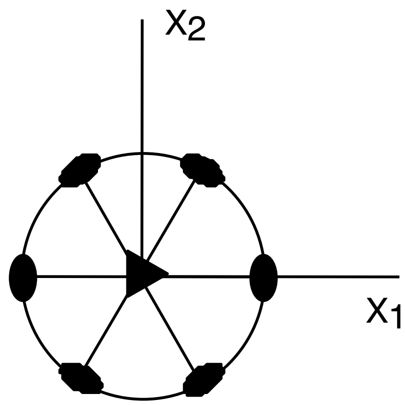
Due to excellent thermal stability of its mechanical properties, quartz single crystals are used for frequency control and related applications (filters, time measurements…)

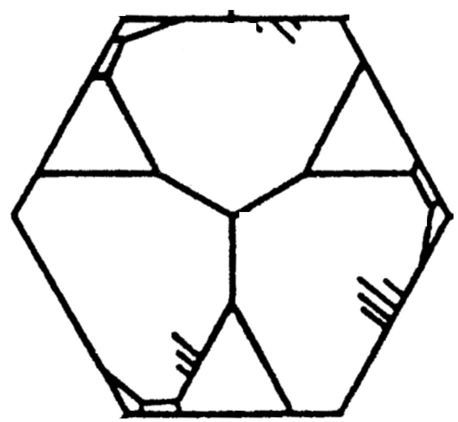


Example- Quartz

SiO_2 32 **non-centrosymmetric , non-polar**







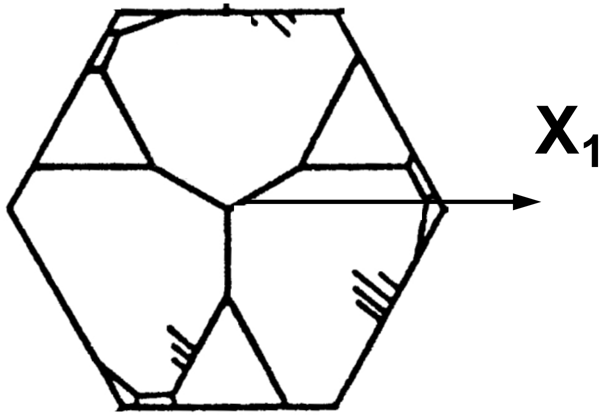
Right

Right-handed quartz is more common in nature
Industry has standardized the use of right-handed quartz to maintain consistency in crystal-cutting, oscillator behavior, and frequency response

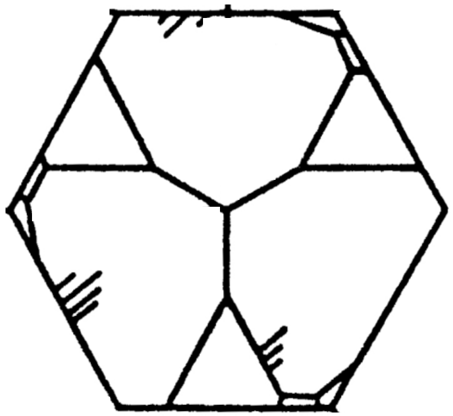
Example- Quartz

Piezocoefficients (piezomoduli)

$$
\begin{array}{c|cccccc}
 & \sigma_1 & \sigma_2 & \sigma_3 & \sigma_4 & \sigma_5 & \sigma_6 \\
P_1 & d_{11} & -d_{11} & 0 & d_{14} & 0 & 0 \\
P_2 & 0 & 0 & 0 & 0 & -d_{14} & -2d_{11} \\
P_3 & 0 & 0 & 0 & 0 & 0 & 0
\end{array}
$$



Right



Left

Linked by reflection by the pane normal to X_1

$$
\begin{pmatrix} 2.3 & -2.3 & 0 & 0.67 & 0 & 0 \\ 0 & 0 & 0 & 0 & -0.67 & 4.6 \\ 0 & 0 & 0 & 0 & 0 & 0 \end{pmatrix}
\quad
\begin{pmatrix} -2.3 & 2.3 & 0 & -0.67 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0.67 & -4.6 \\ 0 & 0 & 0 & 0 & 0 & 0 \end{pmatrix}
\quad
\left[\frac{pC}{N}\right]
$$

Example- Quartz

How strong is the effect?

$$P_1 = d_{11}\sigma_1$$

$$d_{11} = 2.3\times 10^{-12} C/N$$

$$P_1 = \varepsilon_0(K_{11}-1)E_1$$

$$K_{11} = 4.5$$

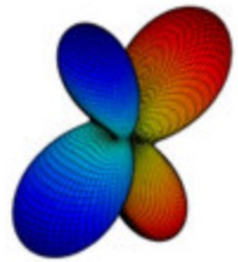
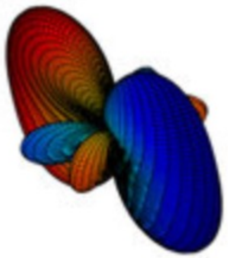
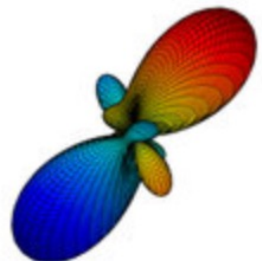
$$\sigma_1 = 2\ \mathrm{kg/cm^2}$$

equivalent to

$$E_1 = d_{11}\sigma_1/\varepsilon_0(K_{11}-1) \approx 150\ \mathrm{V/cm}$$

Anisotropy of piezoelectric effect

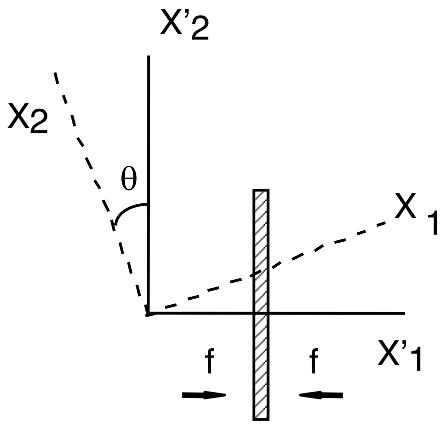
longitudinal piezoelectric modulus in 3D

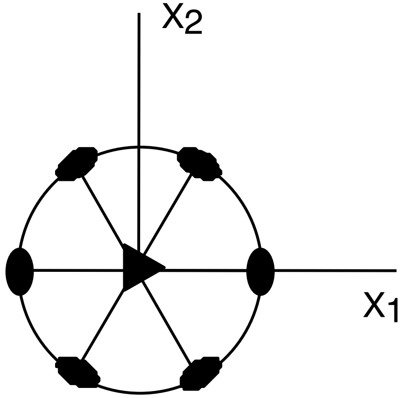
Orthorhombic	222	$\begin{pmatrix} 0 & 0 & 0 & e_{14} & 0 & 0 \\ 0 & 0 & 0 & 0 & e_{25} & 0 \\ 0 & 0 & 0 & 0 & 0 & e_{36} \end{pmatrix}$	
Monoclinic	m	$\begin{pmatrix} e_{11} & e_{12} & e_{13} & 0 & e_{15} & 0 \\ 0 & 0 & 0 & e_{24} & 0 & e_{26} \\ e_{31} & e_{32} & e_{33} & 0 & e_{35} & 0 \end{pmatrix}$	
Monoclinic	2	$\begin{pmatrix} 0 & 0 & 0 & e_{14} & 0 & e_{16} \\ e_{21} & e_{22} & e_{23} & 0 & e_{25} & 0 \\ 0 & 0 & 0 & e_{34} & 0 & e_{36} \end{pmatrix}$	
Triclinic	1	$\begin{pmatrix} e_{11} & e_{12} & e_{13} & e_{14} & e_{15} & e_{16} \\ e_{21} & e_{22} & e_{23} & e_{24} & e_{25} & e_{26} \\ e_{31} & e_{32} & e_{33} & e_{34} & e_{35} & e_{36} \end{pmatrix}$	

http://www.nature.com/articles/sdata201553/figures/3

Anisotropy of piezoelectric effect

Let us find effective longitudinal piezoelectric coefficient





- cut from the crystal a sample with faces parallel to X_3
- force perpendicular to the faces
- Rotation axis - X_3:

$$\begin{bmatrix} \cos\theta & -\sin\theta & 0 \\ \sin\theta & \cos\theta & 0 \\ 0 & 0 & 1 \end{bmatrix}$$

$$P_1' = d_{111}'\sigma_{11}'$$

- **Find the angular dependence of d_{111}**

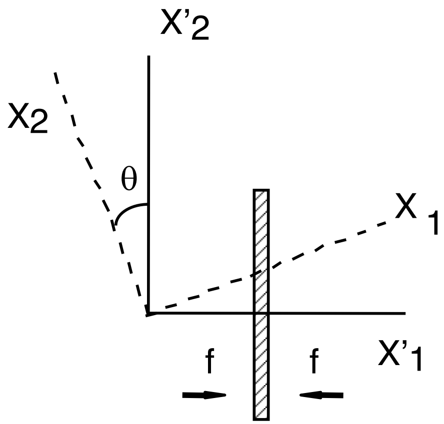
This is the tensor to be transformed:

	σ_1	σ_2	σ_3	σ_4	σ_5	σ_6
P_1	d_{11}	$-d_{11}$	0	d_{14}	0	0
P_2	0	0	0	0	$-d_{14}$	$-2d_{11}$
P_3	0	0	0	0	0	0

- Way to proceed: apply the vector component transformation in the form: ***pqq***

Anisotropy of piezoelectric effect

Let us find effective longitudinal piezoelectric coefficient



$$P_1' = d_{111}' \sigma_{11}'$$

$$\begin{bmatrix} \cos\theta & -\sin\theta & 0 \\ \sin\theta & \cos\theta & 0 \\ 0 & 0 & 1 \end{bmatrix}$$

$$P_1' = P_1 \cos\theta - P_2 \sin\theta$$

$$d'_{111}$$

$$p'_1 (q'_1)^2 = (p_1 \cos\theta - p_2 \sin\theta)(q_1^2 \cos^2\theta + q_2^2 \sin^2\theta - 2 q_1 q_2 \cos\theta \sin\theta)$$

Anisotropy of piezoelectric effect

$$p'_1(q'_1)^2 = p_1 q_1^2 \cos^3\theta + p_1 q_2^2 \cos\theta \sin^2\theta$$

$$-2 p_1 q_1 q_2 \cos^2\theta \sin\theta - p_2 q_1^2 \cos^2\theta \sin\theta$$

$$- p_2 q_2^2 \sin^3\theta + 2 p_2 q_1 q_2 \sin^2\theta \cos\theta$$

$$d'_{111} = d_{111}\cos^3\theta + d_{122}\cos\theta\sin^2\theta$$

$$\cancel{-2d_{112}\cos^2\theta\sin\theta}\ \cancel{-d_{211}\cos^2\theta\sin\theta}$$

$$\cancel{-d_{222}\sin^3\theta} + 2d_{212}\sin^2\theta\cos\theta$$

	σ_1	σ_2	σ_3	σ_4	σ_5	σ_6
P_1	d_{11}	$-d_{11}$	0	d_{14}	0	0
P_2	0	0	0	0	$-d_{14}$	$-2d_{11}$
P_3	0	0	0	0	0	0

$d_{111} \equiv d_{11}$

$d_{122} \equiv d_{12} = -d_{11}$

$d_{112} \equiv d_{16} = 0$

$d_{211} \equiv d_{21} = 0$

$d_{222} \equiv d_{22} = 0$

$d_{212} \equiv 0.5 d_{26} = 0.5(-2d_{11}) = -d_{11}$

$$d'_{111} = d_{11}(\cos^3\theta - 3\cos\theta\sin^2\theta)$$

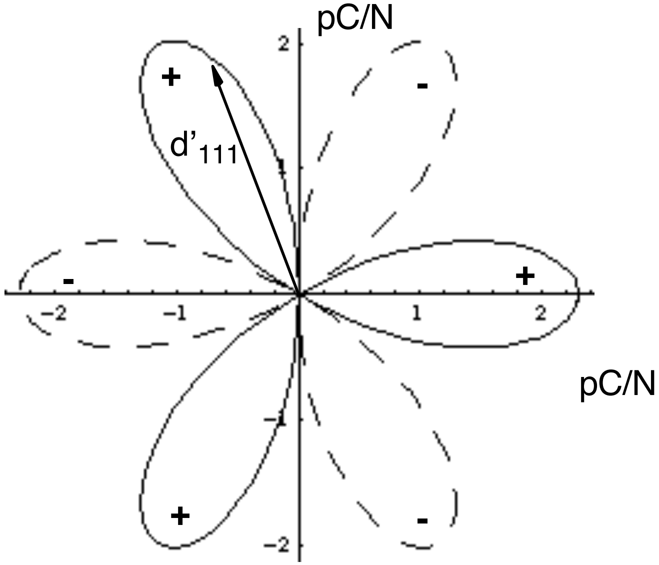
$$= d_{11}\cos 3\theta$$

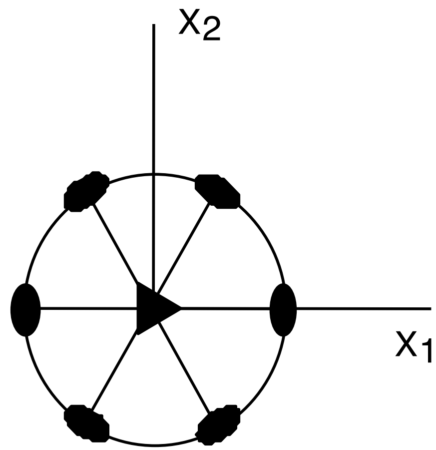
Anisotropy of piezoelectric effect

Quartz

$d_{11} = 2.3\,\mathrm{pC/N}$

$$d'_{11} = d_{11}\cos 3\theta$$





Electrostriction

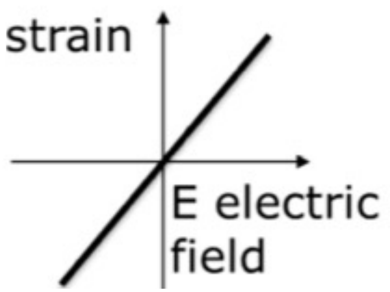
Can we expect any electromechanical coupling in general case, for all materials (even if centro-symmetrical)?

- **Yes, however the effect is quadratic (not linear like piezoelectricity)**

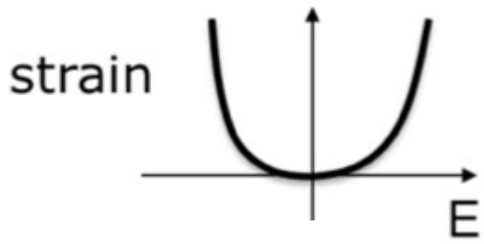
$$\varepsilon_{ij} = Q_{ijkl} P_k P_l$$

- Normally this effect is weaker than piezoelectricity
- The strain sign is independent of the voltage/field polarity!

Piezoelectricity



Electrostriction



Conclusions for piezoelectricity: part - I

1. The piezoelectric response can be successfully treated with the Neumann principle.

2. The 3rd–rank tensor which controls the piezoelectric effect is sensitive the presence of the inversion in the point group → piezoelectricity is forbidden in centrosymmetric materials.

3. Tensor and matrix forms are used for description of piezoelectric response