Lecture 14 (26-27 May 2025)

- Review and summary of the course
- Some questions/answers
- Practical issues / exam

Q&A before the exam: Monday 16.06, 14:00, ELB 328
Exam: 17.06, 9:15

Semaine du 16.06.2025 au 22.06.2025

	Lu	Ma	M
8h - 9h			
9h - 10h		**Crystalline materials: structures and properties** GCA330 (MSE-306) Ecrit	
10h - 11h		**Crystalline materials: structures and properties** GCA330 (MSE-306) Ecrit	
11h - 12h		**Crystalline materials: structures and properties** GCA330 (MSE-306) Ecrit	

Written exam: duration - 3h, “open book”: all printed/handwritten materials are permitted, simple calculator recommended, **smartphones/laptops/tablettes and other electronic devices are not allowed**

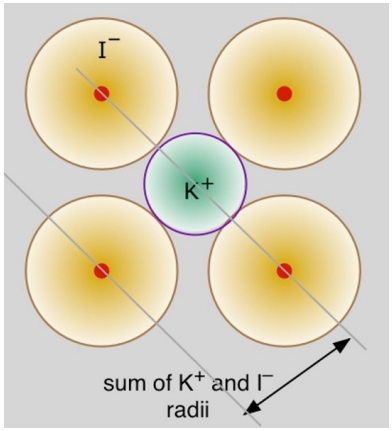
Main topics addressed in the course

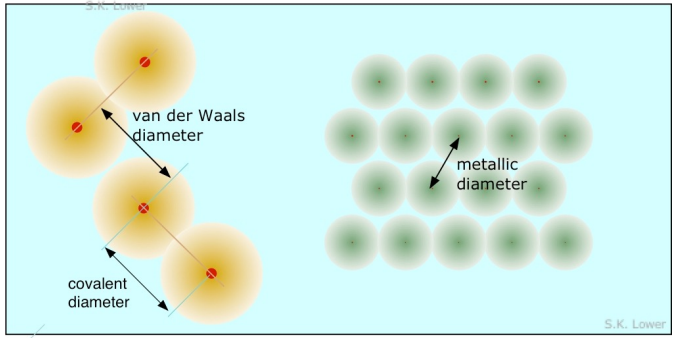
- Crystalline structures, bonds, symmetry
- Tensors: a tool for analysis of anisotropic properties
- Equilibrium properties of materials:
  - dielectric, elastic, piezoelectric, thermoelectric responses
  - Cross-coupled phenomena - thermo-electro-mechanics
- Transport properties of materials: thermal & electric transport
- Defects in crystalline materials – in relation with properties
- Phase transitions – in relationship with symmetry and properties
- Static vs. Dynamic response (dielectric and mechanic response)
- Applications (electronics, sensors, actuators…)
- Relation with current topics of interest – examples, devices, publications…

Bonds and structures

Key concepts:

- Atomic/ionic radii (changes vs type of bond, charge state)





Reference: shannon-prewitt_crystal_radius

- Covalent structure: directional bonds, configuration of orbitals for valent electrons is needed
- Ionic structure: coulomb interaction (omnidirectional)

2 ions:

$$E_{bond}(r_0) = -\frac{e^2 Z_1 Z_2}{4\pi\varepsilon_0 r_0}\left(1-\frac{1}{n}\right) \qquad E_{lattice}(r_0) = -\frac{N_A e^2 Z_1 Z_2 \alpha}{4\pi\varepsilon_0 r_0}\left(1-\frac{1}{n}\right)$$

- other types of bonding: metallic, VdW, hydrogen bonds

Question: Bonds and structures

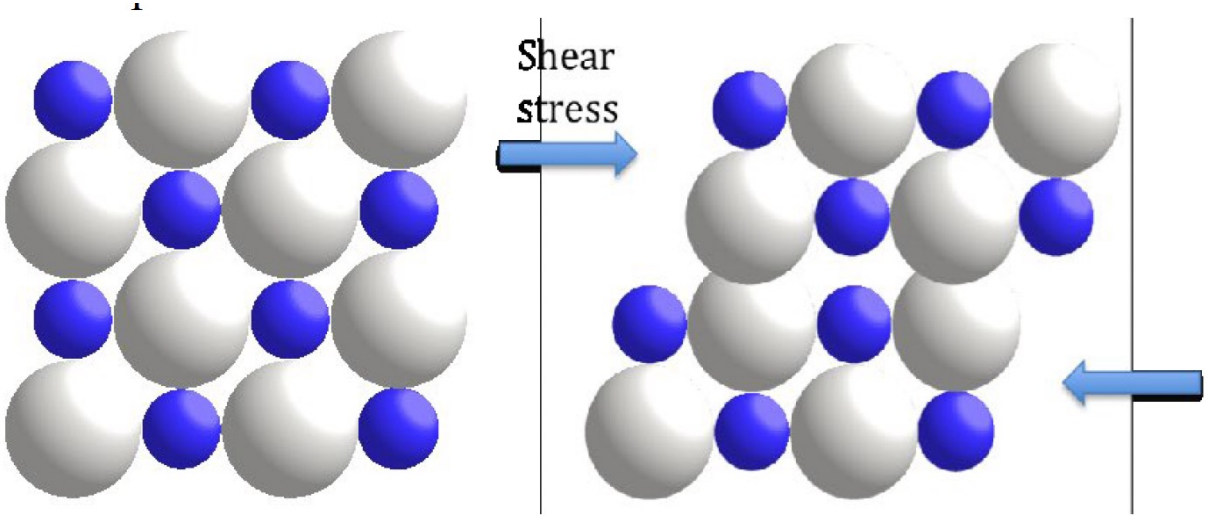
Why is Cu ductile, while MgO is brittle?

Question: Bonds and structures

Why is Cu ductile, while MgO is brittle?

Ductility in metals occurs the process of slip. Slip occurs along the close-packed planes by sliding one plane of atoms past the other; this process occurs when the bonding is metallic, as this bonding is non-directional. (Cu is an FCC metal, wherein the close – packed planes are the {111} family of planes).

In contrast, MgO is a ceramic. In most orientations, if one plane of atoms tried to slip past another, like charges would be brought into contact, as shown in the figure below. The resulting high energy penalty would result in the material failing in a brittle fashion, rather than slip.



Summary: Bonds and structures

Ionic structures: effect of ion size and valence:

- hardness
- melting point
- thermal dilatation

Example: hardness vs. size and valence

	BeO	MgO	CaO	SrO	BaO	
Distance (Å)	1.65	2.10	2.40	2.57	2.77	size
Hardness	9.0	6.5	4.5	3.5	3.3	

	NaF (1)	MgO (2)	ScN (3)	TiC (4)	
Distance (Å)	2.31	2.10	2.23	2.23	valence
Hardness	3.0	6.5	7-8	8-9	

Prediction of ionic structures: Pauling rules

Arguments involve ionic radii, ionic valence and electrostatic forces among ions

- **Rule 1: Each cation is surrounded by a polyhedron of anions. The coordination number of cation is determined by the ratio of radius of cation and anion (r_{cation}/r_{anion}).**

CN	Arrangement of ions	Radio of cation/anion radii
12	cuboctahedral	>1
8	cubic	>0.732
6	octahedral	>0.414
4	tetrahedral	>0.225

- **Rule 2: In a stable structure, the sum of the bond strengths to an anion is equal to anion's valence (preservation of neutrality).** Bond strength =Valence of cation/cation coordination number
- **Rule 3**: The bond is strongest when coordination polyhedra share corners, less stable when they share edges, and least stable when they share faces.
- **Rule 4**: Coordination polyhedra of small cations with large charge tend to share corners (or not share any elements
- **Rule 5**: Simpler structures are more likely than complex (the rule of parsimony)

Crystalline symmetry basics

Key elements and concepts:

- Unit cell
- Crystalline lattice
- Translation vectors
- Bravais lattice
- **Symmetry operations**

Notations:

- Symmetry operations
- Miller indices, planes, directions
- Equivalent directions/planes

Graphic representation of 3D directions on 2D – Stereographic projection

Symmetry operations:

Space groups

Point groups

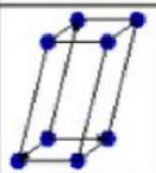
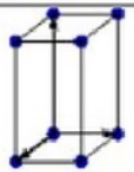
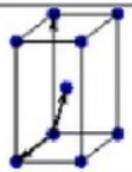
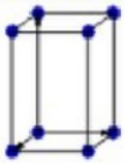
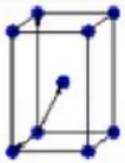
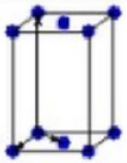
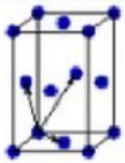
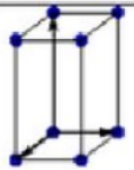
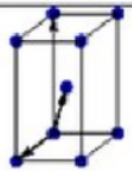
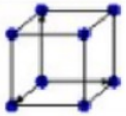
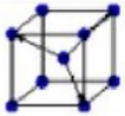
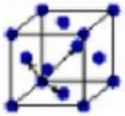
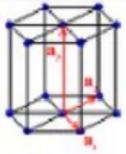
Curie groups

Minimum operations set vs full set

Understand!

Check exercises! Determination of the point group of objects/lattices

Crystalline symmetry basics: types of Bravais lattices

Bravais lattice	Parameters	Simple (P)	Volume centered (I)	Base centered (C)	Face centered (F)
Triclinic	$a_1 \neq a_2 \neq a_3$ $\alpha_{12} \neq \alpha_{23} \neq \alpha_{31}$				
Monoclinic	$a_1 \neq a_2 \neq a_3$ $\alpha_{23} = \alpha_{31} = 90°$ $\alpha_{12} \neq 90°$				
Orthorhombic	$a_1 \neq a_2 \neq a_3$ $\alpha_{12} = \alpha_{23} = \alpha_{31} = 90°$				
Tetragonal	$a_1 = a_2 \neq a_3$ $\alpha_{12} = \alpha_{23} = \alpha_{31} = 90°$				
Trigonal	$a_1 = a_2 = a_3$ $\alpha_{12} = \alpha_{23} = \alpha_{31} < 120°$				
Cubic	$a_1 = a_2 = a_3$ $\alpha_{12} = \alpha_{23} = \alpha_{31} = 90°$				
Hexagonal	$a_1 = a_2 \neq a_3$ $\alpha_{12} = 120°$ $\alpha_{23} = \alpha_{31} = 90°$				

Bravais lattice:

- Built on translation vectors
- Disregards atomic pattern (motif)
- Symmetry groups are classified based on 7 types of lattices
- Anisotropic properties and tensor structures are conveniently classified based on 7 types of lattice

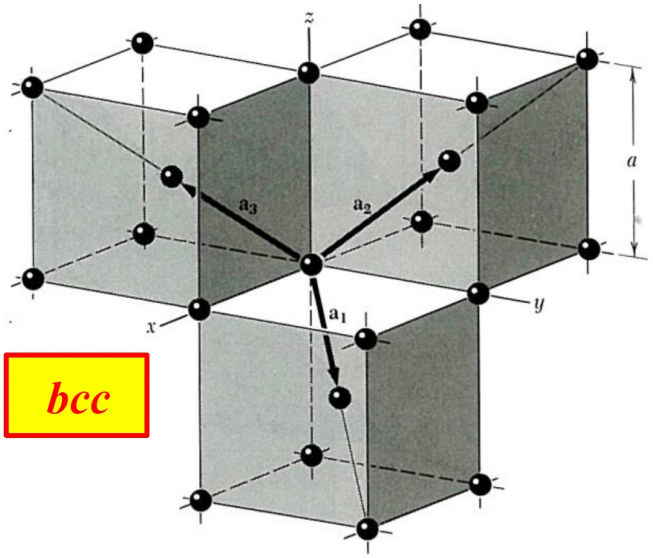
Crystalline symmetry basics: types of Bravais lattices

Question: are the edges of cells of Bravais lattice shown in previous slides always correspond to primitive vectors of translation?

Crystalline symmetry basics: types of Bravais lattices

Question: are the edges of cells of Bravais lattice shown in previous slides always correspond to primitive vectors of translation?

Answer: No! (look at non-primitive Bravais lattices)



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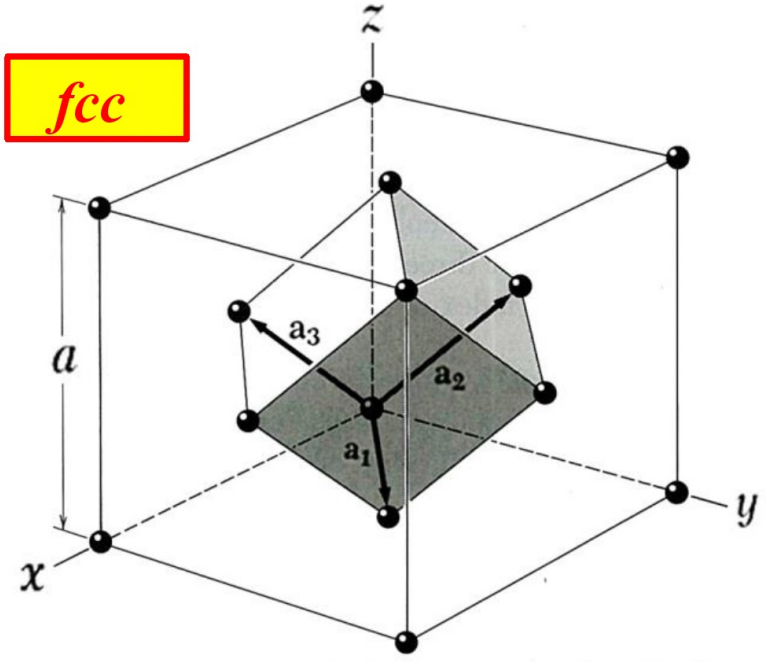

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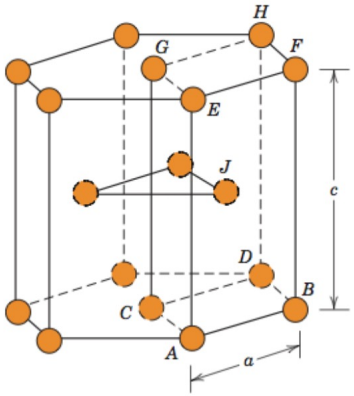
The choice of unit cell is often made in a way to represent symmetry

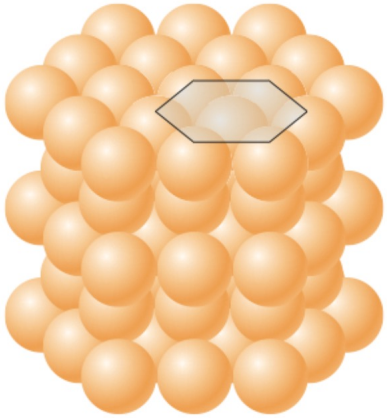
Table of point groups with ALL symmetry elements

Question:

Zn crystallizes in hexagonal lattice, point group is 6/mmm

Where is the 6-fold axis?





Stacking A + B + A + B

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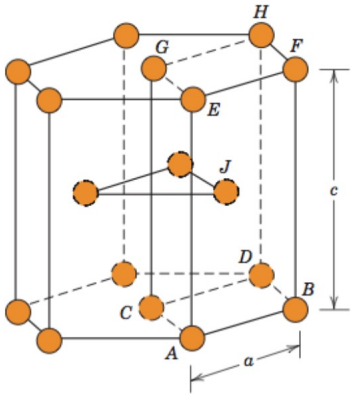
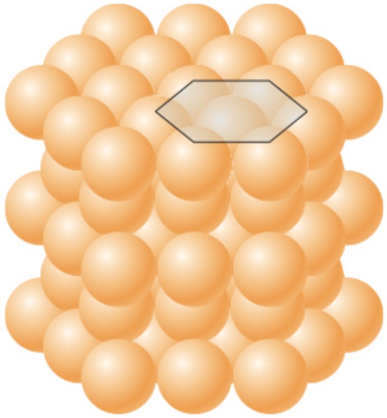
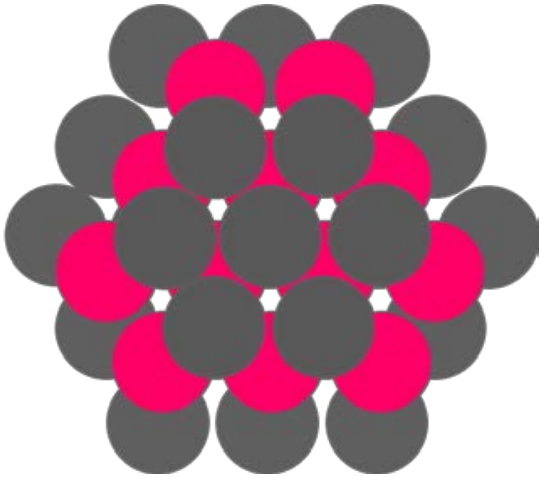




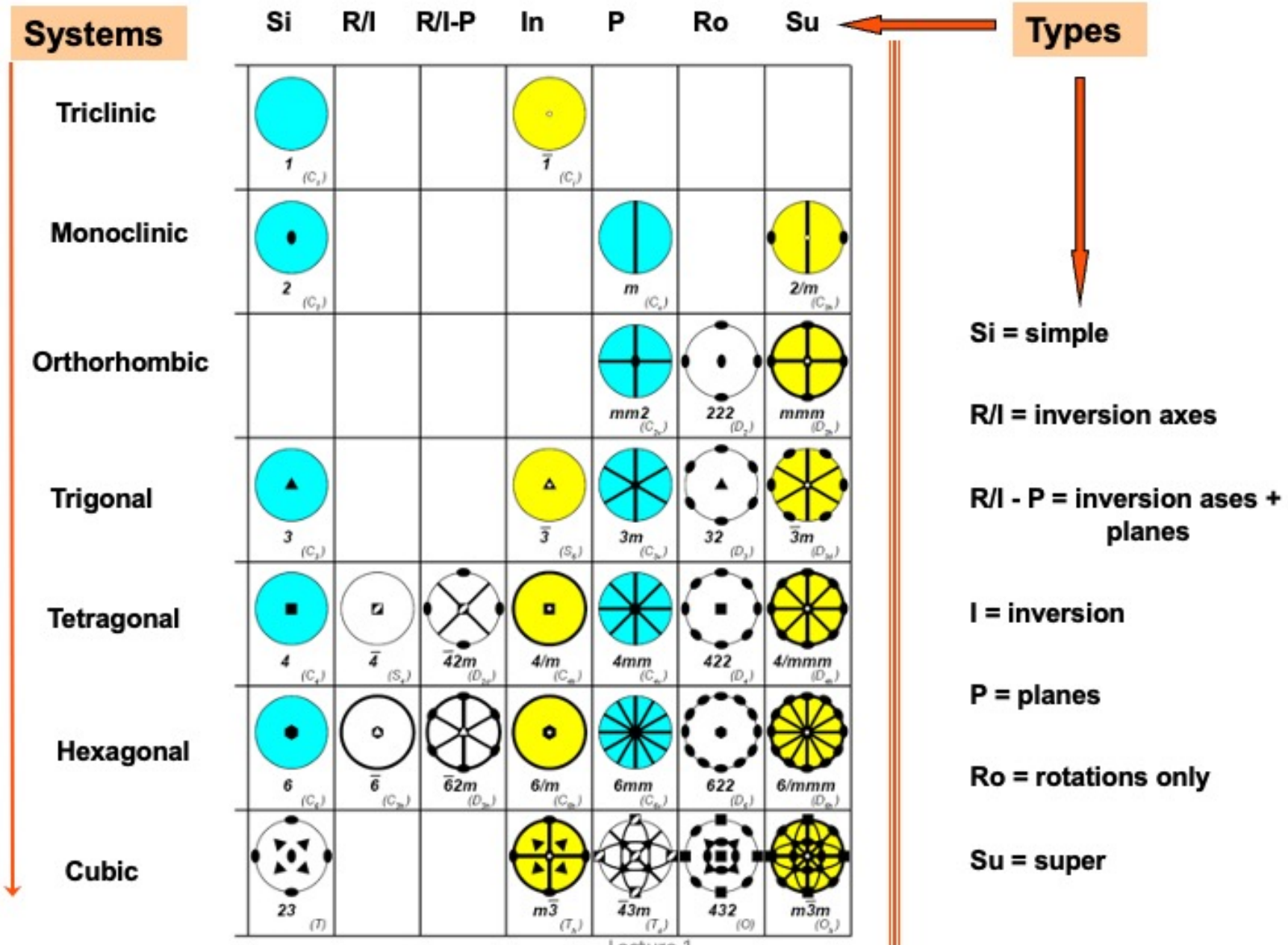
Stacking A + B + A + B

Answer:

- There is no “simple” 6-fold axis
- There is a 6-fold screw axis
- This axis does not pas through atoms
- the axis passes through “C” points for the ABABAB…structure



Point groups: representation of ALL symmetry elements



Tensors: transformation rule

Table of direction cosines

	X_1	X_2	X_3
X_1'	a_{11}	a_{12}	a_{13}
X_2'	a_{21}	a_{22}	a_{23}
X_3'	a_{31}	a_{32}	a_{33}

$$a_{ij} = \cos(X_i' \wedge X_j)$$

new old

$$a_{12} = \cos\phi_2 = \cos(X_1' \wedge X_2)$$

E_i – 1st rank tensor = vector

$$E_i' = a_{ij} E_j$$

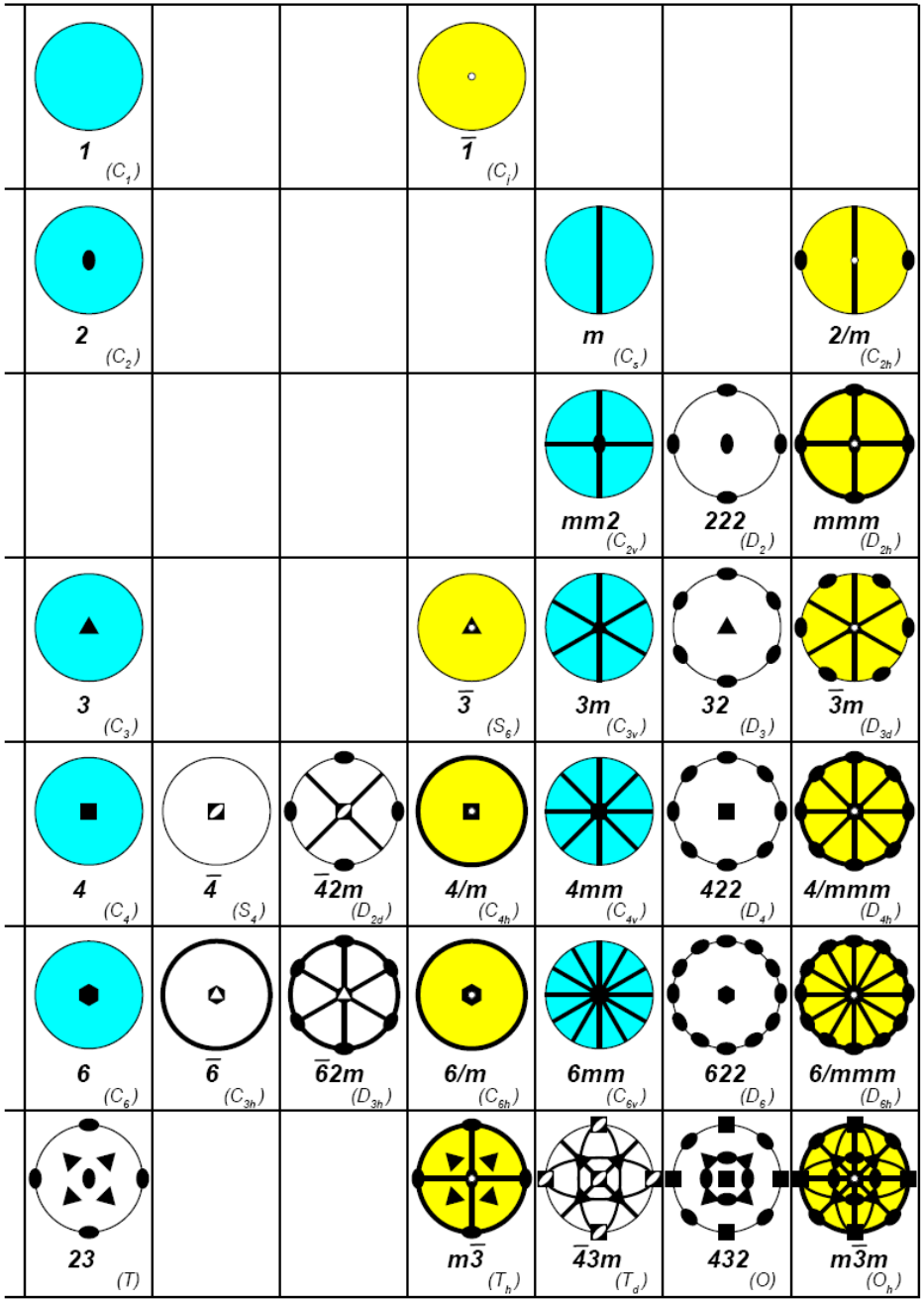
T_{ij} – 2nd rank tensor

$$T_{ip}' = a_{ij} a_{pq} T_{jq}$$

n^{th} rank tensor $M'_{ij\underbrace{.....pt}_{n}} = a_{ii'} a_{jj'} \underbrace{.....a_{pp'} a_{tt'}}_{n} M_{i'j'\underbrace{.....p't'}_{n}}$

Understand and master vector components technique for tensor transformation for simple symmetry operations

Neumann principle: structures of K-tensor



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

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

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

$$\begin{pmatrix} K_1 & 0 & 0 \\ & K_1 & 0 \\ & & K_3 \end{pmatrix}$$

$\infty \quad \infty m \quad \infty 2$

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

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

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

18

Neumann principle: structures of K-tensor

• 3 types of dielectric anisotropy = 3 types of symmetry of dielectric response:

mmm $\qquad\qquad$ ∞ / mm $\qquad\qquad$ $\infty\infty m$

• 3 types of symmetry but 5 types of tensor structure (this is due to the choice of the reference frame where the tensor is diagonalized)

• Same analysis using Neumann principle for all symmetric second rank tensors

Dielectric response: origins

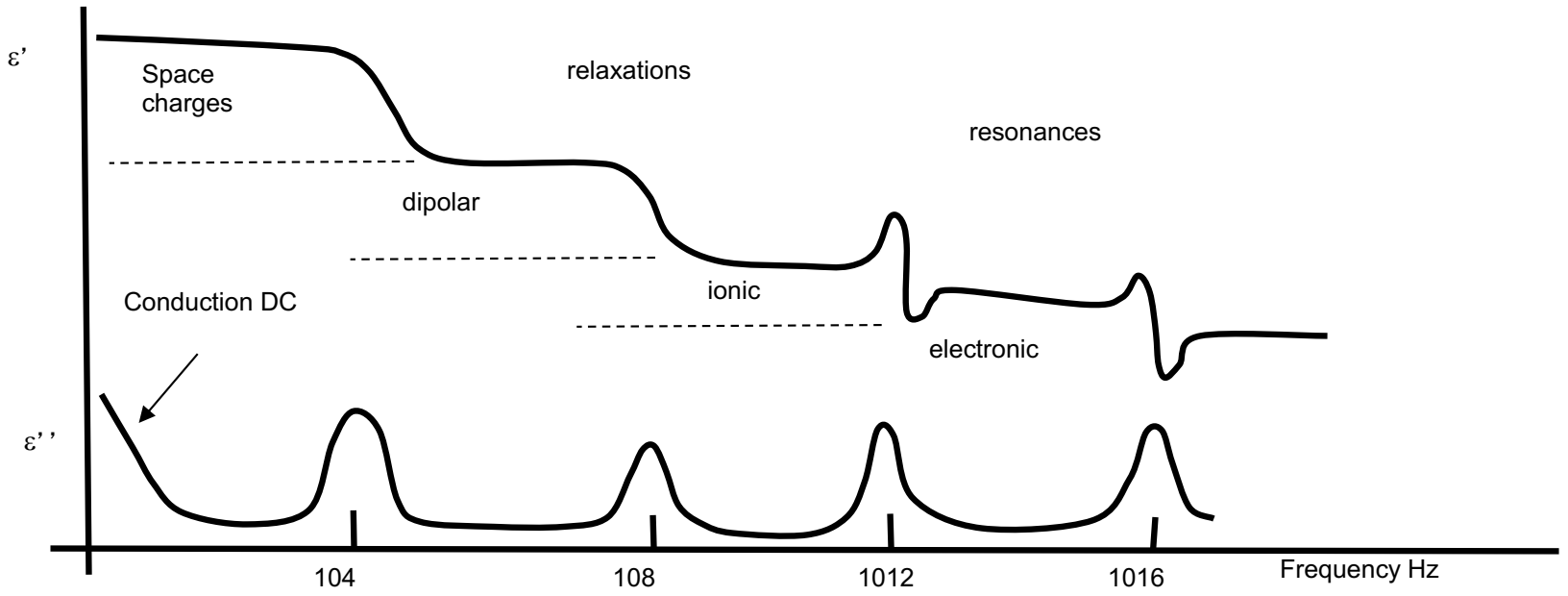
• Electronic polarizability: This occurs as the electron cloud of an atom displaces with respect to the nucleus due to the applied electric field.

• Ionic polarizability: This is a result of relative displacement of cations and anions in response to the applied electric field. That is, the cations try to displace parallel to the field, while the anions try to move in the opposite direction. Because the atoms are held in place by bonds, the displacement is not large, and will have the effect of compressing some bonds and expanding others.

• Dipolar polarizability: This mechanism describes the reorientation of existing dipoles in the material in response to the applied electric field.

• Space charge polarizability: This occurs when mobile carriers (e.g. free electrons and holes or polarons) move in response to the applied electric field until they are blocked by some insulating interface.

Dielectric response: origins



Debye relaxation model

$$E = E_{ac}\cos\omega t$$

$$\tilde{P} = (\chi' - i\chi'')\tilde{E}$$

$$\chi'' = \gamma^{-1}\frac{\omega}{\omega_r^2 + \omega^2}$$

$$D = D_{ac}\cos(\omega t - \delta)$$

$$\chi' = \gamma^{-1}\frac{\omega_r}{\omega_r^2 + \omega^2}$$

$$\tan\delta = K''/K' \qquad D_{ac} = \varepsilon_0\sqrt{K'^2 + K''^2}\,E_{ac}$$

ω_r-relaxation frequency, γ- [F/m sec]

Understand Cole-Cole plots

Dielectric response: question

The low-frequency relative permittivity of water varies from 88.00 at 0° C to 55.33 at 100° C. Explain this behavior.
Over the same range in temperature, the index of refraction goes from roughly 1.33 to 1.32 (electronic polarizability). Why is the change in the refractive index so much smaller?

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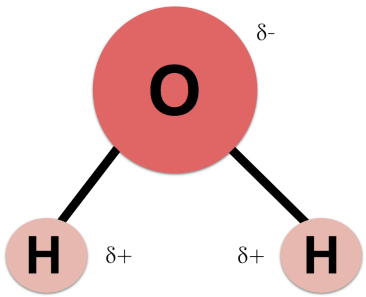
For liquid water, electronic, ionic, and dipolar polarizabilities should all contribute. The dipole moment arises as a consequence of the bent shape of the water molecule. The dipolar polarizability is the largest contributor to the dielectric constant at low frequencies. The majority of the temperature dependence thus arises from the effect of temperature on the dipole mechanism. At lower temperatures, an electric field can help temporarily reorient the dipoles (note that water is not a ferroelectric). As the temperature increases, it acts to randomize the dipole orientation, decreasing the alignment that can be induced by an electric field. Thus, the dielectric constant drops.

At the frequencies of visible light, only electronic polarizability can contribute to the refractive index.



Dielectric response

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

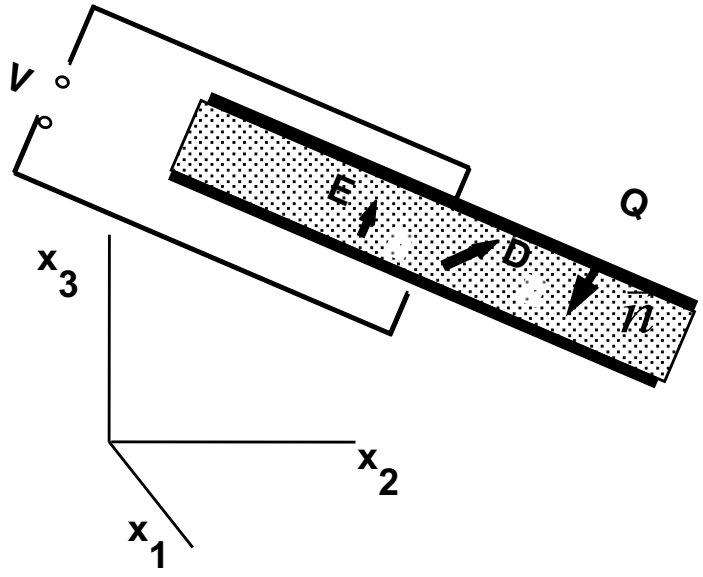
P_i - polarization [C/cm-2]; χ_{ij} – dielectric susceptibility [F/m], E- electric field

$$D_i = \varepsilon_o E_i + P_i \qquad D_i = \varepsilon_0 K_{ij} E_j \qquad \varepsilon_0 K_{ij} = \varepsilon_0 \delta_{ij} + \chi_{ij}$$

D_i - Electric displacement field, ε_0- permittivity of vacuum (8.85x10-12 F/m)

K_{ij} - tensor of dielectric response

Calculation of effective relative dielectric constant in anisotropic materials for a direction ***n***



$$K_{eff} = n_i K_{ij} n_j \text{ ou } K_{eff} = \vec{n} \underline{K} \vec{n}$$

Elastic response

Stain tensor

$$\delta l_i = \varepsilon_{ij} l_j$$

Stress tensor [Pa]

$$f_i = \sigma_{ij} n_j$$

Hook's law

$$\varepsilon_{ij} = s_{ijkl} \sigma_{kl}$$ **Compliance tensor**

$$\sigma_{ij} = c_{ijkl} \varepsilon_{kl}$$ **Stiffness tensor**
Young's modulus

Young modulus is typically defined as $1/s_{33}$ which is not equal to c_{33}

- 3 types of symmetry of suffixes
- Tensorial and matrix form
- Only tensorial form is usable for analysis of symmetry-related properties
- One should be able to switch between tensor and matrix notation

Elastic response, matrix description

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

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

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

$$\sigma_n = c_{nm}\varepsilon_m \qquad \varepsilon_n = s_{nm}\sigma_m$$

$$c_{ijkl} = c_{nm} \qquad s_{ijkl} = s_{nm} \qquad m,n = 1,2,3$$

$$s_{ijkl} = s_{nm}/2$$

one suffix 1, 2, 3 and one suffix 4, 5, 6

$$m,n = 1.....6$$

$$s_{ijkl} = s_{nm}/4$$

both suffixes 4, 5, 6

Piezoelectric response

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

$D_i = d_{in}\sigma_n$ $\varepsilon_n = d_{in}E_i$ **Direct/converse: pay attention to the order of suffixes**

$$d_{ijk} = d_{ikj}$$ [C/N] or pm/V

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

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

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

Piezoelectric response: question

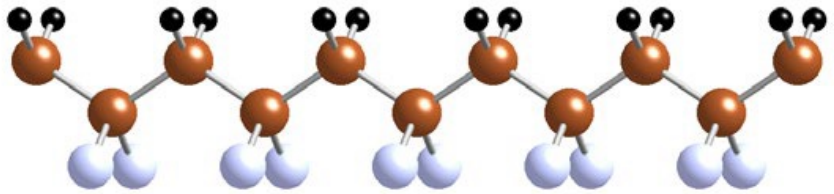
- **Can longitudinal piezoelectric coefficient d33 be negative?**

Piezoelectric response: question

- **Can longitudinal piezoelectric coefficient d33 be negative?**

There are no fundamental restrictions for sign of piezoelectric coefficients
This is unlike dielectric response – the dielectric response components are positive

Negative d_{33} is uncommon but possible. In PVDF polymers (polyvinylidene flouride) very long molecules have dipole moments oriented from fluorine group towards H-group.



The interaction between the molecular chains is of van der Waals type.

In this material, d_{33} is negative because the distance between the chains decreases as a result of poling

Piezoelectric response: question

- Can you induce any mechanic strain by electric field in centrosymmetric materials?

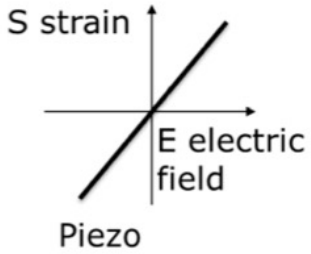
Piezoelectric response: question

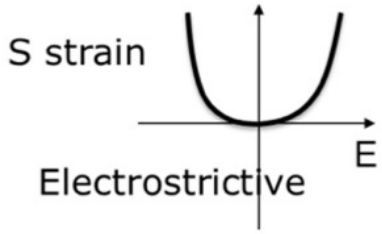
• Can you induce any mechanic strain by electric field in centrosymmetric materials?

Answer: yes

- There will be no piezoelectricity i.e. no ***linear*** electro-mechanic coupling
- However, the second-order electrostriction effect is always there

$\varepsilon_{ij} = Q_{ijkl}P_kP_l$





Disregarding the tensorial nature of electrostriction effect:

$\varepsilon_{ij} = QP^2$

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

• Is there electrostriction in polar materials? Yes, it causes piezoelectricity!

$x = Q(P_s \pm \delta P)^2 = QP_s^2 + 2QP_s\delta P + Q\delta P^2 = QP_s^2 + 2QP_s\varepsilon\varepsilon_0E_{ac}$, where E_{ac} is a small ac electric field (small means it weakly modulates Ps)

$2QP_s\varepsilon\varepsilon_0$ is a piezoelectric coefficient (m/V)

Ferroelectricity, Ginzburg-Landau theory

Ginzburg-Landau equation of state of ferroelectric

$$E = \alpha P + \beta P^3$$

$$\alpha = A(T - T_c)$$

$T > T_c \quad \alpha > 0 \rightarrow P = 0$

$T < T_c \quad \alpha < 0 \rightarrow P = P_0 \equiv \sqrt{-\alpha/\beta}$

unstable

~~$P = 0$~~

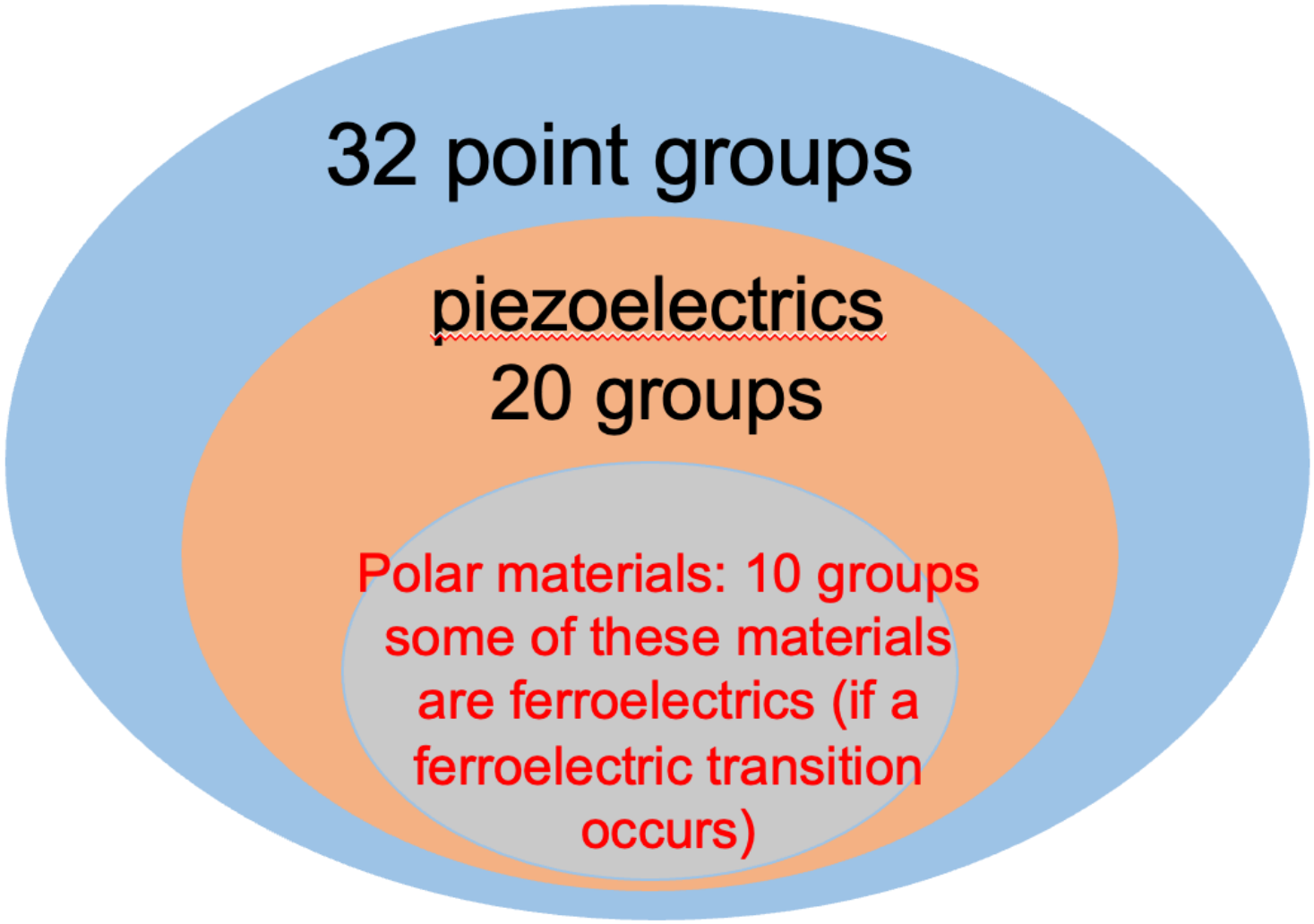
$$P_0 = \sqrt{A(T_c - T)/\beta}$$

PYROELECTRIC COEFFICIENT:

$$p_3 = -\frac{A/\beta}{2}\frac{1}{\sqrt{A(T_c - T)/\beta}}$$

Curie-Weiss constant:

$$C_{\mathrm{CW}} = \frac{1}{\varepsilon_0 A}$$


32 point groups
piezoelectrics
20 groups
Polar materials: 10 groups
some of these materials
are ferroelectrics (if a
ferroelectric transition
occurs)

Constitutive equations

piezoelectric effect

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

pyroelectric effect

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

Thermal expansion

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

Electrocaloric effect

Piezocaloric effect

Be sure you understand and feel comfortable with the exercises on cross-coupled thermo-electro-mechanic effects

- Choose right equations
- Apply the right boundary conditions
- Make use of symmetry to reduce number of unknown variables

Transport properties

Electrical Conductivity

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

τ- electr. conductivity[1/Ohm cm]

Thermal Conductivity

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

h_i - heat flux, k_{ij} ("kappa") – thermal conductivity[J/(m K sec)

$$E_i = \rho_{ij} J_j + \Sigma_{ij} \frac{\partial T}{\partial x_j} \qquad \rho_{ij} = \tau^{-1}{}_{ij}$$

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

$\sum_{ij}$ Thermoelectric tensor (Seebeck coefficients, **[V/K]**) $\qquad \sum_{ij} \neq \sum_{ji}$

$$V = (\Sigma_{II} - \Sigma_I)(T_2 - T_1)$$

Seebeck effect (no current, temperature dependence of Σ is neglected)

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

Peltier effect

Question: specify the main contributions to electric conductivity, to thermal conductivity

Law of mass action for defects in solids

Intrinsic electron/hole concentration

$$Nul \leftrightarrow e' + h^{\bullet}$$

$$K_i = \left[h^{\bullet}\right]\left[e^{'}\right] \equiv pn = N_V N_C \exp(-\Delta E_g / kT)$$

K- equilibrium constant

Formation of defects

$$\alpha A + \beta B \leftrightarrow \gamma C + \delta D$$

$$K = \frac{[C]^{\gamma}[D]^{\delta}}{[A]^{\alpha}[B]^{\beta}}$$

In our analysis K in typically normalized to 1

Example: oxygen vacancies

$$M_M + O_O \xleftrightarrow{MO} V_M^{''} + V_O^{\bullet\bullet}$$

$$K = \frac{[V_M^{''}][V_O^{\bullet\bullet}]}{[M_M][O_O]}$$

$$but\ [M_M]\ et\ [O_O] \approx 1$$

$$[V_M^{''}] = [V_O^{\bullet\bullet}] = \sqrt{K}$$

$$Nul \xleftrightarrow{MO} V_O^{\bullet\bullet} + V_M^{''}$$

$$K_S = \left[V_O^{\bullet\bullet}\right]\left[V_M^{''}\right] = \exp(-\Delta g_S / kT)$$

Δg_S – Energy of defect formation

What we have learned (hopefully)

- **Reading/understanding/interpreting papers/documents including tensor notation, defect chemistry formulas, analysis of properties**
- **Describing/visualizing structures (Vesta), using crystallographic databases**
- **Understanding what you measure (e.g. dielectric response or conduction vs. frequency**
- **Quantitative estimations, calculation of anisotropic properties**
- **Importance and application of boundary conditions**
- **use of reference data, tables, prediction of properties**
- **practical considerations for making materials with required properties (conduction/dielectric response/electromechanical coupling…)**

Some takeaway (incomplete list)

- "Rules" maybe overcome in some cases if new principles are implemented (e.g. restrictions of "centrosymmetric materials")
  - Symmetry can be broken/changed by introducing defects, strain, changing dimension (films, nanostructures)

- A measurement should be treated as a physical experiment
  - the outcome is just a number(s), but to make them relevant many things are to be considered
  - Dielectric response& mechanic response are simple examples

- the analysis should include:
  - Frequency range, dynamics
  - Symmetry consideration, directions
  - Anisotropy vs temperature, possibility of a phase transition
  - If piezoelectric, electrical boundary condition
  - Mechanic, temperature boundary conditions

Some takeaway (incomplete list)

For analysis of functional properties, look into structure (different levels and scales)

- **Anisotropy –properties depend on crystallographic directions!**
- **Ceramics: texture (preferential orientation) is important**
- **Ceramics: grains, grain boundaries, processing conditions (defect chemistry)**
- **Same analysis can be developed without knowing the microscopic mechanisms and atomic structures**
  - **Symmetry consideration (how many moduli, what direction)**
  - **Anisotropy vs temperature**
  - **boundary condition (electrical, mechanical, thermal)**
  - **Frequency range**

Exam checklist

- Structure, chemical bonding, ion radius
  - Pauling rules - prediction of simple structures
  - Understanding different bonding @properties
  - Ionic radius @ properties
  - Basic predictions of properties (hardness, melting point, thermal expansion…)

- Symmetry and Neumann principle
  - Understanding symmetry elements, point groups and use of stereographic projection (use of table of point groups)
  - Use of Neumann principle for analysis of properties (see examples & exercises)
  - Understanding tensorial properties of crystalline materials (exercises)
  - Operations with tensors, transformation of tensor components using Neumann principle (see examples & exercises)
  - Use of vector components rule for simple tensor transformations
  - Simple analysis of anisotropy of properties (see examples)
  - Tensor and matrix formalism (including tensors of ranks 3 and 4)

Exam checklist

- **Phase transitions (simple prediction of properties based on Landau theory of second order phase transitions) – see examples**

- **Cross-coupled effects – understanding, formalism, simple calculations**
  - **Electromechanics (piezoelectricity) – direct, converse effect**
  - **Pyroelectricity**
  - **Thermal expansion**
  - **Thermoelectromechanics**

- **Cross-coupled effects in relationship with symmetry**

Exam checklist

- **Use of constitutive equations for analysis of thermoelectromechanical effects (examples and exercises)**

- **Understanding and use of simple boundary conditions**

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

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

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

Adiabatic ←→ Isothermal **Clamped ← → Mechanically free** **Short-circuit ←→ Open-circuit**

Exam : some possible types of questions (not exhaustive list)

- Exercises - Neumann principle, determination of structure of some tensor, or properties of some tensor element (examples:
- Exercises: qualitative analysis of properties (e.g. is some property possible for a given point group/crystallographic direction)
- Defect chemistry: simple equations describing defects of Schottky and Frenkel type (like Ex. 12-1), understanding principles of defect formation
- Simple analysis of anisotropy (response at a given direction) like Lecture
- Simple qualitative (symmetry) or quantitative analysis of properties (dielectric/mechanical/pyroelectric/conduction responses…)

Exam : possible types of questions (not exhaustive list)

- Cross-coupled effects, use of constitutive equations for analysis of thermo-electro-mechanical effects (see examples and exercises)
  - Use of simple boundary conditions

- General understanding of principle concepts: yes/no type of questions

Exercises from the course and examples discussed in the lecture are usable as guidelines for preparation

Good luck!