

B. Materials for Devices

No. ✓1

Date 10.12.18

Liquid Crystals & Optical Polarisation

- Crystalline materials are anisotropic: their long range order means that their properties may differ depending on the direction of measurement.
- By contrast, liquids are isotropic - invariant w.r.t direction
- Liquid crystals are anisotropic liquids:
 - typically rod-shaped molecules with a rigid long axis but flexible tail



- the molecules can flow past each other \Rightarrow no long-range positional order
- but their shape leads to some orientational order as the molecules tend to align on the long axes.
- this leads to the Nematic LC structure, wherein orientational order is defined by a Director \vec{D} .



- The degree of orientational order is temp-dependent.
 - at sufficiently high temp, random thermal agitation overcomes alignment interactions so the LC \rightarrow isotropic liquid
 - at very low temp LC \rightarrow normal crystal
 - so there is a given band of temperatures for a particular LC material to have LC properties.

- We can describe the degree of orientational order with the order parameter Q , where

$$Q = \frac{3\langle \cos^2\theta \rangle - 1}{2}$$

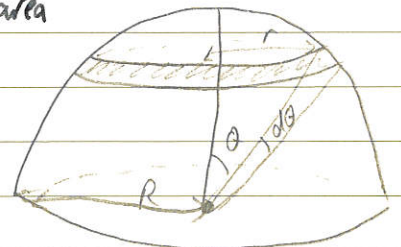


- for perfect alignment, $\langle \cos^2\theta \rangle = 1 \Rightarrow Q = 1$.

- for isotropic liquids, $\langle \cos^2\theta \rangle = 1/3 \Rightarrow Q = 0$.

- this can be derived by considering the area of a small band: $dA = 2\pi r \cdot R d\theta$

$$\text{then } \langle \cos^2\theta \rangle = \frac{\int_0^{\pi/2} \cos^2\theta \cdot 2\pi R^2 \sin\theta d\theta}{2\pi R^2} = \frac{1}{3}$$



surface area of hemisphere.

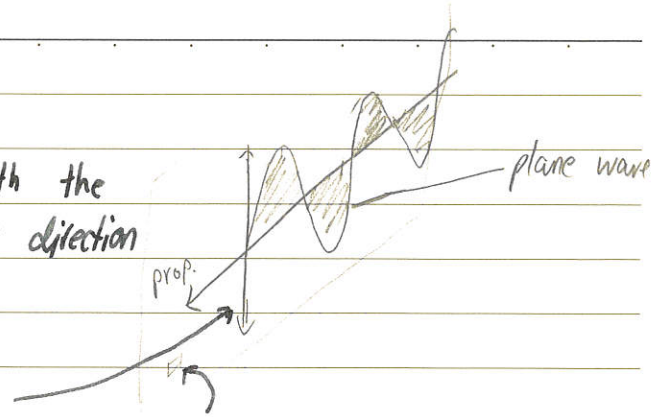
A'ZONE

Polarised light

- Light is a transverse EM wave with the E field oscillating orthogonal to the direction of propagation

- the direction of polarisation is the vibration axis of the E field

- the plane of polarisation contains the directions of prop. and polarisation



- EM waves incident on a single polymer molecule will couple strongly in one direction (not necessarily the long axis) and weakly through the perp. direction.

- in an isotropic polymer sample (e.g. high temp), there will be no effect on polarisation.

- but in a nematic LC there will be a direction with strong coupling (slow axis) and a direction with weak coupling (fast axis)

- these permitted vibration directions (PVDs) are the only axes on which the transverse E field can oscillate.

- Because the speed of light is different for each PVD, the refractive index is different. The birefringence is the difference between the refractive indices: $\Delta n = n_1 - n_2$

- Polarised materials (polaroids) are made from polymers with such strong coupling along the director that only light vibrating perpendicular can be transmitted.

- When polarised light is incident on a birefringent material, it is split into a component for each PVD.

- because of birefringence, there is an optical path difference when they come out the other side

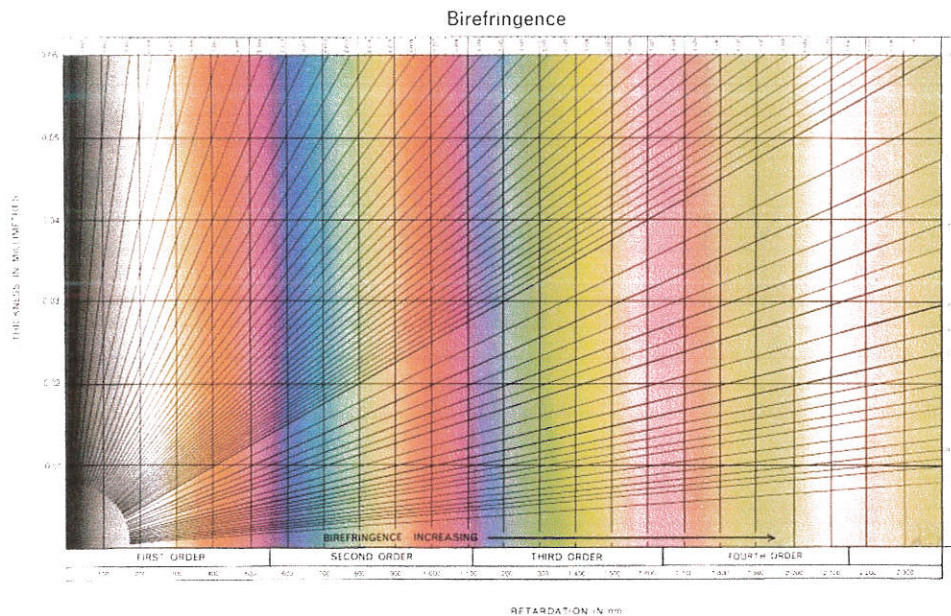
- if the thickness is t : $\text{o.p.d.} = \Delta n \cdot t$



- The phase difference δ is then given by

$$\frac{\delta}{2\pi} = \frac{\Delta n \cdot t}{\lambda} \quad \text{— wavelength in free space.}$$

- Birefringent materials can rotate the plane of polarisation because of this phase difference
 - if o.p.d = $\lambda/2$ (i.e. $\delta = \pi$), the resulting plane of pol. will be perpendicular to the original
 - ↳ light will be transmitted even through crossed polars.
 - if $\delta = 2\pi$, the plane of pol. will be rotated 360° back to the original so no light through crossed polars.
- If a birefringent sample is illuminated with polychromatic light, one wavelength will be lost (λ for which $\delta = 2\pi$).
 - ↳ we will observe the complementary colour.



- The Michel-Lévy chart shows the complementary spectrum for increasing birefringence retardation (o.p.d) which is affected by birefringence and thickness
- On the far left, there is little retardation so light is not transmitted.
- Moving across, there are higher order colours as $\text{o.p.d} = \lambda, 2\lambda, 3\lambda \dots$
- For high retardations, several wavelengths are lost as $\text{o.p.d} = 2\lambda, 3\lambda$, so the colours become more washed out.

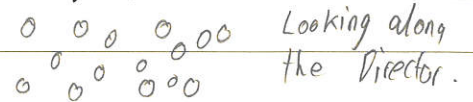
- If a quartz wedge is placed between crossed polars, it will display the M-L chart because it is a material with constant Δn but increasing thickness.

Extinction positions

- If incident light has its plane of pol. parallel to a PVD, there will be no component in the direction of the other PVD.
 \rightarrow no phase diff \Rightarrow no rotation \Rightarrow extinction between X polars.
- Thus the PVDs can be determined by rotating a sample between X polars: max intensity when PVDs at 45° .
- Which PVD is fast/slow (i.e. the sign of the birefringence) can be determined by adding a compensator, an anisotropic sample with known Δn , on top of the sample both at 45° .
 \rightarrow ADDITION: higher colour \Leftrightarrow o.p.d increase \Leftrightarrow fast direction parallel
 \rightarrow SUBTRACTION: lower colour \Leftrightarrow o.p.d decrease \Leftrightarrow fast directions antiparallel.

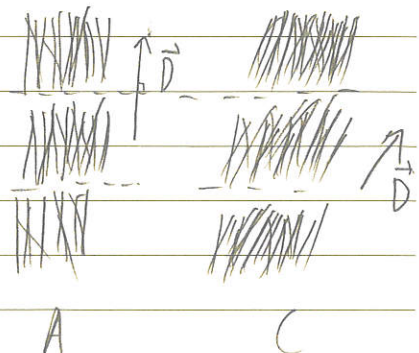
e.g. Quartz

- In an LC, PVDs will be aligned with the director.
- But a nematic LC sample may not have a uniform director: domains with different orientations.
- There will be disclinations where domains meet, forming a schlieren texture between X polars.
- Dark whenever the director aligns with the polariser or analyser.
- Also dark if director is parallel to light path, because an LC is isotropic along the optic axis.



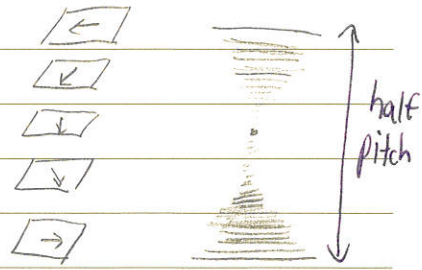
Smectic LCs

- Smectic LCs have some overall positional order, with molecules organising into layers.
- No pos. order within layers
- Smectic A: director parallel to layer normal
- Smectic C: director nonparallel to layer normal

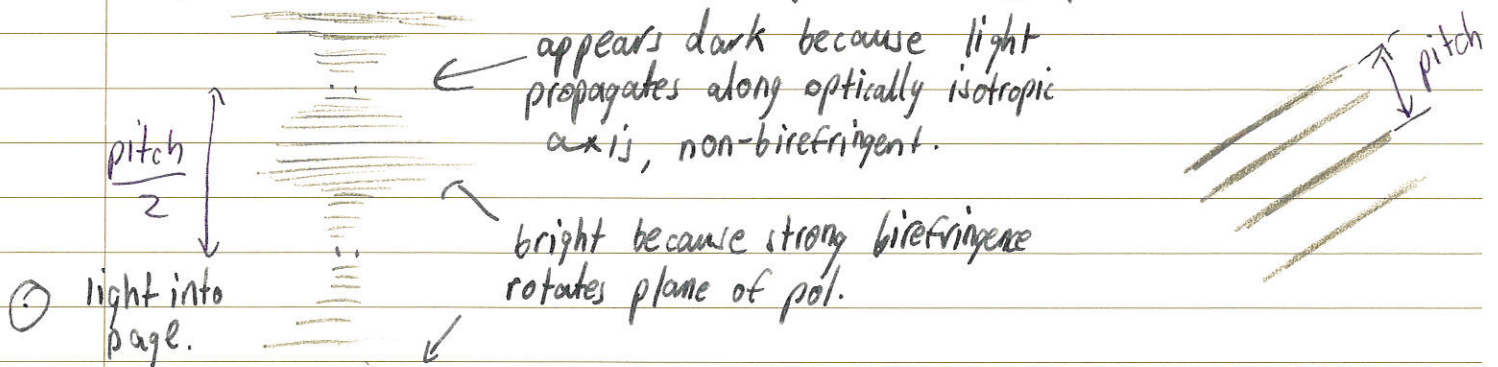


Chiral Nematic LCs

- Molecules in a chiral nematic (cholesteric) LC have their director in a plane, which rotates along the axis perpendicular to the plane to trace out a helix
- Polarised light propagating along this axis will have its plane of pol. rotate with the director.
- The pitch is the distance required for \vec{D} to rotate 360°
- Generally, higher temperatures lead to more twisting so pitch is reduced.
- The twisted structure occurs because the molecules are chiral (e.g. asymmetric α -helix), leading to a twisting alignment.
 - ↳ shorter molecules tend to be more strongly asymmetric, thus have more twist and lower pitch.

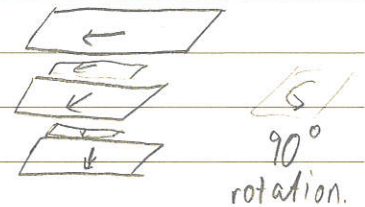


- Observing a chiral nematic LC between crossed polars (with light perp. to the axis of the helix) gives a stripy pattern



LCDs

- The director of an LC can be encouraged to lie along a direction using a grooved surface.
- Sandwiching an LC between 2 plates with \perp grooves leads to a precise twisted nematic structure. Normally requires addition of a chiral nematic dopant.



- When viewed between crossed polars (along the axis of rotation), sample will be bright because the twisted nematic structure rotates the plane of pol. by 90° .

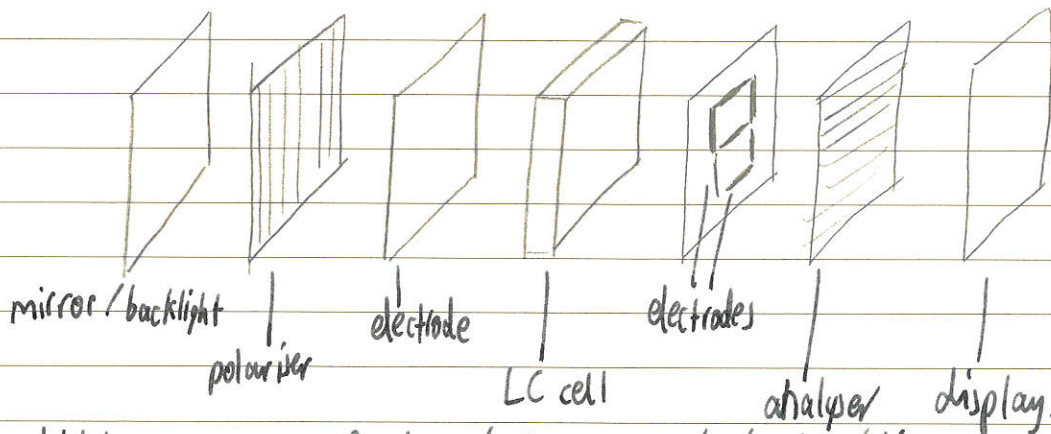
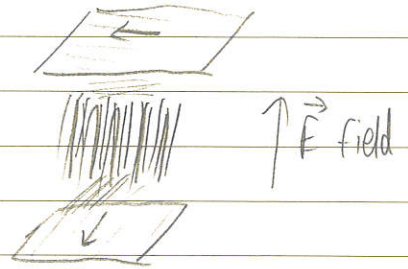
↳ this is the ON state for an LC cell.

- Applying an \vec{E} field causes the molecules to align normal to the grooved plates, in the Fredericksz transition

↳ molecules near grooves stay aligned but the rest become parallel to the \vec{E} field

↳ optically isotropic \Rightarrow no rotation \Rightarrow dark cell

↳ this is the OFF state.



• Light enters from front and is reflected by ~~backlight~~ mirror.

• By default, plane of pol. twisted by LC so everything bright.

• When a p.d. is applied across the electrode plate and a shaped electrode (all transparent), light is blocked and an image appears.

• Colour LCD can be made with backlighting and colour filters to make RGB sub-pixels.

Polymers

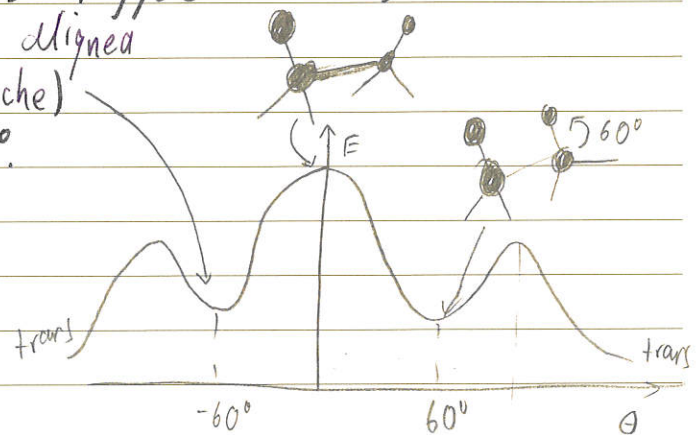
- Polymers are macromolecules made from long chains of monomers.
- The chains are generally twisted and coiled, with branches and cross-linking.



- Rotation about the C-C bond leads to changes in conformation
 - lowest energy when C-C bonds staggered (trans)
 - highest energy when C-C bonds aligned
 - intermediate conformations (gauche) with bonds misaligned by 60° .

- In reality, a molecule will have many different conformations.

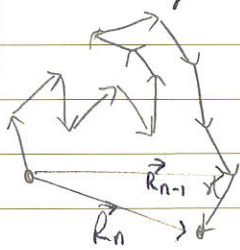
- Increasing temp allows for more conformational change (can climb the energy barrier)



↳ polymers become more flexible when heated.

Size of polymer molecules

- A polymer molecule can be modeled as a random walk of n segments of length l (i.e. assume free rotation)
- the length is then the root mean square of the end-end vector \vec{R}_n .



$$\vec{R}_n = \sum_{i=1}^n \vec{r}_i \quad \text{and} \quad \vec{R}_n = \vec{R}_{n-1} + \vec{r}_n$$

$$|\vec{R}_n|^2 = (\vec{R}_{n-1} + \vec{r}_n) \cdot (\vec{R}_{n-1} + \vec{r}_n) = R_{n-1}^2 + 2R_{n-1}l \cos \alpha + l^2$$

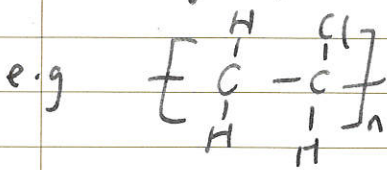
$$\therefore \langle R_n^2 \rangle = \langle R_{n-1}^2 \rangle + l^2 \quad \text{since} \quad \langle \cos \alpha \rangle = 0$$

By induction, $\langle R_n^2 \rangle = n l^2$

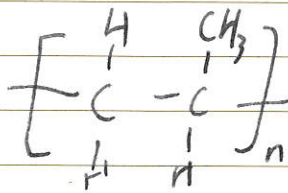
$$\therefore \text{RMS} : \langle R_n^2 \rangle^{1/2} = L \sqrt{n}$$

- Because of steric hindrance, real polymer chains have some stiffness. We can improve the model by redefining l as the length scale below which the chain is straight and rigid (rather than the monomer length). Must reduce n accordingly.
- This is the Kuhn length, and is sometimes written as $K \times \text{C-C length}$. Higher K means stiffer.

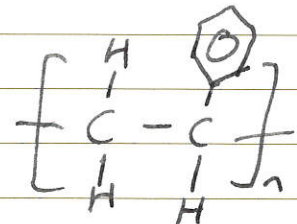
Side groups



PVC

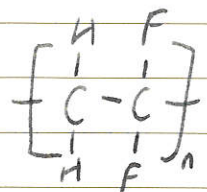


polypropylene



polystyrene

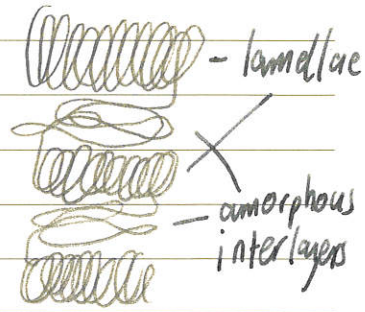
- The molecule's configuration/tacticity refers to the arrangement of the side groups along the chain.
- Isotactic - side group always on the same side
- Syndiotactic - side group on alternate sides
- Atactic - side groups distributed randomly.
- These affect charge distribution. In an extreme case like polyvinylidene fluoride (PVDF), the charge imbalance leads to important properties.



Polymer microstructure

- At higher temperatures, chains can flex, coil, slide. As temp lowers, there is less conformational change and less space for movement, so viscosity increases until the glass temperature is reached.
- A rubber is a cross-linked polymer: chain segments can undergo conformational change but cannot slide past each other to give permanent shape changes.
- Plasticisers are small molecule additives which space out the chains and increase mobility.

- Polymers can exist in a partially crystalline form when chains fold and pack into a regular structure.
- Alternates between crystalline layers called lamellae and amorphous regions.
- The relative thickness of the layers defines the percentage crystallinity of such a polymer.
- Crystallisation is easier for polymers with very regular chains (e.g. isotactic/syndiotactic); bulky side groups or atacticity hinder packing.
- Highly crystalline polymers are stiffer or more brittle, and generally more opaque because of light scattering between layers.



Electrical Polarisation

- A dielectric is an insulator that is electrically polarisable.
- Polarisation occurs by the creation of electric dipoles (i.e. charge sep.):
 - electronic pol.: distortion of electron cloud when \vec{E} field applied
 - ionic: elastic distortion of ionic bonds
 - orientational/molecular: rotation of pre-existing permanent dipole moments, especially common in polar liquids

- For equal but opposite charges separated by \vec{r} , the dipole moment is defined by: $\vec{\mu} = q \vec{r}$



- The polarisation is the dipole moment per unit volume
 $\vec{P} = n \vec{\mu}$ (C m^{-2}), where $n \equiv$ no. of dipoles per unit volume.

- Alternatively, it is the charge per unit surface area: $P = Q/A$.

- When an \vec{E} field is applied to a dielectric, a charge density \vec{D} will develop, with a magnitude depending on the material's permittivity ϵ .

$$\vec{D} = \epsilon \vec{E} = \kappa \epsilon_0 \vec{E} \quad \kappa \equiv \frac{\epsilon}{\epsilon_0} \text{ is the Dielectric Constant of the material}$$

- We can consider \vec{D} (a.k.a. displacement field) to be made from 2 components: free space and the polarisation of the material

$$\text{i.e. } \vec{D} = \epsilon_0 \vec{E} + \vec{P}$$

- Equating this to the previous result gives \vec{P} in terms of \vec{E} and κ

$$\vec{P} = \vec{D} - \epsilon_0 \vec{E} = \epsilon_0 \vec{E} (\kappa - 1)$$

- A capacitor stores charge. The capacitance is defined as $C = \frac{Q}{V}$.

- For an empty parallel-plate cap.

↳ charge density between plates is $\epsilon_0 E$, so $Q = \epsilon_0 E A$ — area of plate

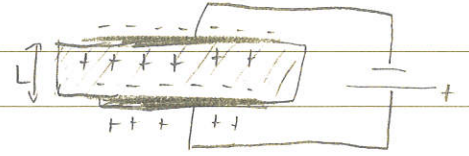
↳ if plates separated by distance L , $V = EL$

$$\therefore C = \frac{Q}{V} = \frac{\epsilon_0 EA}{EL} \Rightarrow C = \frac{\epsilon_0 A}{L}$$

- With a dielectric, there is a higher charge density so more charge on the plates

$$D = \epsilon_0 E + P \Rightarrow Q' = (\epsilon_0 E + P) A$$

$$= \epsilon_0 E \kappa A$$

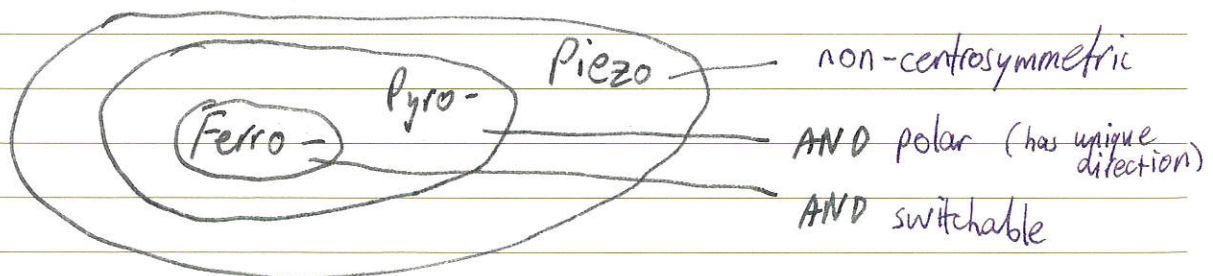


$$C' = \epsilon_0 \kappa \frac{A}{L}$$

- Thus a dielectric increases capacitance:
 - when battery connected, V constant but $Q \uparrow$, so $C \uparrow$
 - when disconnected, Q constant but $E \downarrow$ and $V \downarrow$, so $C \uparrow$.
- Though we model dielectrics as the constant of proportionality in a linear relationship between \vec{P} and \vec{E} , for very high fields the dielectric may allow current to flow: dielectric breakdown. The maximum field that can be sustained is the dielectric strength.

Dipole formation & symmetry

- If a crystal is centrosymmetric (has a centre of symmetry), then any line through the centre will connect equivalent faces/atoms.
- A unique direction is a lattice vector which is not repeated by the present symmetry.
- Centrosymmetric crystals have no unique direction, so there cannot be a net electric dipole without an external E field.
- Non-centrosymmetric crystals do not necessarily have a unique direction, e.g. sphalerite (ZnS).
- A polar material, which can demonstrate dielectric polarisation, must have a unique direction.
- Electrical properties depend on this asymmetry



Piezoelectrics

- Piezoelectricity is the change in polarisation on application of stress

$$P = d\sigma$$

$d \equiv$ piezoelectric coefficient $C N^{-1}$

$\sigma \equiv$ stress (tension or compression) $N m^{-2}$

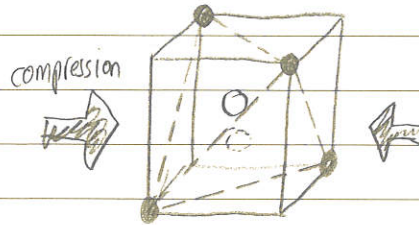
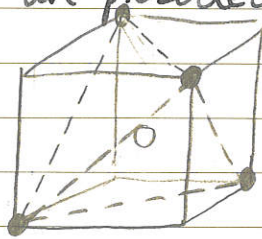
$$P = \frac{Q}{A} = \frac{CV}{A} = \frac{\epsilon_0 K V}{L}$$

$$\therefore V = \frac{d\sigma L}{K\epsilon_0} \leftarrow \text{RESULTANT VOLTAGE}$$

(not applied).

- Quartz and crystals containing tetrahedral groups, e.g. sphalerite \rightarrow ZnS are piezoelectric because stress distorts the tetrahedron

○ = Zn
● = S



- the centre of mass (and charge centre) of the S^{2-} ions doesn't move during compression
- but the Zn^{2+} ion moves to maintain equal bond lengths
- generator effect: stress changes P and leads to voltage
- e.g. igniters: pressure induces $\sim kV$ which causes dielectric breakdown across an air gap ($\sim 1mm$).
- The motor effect is when applying an E field leads to a structural change in a piezoelectric, e.g. watches.

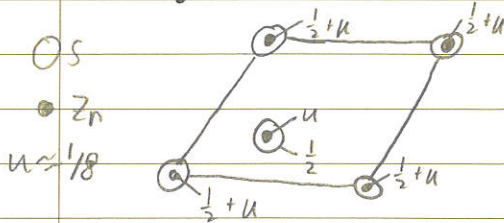
Pyroelectrics

- Pyroelectricity is the change in polarisation due to a change in temp.
- Adsorption of polar impurities masks the true surface polarisation, so we measure ΔP :

$$\Delta P = p\Delta T \Rightarrow \Delta V = \frac{p\Delta TL}{K\epsilon_0}$$

where $p \equiv$ pyroelectric coefficient $C m^{-2} K^{-1}$

e.g. in Hex P ZnS (wurtzite):



- non ideal c/a

- only upward-pointing tetrahedra are filled

- [001] is a unique direction

• can be applied in burglar alarms (or IR detectors)

- one sample behind IR filter/reflector, another exposed.

- voltage difference between both must be due to IR

- used to isolate the ~60W of IR from a burglar.

Ferroelectrics

• Ferroelectricity is stable spontaneous net polarisation which can be reversed by an external E field.

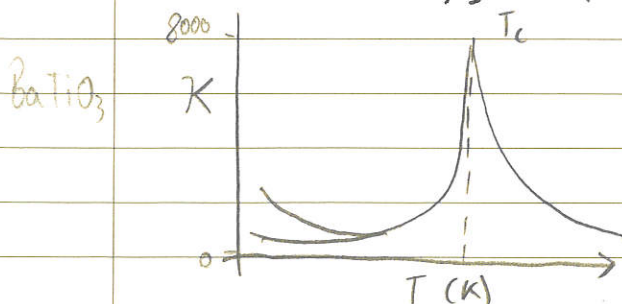
• At higher temps, crystals tend to be more symmetric. Some compounds have a Curie temperature T_c . When cooled below T_c , they undergo a displacive phase transition

• e.g. the ABO_3 perovskite structure with smaller B cations.
↳ more room for B to move in the BO_6 octahedron.

• e.g. $BaTiO_3$: cubic $\xrightarrow{\text{cool}}$ tetragonal $\xrightarrow{\text{cool}}$ orthorhombic
 T_c between cubic/tetragonal $\langle 001 \rangle$ $\langle 110 \rangle$ $\downarrow \text{cool}$
rhombohedral $\langle 111 \rangle$

• In FE materials, K depends on the E field, so polarisation is nonlinear with the field.

• K is also strongly temperature dependent

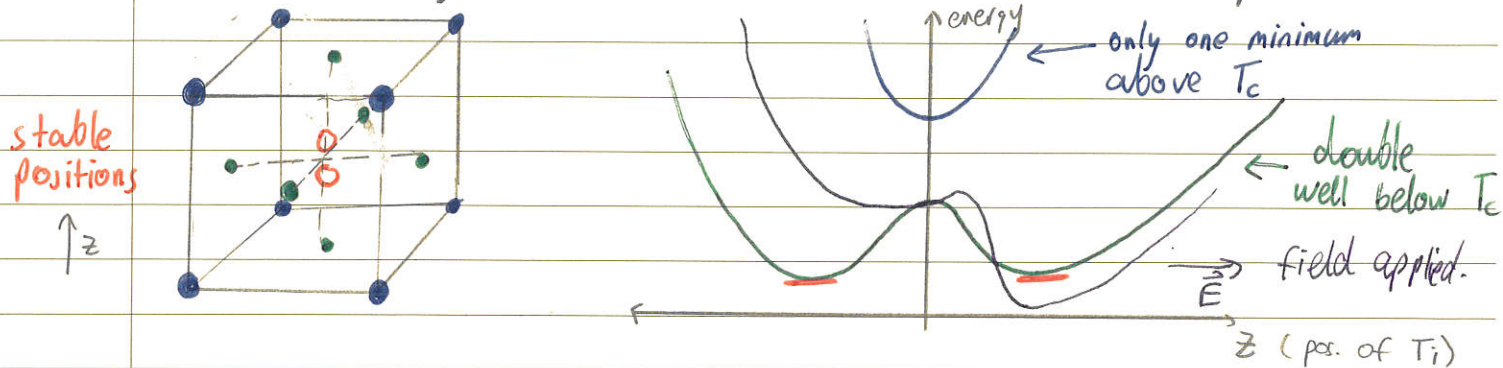


- at the peak, the central ion can easily move, hence easy to induce dipole.

- two K values because tetragonal phase is electrically anisotropic.

• Impurities or dopants can lead to significant variations in dielectric properties.

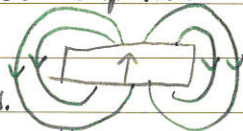
Ferroelectricity occurs when ions sit in double-well potentials



- (below T_c)
- in the absence of an E field, both **stable minima** are equally likely.
 - when \vec{E} applied, one minimum will be much more favourable
 - ion will remain in that position once the field is removed.

A domain is a local region with aligned dipoles.

Stray fields have an energy cost, which encourages differently-oriented domains.



But this must compromise with domain wall energy.

↳ depends on orientation: can be polarised along any $\langle 100 \rangle$.

↳ tend to form at oblique angles



The polarisation of a FE can be switched with an E field.

↳ cycling E field leads to hysteresis loop

① Unpolarised, randomly oriented. Behaves like a linear dielectric for very small \vec{E} .

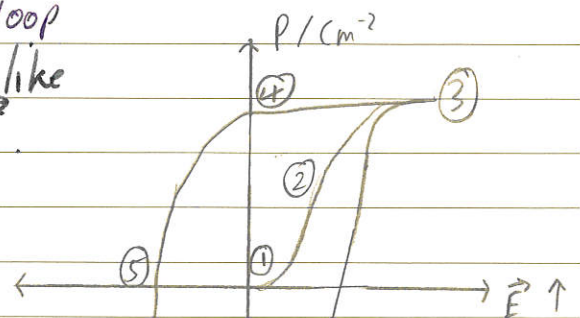
② Favourably aligned domains grow

③ Saturation polarisation (P_{sat}): one aligned domain in sample.

④ Even with zero field, there is a remnant polarisation P_r .

⑤ As field is reversed, opposite domains nucleate and grow. The field required to return to $P=0$ is the coercive field E_c .

⑥ Saturation in opposite direction.



Energy \propto area

crystal defects may result in domain walls being pinned \Rightarrow higher E_c

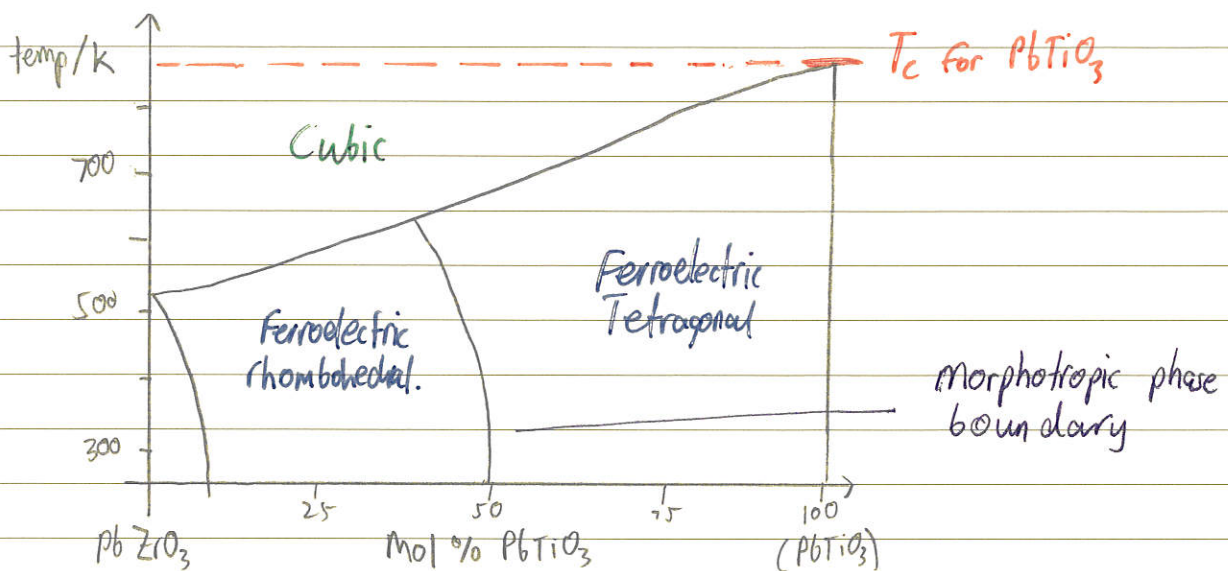
Applying ferroelectrics

- Often, FE properties ignored and they are just used as dielectrics, e.g. BaTiO_3 has high κ values and is used for camera flash capacitors.
- Switchable states can be used in FE-RAM - non-volatile, low voltage, radiation hard.

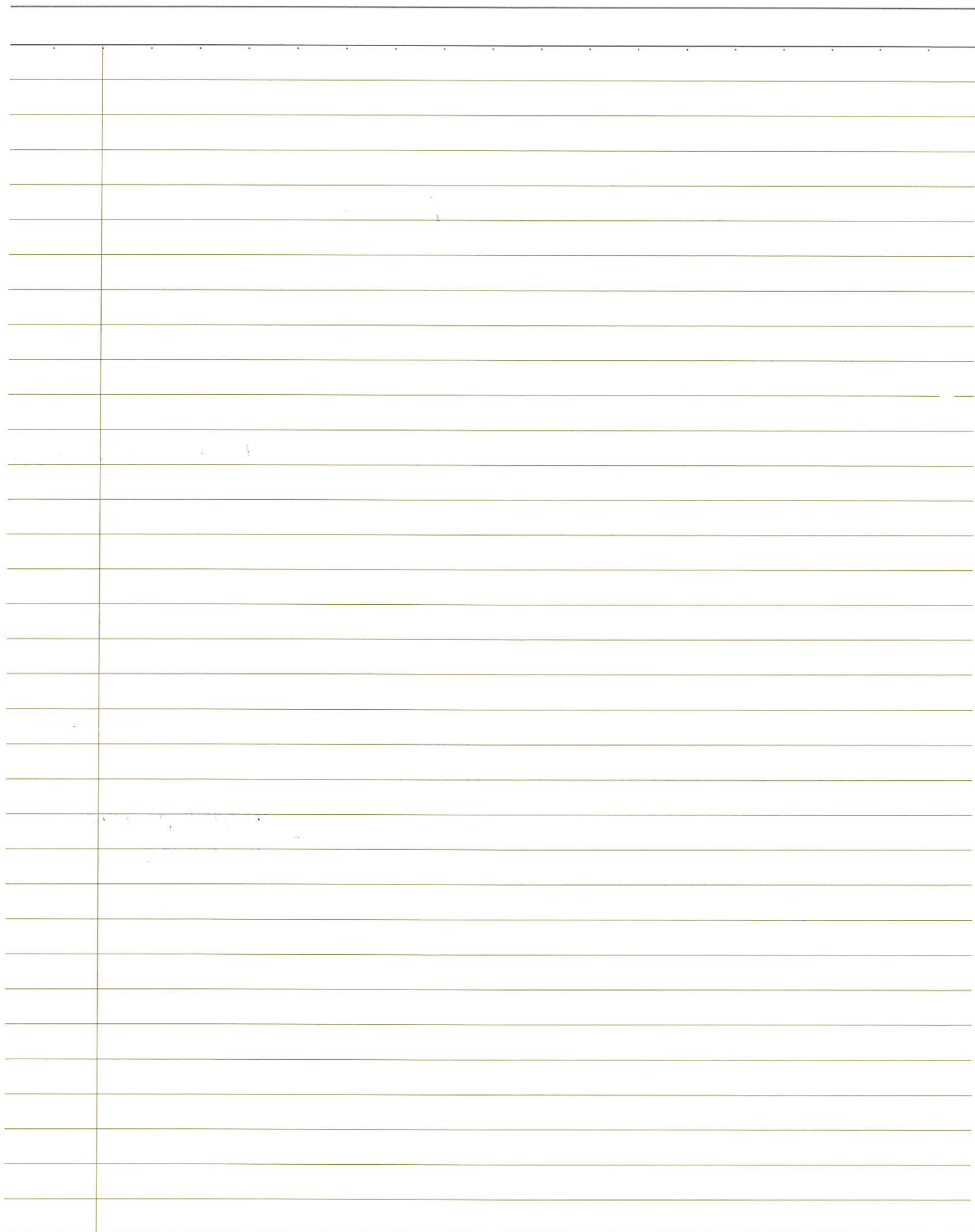
↳ needs high P_{sat} and P_r , high κ and low E_c , high T_c

- The materials are fabricated as thin films to minimise switching voltage: film e.g. 10-300nm, switch takes ~50ns.
- During the switch, heat is given off.

- One of the most widely used piezoelectrics is PZT - $\text{Pb}(\text{Zr}_x\text{Ti}_{1-x})\text{O}_3$.
 - Zr/Ti ions occupy the perovskite B site.
 - properties changed by varying x .

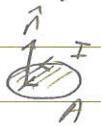
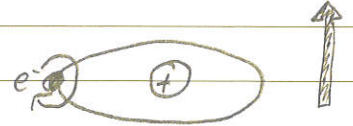


Along the morphotropic phase boundary, polarisation states can form along the 6 possible $\langle 100 \rangle$ tetragonal distortions OR the 8 possible $\langle 111 \rangle$ rhombohedral distortions.
 ↳ 14 possible orientations \Rightarrow easy to pole and switch.



Magnetic materials

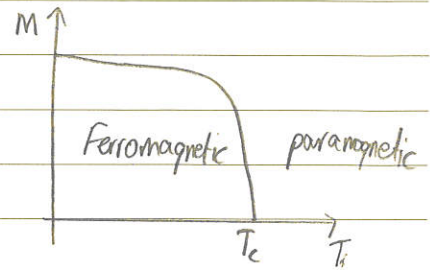
- Magnetic moments are produced by spinning electrons orbiting the nucleus.
 - The net magnetisation of a material depends on the strength and alignment of individual moments
 - ↳ depends on valence electrons because e^- pairs in complete shells have opposite spin.
 - The magnetic moment on a current loop: $\vec{M} = IA\hat{n}$
 - The magnetisation M is the magnetic moment per unit volume, $A m^2$ per m^3 i.e. $A m^{-1}$.
- $M = \chi H$ $\chi \equiv$ susceptibility (dimensionless).
 $H \equiv$ magnetic field ($A m^{-1}$)



- Diamagnetism: shells filled, so no unpaired e^- and no net moment in the absence of a field. When an external mag. field is applied, electron orbits move to oppose flux, developing an opposite moment i.e. χ is negative e.g. -10^{-5} (noble gases, graphite).
- Paramagnetism: some unpaired e^- so dipoles exist, but are non-interacting and randomly oriented. No overall moment when $H=0$.
 - when $H > 0$, there is partial alignment of moments
 - χ is positive but small e.g. $\sim 10^5$ (most metals).
- Ferromagnetism: many unpaired e^- . Because of QM effects (the exchange interaction), moments tend to align and there is long range magnetic order.
 - χ large, e.g. 5×10^3 for Fe
 - moments remain aligned even with no external field.
- Antiferromagnetism: many moments, but they interact such that an antiparallel arrangement is most favourable. No net dipole. e.g. Cr
- Ferrimagnetism: a material with two ferromagnetic sublattices oppositely oriented \Rightarrow net magnetisation
 - behaves like ferromagnet with low susceptibility ($\chi \approx 0.1$)
 - e.g. magnetite (Fe_3O_4).

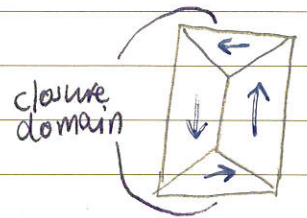
Ferromagnetic materials



- Above the Curie temp, thermal agitation overcomes the exchange interaction because of the phase transition.
- χ becomes large when $T \rightarrow T_c$, as the magnetic moment can easily be changed.

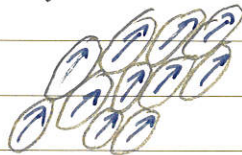


- The preferred direction of the magnetic moment depends on the crystal. Magnetocrystalline anisotropy means that there will be easy and hard crystallographic axes (but hard to know a priori).

- Because stray fields have an energy cost, magnetic domains form
- One consequence of this is shape anisotropy: lower energy for magnetisation to lie along the length of a long thin sample.



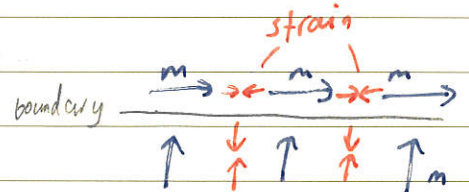
LOWER ENERGY \rightarrow 
 HIGHER ENERGY $\uparrow \uparrow \uparrow$ 



e.g. the elongated grains in a polycrystalline sample may result in strong directional magnetisation.

- On magnetisation, a crystal experiences strain and will change dimensions.
 \hookrightarrow the magnetostriction coefficient Λ is the fractional change in length (in a particular direction) as magnetisation goes from zero to saturation.

- Because neighbouring domains have different dimensional changes, there is high strain at the boundary; elastic strain energy stored.



- The width of a domain wall / Bloch wall is a compromise between:
 - exchange interaction energy \rightarrow wants wide walls with gradual twist of moments
 - magnetocrystalline/anisotropy energy \rightarrow wants abrupt walls so moments align with easy axis.
- The exact value depends on material properties. Typically 5-100nm.

- A domain structure won't form in a small particle/grain if the wall energy $>$ stray field. For a small enough grain, it will have one domain.
 \rightarrow stray fields $\propto r^3$, domain wall energy $\propto r^2$.

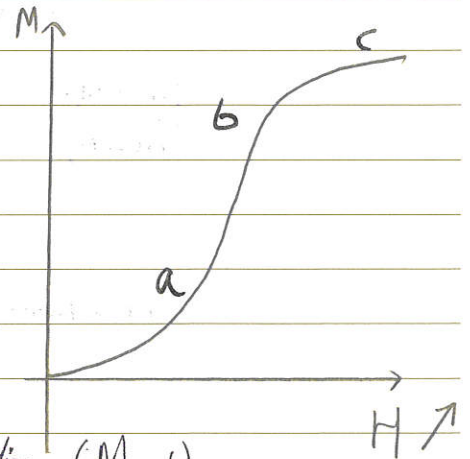
Ferromagnetic hysteresis

When a field is applied:

a) favourably oriented domains (which lie on easy axes) grow by wall motion. This is irreversible, because of pinning imperfections.

b) The whole sample is aligned along the easy axis closest to H 's direction.

c) Moment aligns with H : saturation magnetisation (M_{sat})



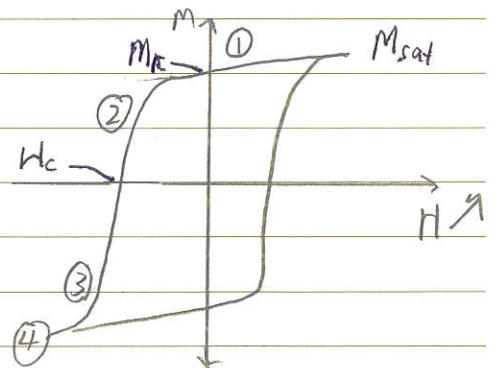
Cycling the field produces hysteresis:

① Moment relaxes to easy crystallographic axis but remains stable as $H \downarrow$: remanent magnetisation.

② As $H \downarrow$, the roughly parallel domains grow. The H for which $M=0$ is the coercive field.

③ Single domain along easy axis

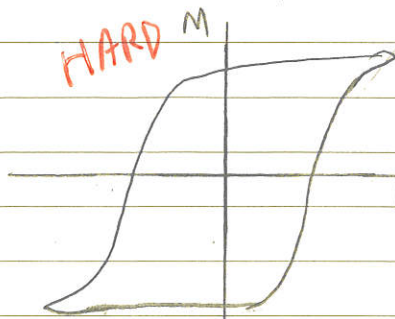
④ Moment rotates to align with H .



• area within loop \propto energy dissipated (i.e. 2x switch energy).

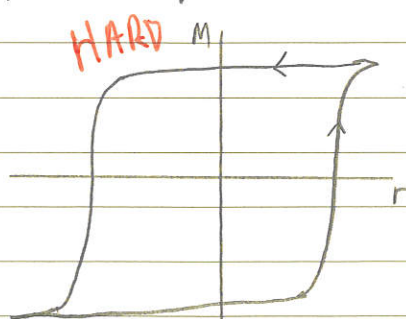
• Imperfections pin domain walls \rightarrow increased coercive field.

• Different shapes of hysteresis loop are desirable for different applications



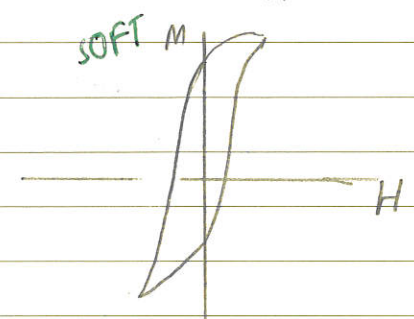
Permanent magnets:

- Need high, stable mag.
- Large M_r and H_c



Memory devices

- Need well-defined switch
- i.e. very steep around H_c



Transformer cores:

- Easy switching
- High M_{sat} , low H_c .

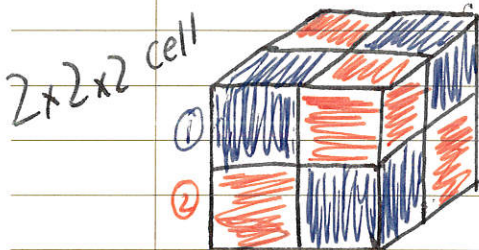
- To make **SOFT** magnetic materials, we need to remove imperfections that would pin domain walls
 - ↳ we annealing to form 'perfect' crystals, or use very homogeneous materials ($H_c \sim 3 \text{ A m}^{-1}$)
- To make **HARD** magnetic materials, incorporate imperfections by:
 - quenching, which doesn't allow grains to reorganise during cooling.
 - sintering \rightarrow compressing fine powders to leave many particles ($H_c \sim 10^6$)

In practice, we don't measure M , we measure the magnetic flux density B (a.k.a. inductance). It has units of Tesla.

$$B = \mu H = \mu_0 (H + m) = \mu_0 H (1 + \chi) \quad \begin{array}{l} \mu \equiv \text{permeability} \\ \mu_0 \equiv \text{permeability of free space} \end{array} \quad (\text{H m}^{-1})$$

Ferrimagnetism

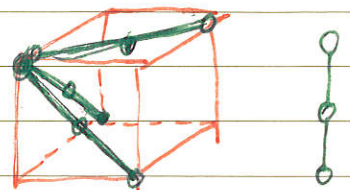
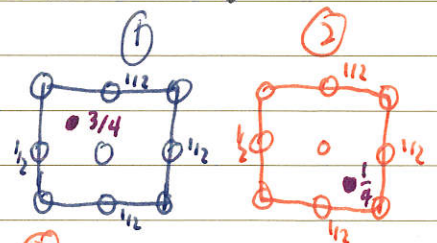
The Spinel structure consists of (almost) ccp oxygen ions with two cation sites. AB_2O_4 with A^{2+} and B^{3+}



- $\frac{1}{8}$ tetrahedral interstices occupied by **(A)**

- $\frac{2}{4}$ octahedral interstices occupied by **(B)**, only in **(2)**.

- tetrahedra unconnected, pointing opposite directions



In the Inverse Spinel Structure, we have $\text{A}(\text{AB})\text{O}_4$.

e.g. in Fe_3O_4 (magnetite), $\text{A} \equiv \text{Fe}^{3+}$, $\text{B} \equiv \text{Fe}^{2+}$.

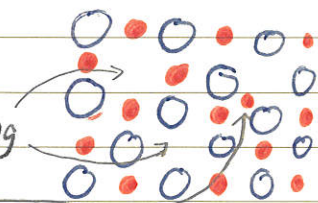
- spin moments of Fe^{3+} on A sites cancel with B sites

- the remaining Fe^{2+} moments align, resulting in a net moment.

- thus, Fe_3O_4 is ferrimagnetic.

Solid Ionic Conductors

- Ceramics are compounds of metallic anions with non-metallic cations, e.g. metal oxides. They generally have high melting points and low electrical conductivity
- Ionic lattices tend to have imperfections
 - Schottky defect: one pair of cation/anion missing
 - Frenkel defect: cation moves into interstice
- These defects mean that ions can move through the lattice, leading to ionic conduction. This can happen because of:
 - a concentration gradient of ions or vacancies, i.e. a diffusion current
 - an external electric field, causing a drift current.
- Mobility depends on the number of vacant sites as well as the energy barrier between lattice sites.



Ionic currents

- The atomic/ionic flux J is the no. of atoms crossing a unit area per second.
- For steady state diffusion in a uniform 1D conc. gradient:

$$J = -D \frac{\partial n}{\partial x} \quad \begin{array}{l} D \equiv \text{diffusivity (m}^2 \text{ s}^{-1}) \\ \partial n / \partial x \equiv \text{conc. gradient (m}^{-4}) \end{array}$$

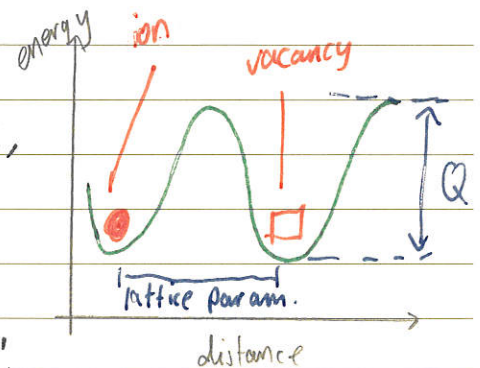
- We can then find the diffusion current density j

$$j = -qD \frac{\partial n}{\partial x} \quad (\text{A m}^{-2})$$

- The diffusivity depends on the probability that an atom/ion can overcome the activation energy Q , given by the Arrhenius equation

$$D = D_0 \exp\left(-\frac{Q}{RT}\right) \quad \text{or} \quad D = D_0 \exp\left(-\frac{Q}{kT}\right)$$

if Q is given in J mol^{-1}
if Q is J atom^{-1}

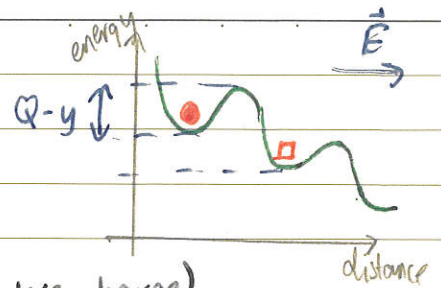


- This can be found empirically by linearising and plotting:
 $\ln D = \ln D_0 - Q/RT$

• When an E field is applied, the activation energy is reduced in one direction.

• The drift current density depends on the field and the conductivity σ ($\Omega^{-1}m^{-1}$)

$$j = -\sigma \frac{\partial V}{\partial x} = \sigma \vec{E} \quad (\text{movement of +ve charge}).$$



• The number of diffusing ions in an electric potential follows a Boltzmann statistic: $n = n_0 \exp(-qV/kT)$.

$$\frac{\partial n}{\partial x} = \frac{\partial n}{\partial V} \frac{\partial V}{\partial x} = -\frac{nq}{kT} \frac{\partial V}{\partial x} = \frac{nq\vec{E}}{kT} \rightarrow \vec{E} \text{ field} \Rightarrow \text{conc gradient}$$

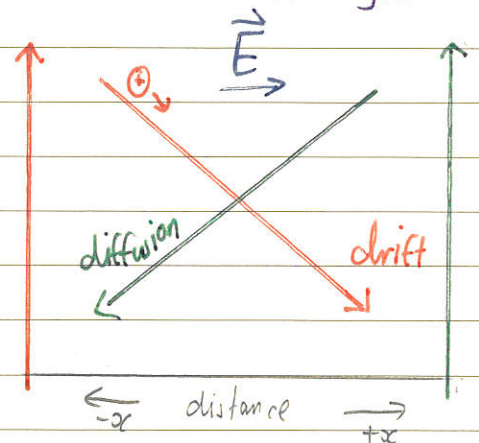
• But in a steady state equilibrium, no ions escape so the diffusion current must balance the drift current: $j_{diff} + j_{drift} = 0$.

$$\therefore qD \frac{\partial n}{\partial x} = \sigma \vec{E} \Rightarrow qD \left(\frac{nq\vec{E}}{kT} \right) = \sigma \vec{E}$$

Leads to the Nernst-Einstein equation

both Temp. dependent.

$$\frac{\sigma}{D} = \frac{nq^2}{kT}$$



• We can use this to find a relationship between σ and temperature:

$$\sigma = \frac{Dnq^2}{kT} = \frac{q^2}{kT} \left[D_0 \exp\left(-\frac{Q}{kT}\right) \right] \left[n_0 \exp\left(-\frac{qV}{kT}\right) \right]$$

oversimplification

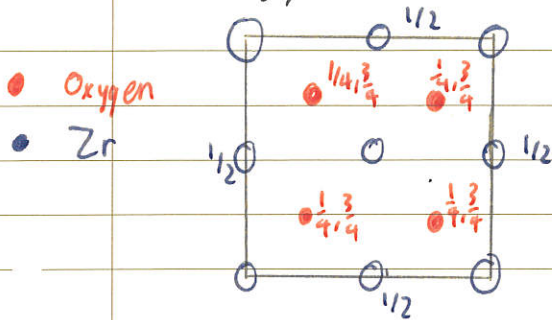
$$\therefore \ln \sigma = \ln \sigma_0 - \left(\frac{Q}{k} \right) \frac{1}{T}$$

$\approx n_0$ when \vec{E} small and $qV \ll kT$.

assuming $\sigma_0 = \frac{D_0 n_0 q^2}{kT} \approx \text{constant}$

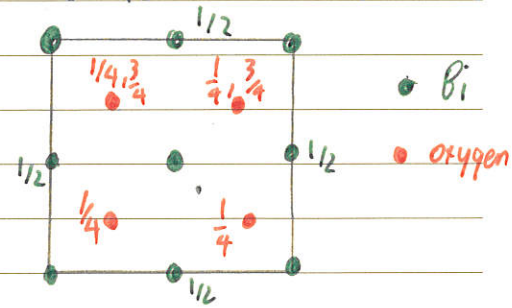
Applications of solid ionic conductors

- The ideal ionic conductor will have many vacancies & defects
- Yttrium-stabilised Zirconia (YSZ) is made by doping ZrO_2 with Y_2O_3 , which creates oxygen vacancies.



- $2 Zr^{4+}$ and $1 O^{2-} \Rightarrow 2 Y^{3+}$
- The doping also leads to a stable cubic fluorite structure, i.e. fcc Zr with O^{2-} ions in most tetrahedral interstices.

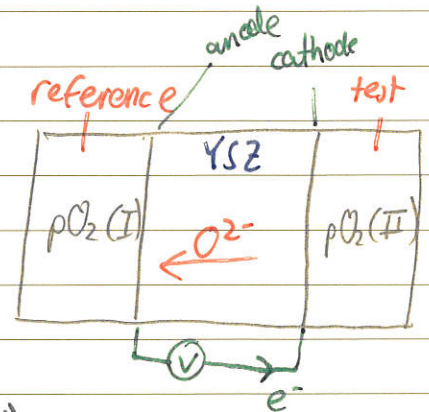
- δ - Bi_2O_3 is another common choice. It has the fluorite structure with two formula units per unit cell



- Thus there are 2 O^{2-} vacancies, which creates a fast-ion channel
- In general, these ionic conductors can replace electrolytes whenever the transferred ion is O^{2-} .

e.g. Oxygen concentration cell

- Monitors O_2 conc: if reference $pO_2 <$ test pO_2 , there will be diffusion and redox
- cathode: $O_2(g) (II) + 4e^- \rightarrow 2O^{2-}$
- anode: $2O^{2-} \rightarrow O_2(g) (I) + 4e^-$



- Electrodes are made of porous platinum (catalyst) i.e. $Pt(s) | O_2(g) (I) | YSZ | O_2(g) (II) | Pt(s)$.

- We can use the electrochemical formula to find the potential:

moles of e^- produced

$$E = - \frac{RT}{nF} \ln \frac{\prod_i (\text{activity of product } i)^{x_i}}{\prod_i (\text{activity of reactant } i)^{y_i}}$$

molar ratios

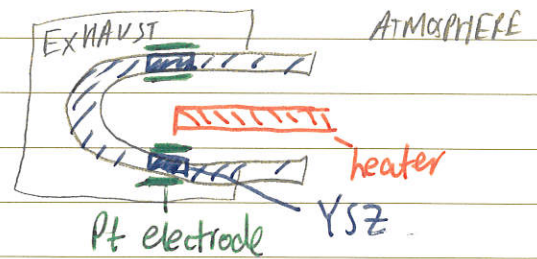
in this case, $E = - \frac{RT}{4F} \ln \frac{pO_2 (I)}{pO_2 (II)}$

• This is used in a Lambda sensor in car exhausts, measuring the O_2 conc in exhaust gas.

- a heating implement maintains constant conductivity for the YSZ

- the potential feeds into the fuel-injection system.

• The ideal air-to-fuel ratio (by weight) for complete combustion is 14.6. Defining $\lambda = \text{measured ratio} / 14.6$, we can plot:



• When pO_2 high, $\lambda > 1$, so fuel should be added

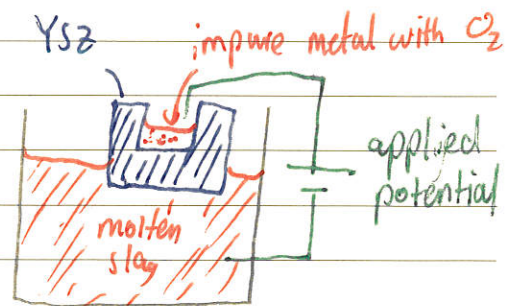
• When pO_2 low, $\lambda < 1$ so air should be added.

• Aiming for $\lambda = 1$.

e.g. Oxygen pump

• To purify some metal, we can place it in a YSZ container in molten slag and apply a p.d

• This drives O^{2-} ions from the metal to the slag, purifying it.



e.g. Fuel cell

• Fuel cells convert chemical energy directly into electrical energy.

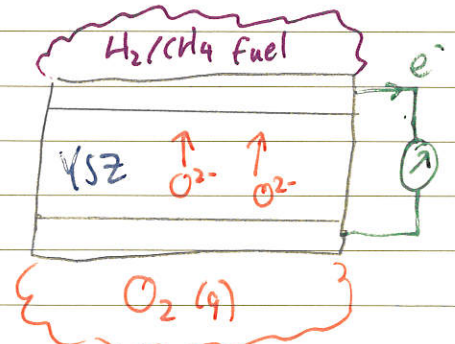
• The fuel is H_2 or CH_4 , which is oxidised to produce a flow of electrons.

• The advantages of a fuel cell are:

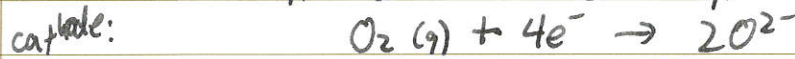
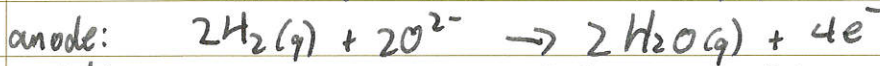
- high efficiency compared to internal combustion engine

- noiseless

- 'clean', i.e. no NO_x or CO .

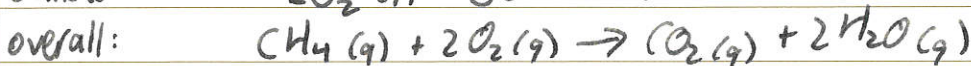
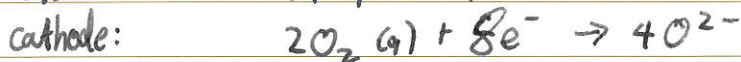


- Using H_2 fuel:



$$E = -\frac{RT}{4F} \ln \frac{(p_{H_2O})^2}{(p_{H_2})^2 p_{O_2}}$$

- Using CH_4 fuel:

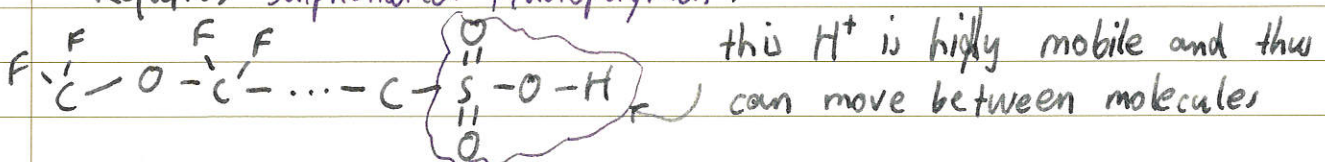


$$E = -\frac{RT}{8F} \ln \frac{p_{O_2} (p_{H_2O})^2}{(p_{CH_4})(p_{O_2})^2}$$

- The YSZ electrolyte needs high temperatures to be effective (1000K).
 \rightarrow this is a challenge because the anode operates in an ~~oxidizing~~ a highly reducing env, and the cathode in a highly oxidizing env.
- The anode is often a conducting ceramic (porous).
- The cathode is often doped porous manganite (doesn't oxidize).

e.g. Polymer Electrolyte Membrane fuel cells

- Because a YSZ fuel cell presents many challenges, PEM fuel cells have been developed, which conduct protons instead of O^{2-} .
- Requires sulphonated fluoropolymers:



- These have much lower running temps ($80^\circ C$) but require expensive Pt-based catalysts.

