Defects in Solids

Last time

Gases and solids

Today

Defects in solids

Next time

Phase transitions

Crystal defects



Blue Moon diamond
(sold for US$48.4m in 2014)



Tesla Power Wall

Crystal defects

In a crystal at absolute zero, all atoms are at rest at their ideal lattice position

Real crystals are imperfect, and their imperfections are called *defects*

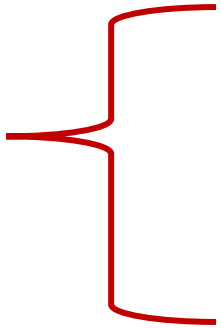
Defects cause or affect many important material properties, including:

- Strength
- Conductivity
- Color

Types of defects

Categorised by geometry:

- Point defects (0 dimensional)
- Linear defects (1 dimensional) (a.k.a. dislocations)
- Planar defects (2 dimensional)
- Bulk defects (3 dimensional)

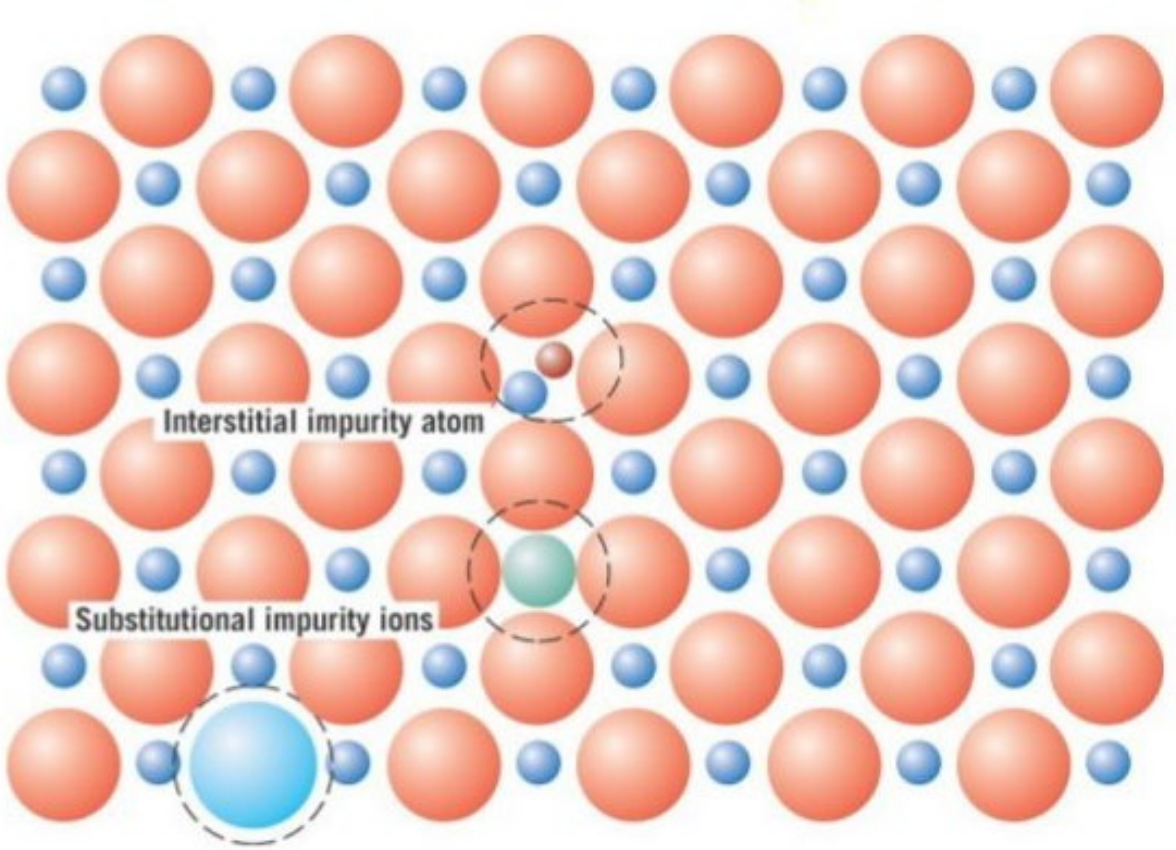


- Intrinsic (caused by thermodynamics)
- Extrinsic (not required by thermodynamics; impurities)

Point defects: Impurities

The most common **extrinsic** defects are impurities

They are *point* defects, because they only affect one lattice site (or a few)



Point defects: Substitutional impurities

Ruby:
corundum with chromium impurities, Al_2O_3:Cr

Sapphire:
corundum with non-chromium impurities, e.g. Al_2O_3:Fe,Ti

Emerald:
beryl with chromium impurities, $Be_3Al_2(SiO_3)_6$:Cr

Blue diamond:
carbon with boron impurities, C:B





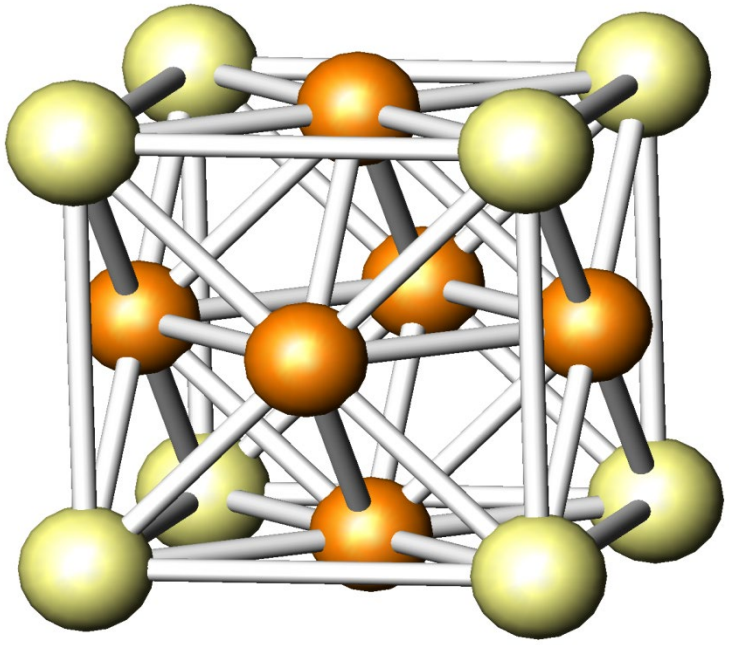


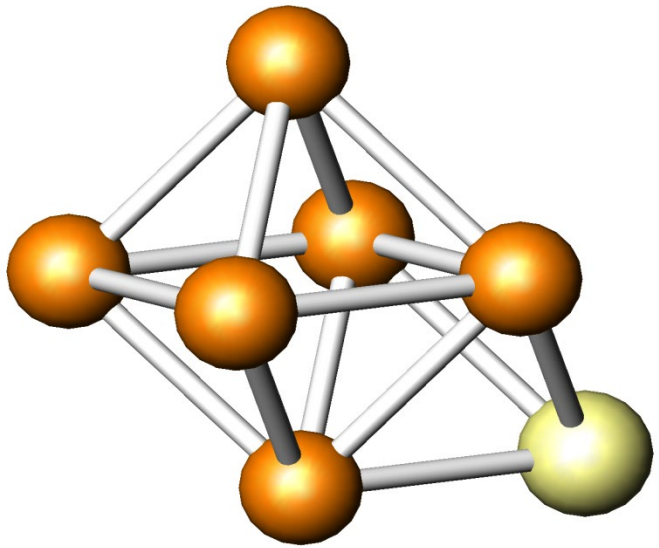


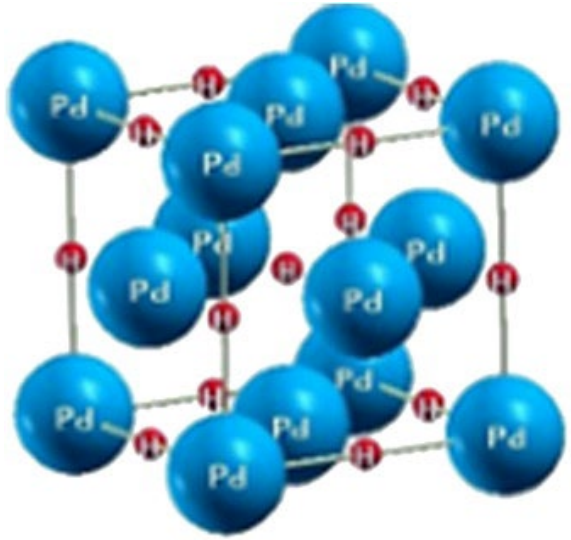
Point defects: Interstitial impurities

Interstitial sites are positions between the regular array of atoms (Lecture 5)

In fcc crystals, there are both octahedral and tetrahedral interstitial holes



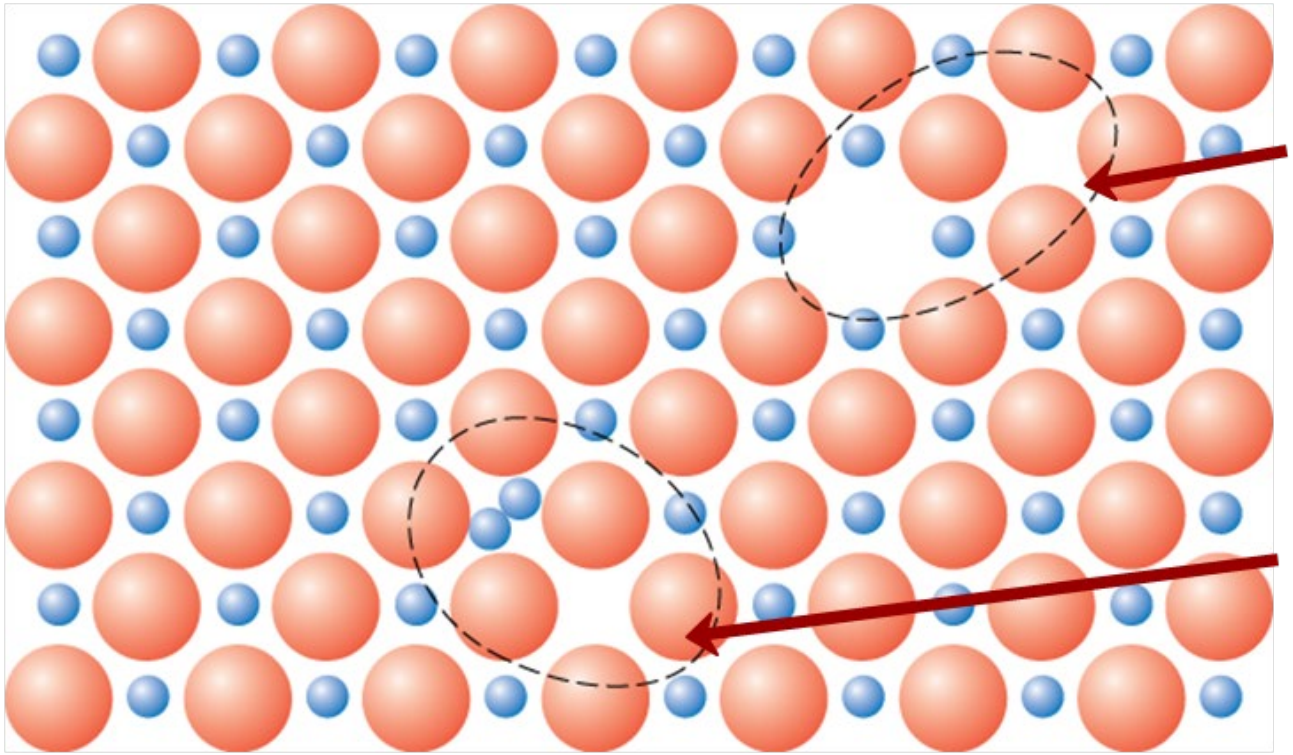




Example: H occupies octahedral sites in Pd

Intrinsic point defects

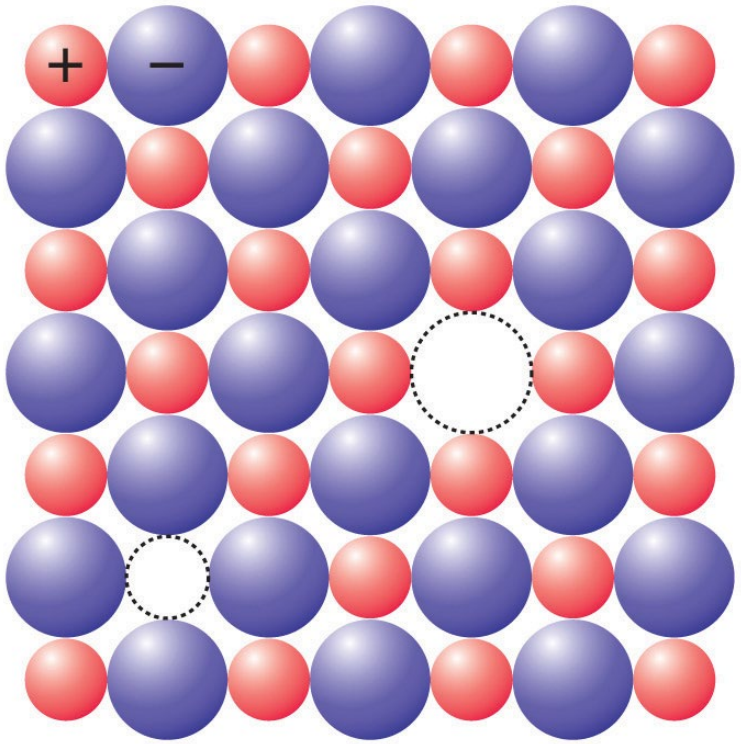
Intrinsic point defects are stoichiometric, and they preserve electroneutrality



Schottky defect: Oppositely charged vacancies are attracted to each other to form pairs

Frenkel defect: Oppositely charged vacancies and interstitial sites are attracted to each other to form pairs

Point defects: Schottky defects



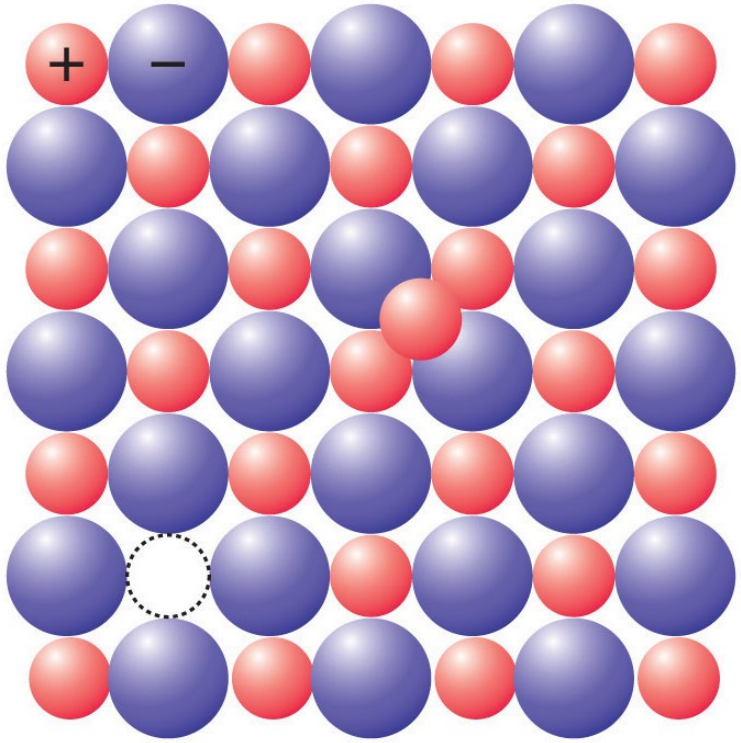
(a) Schottky defect

Example: NaCl — Schottky defects are responsible for its electrical and optical properties

Typically found in materials that are:

- Highly coordinated
- Small difference in the sizes of ions

Point defects: Frenkel defects



(b) Frenkel defect

Example: AgCl

Typically found in materials where the ions are of different size (i.e., large interstitial holes)

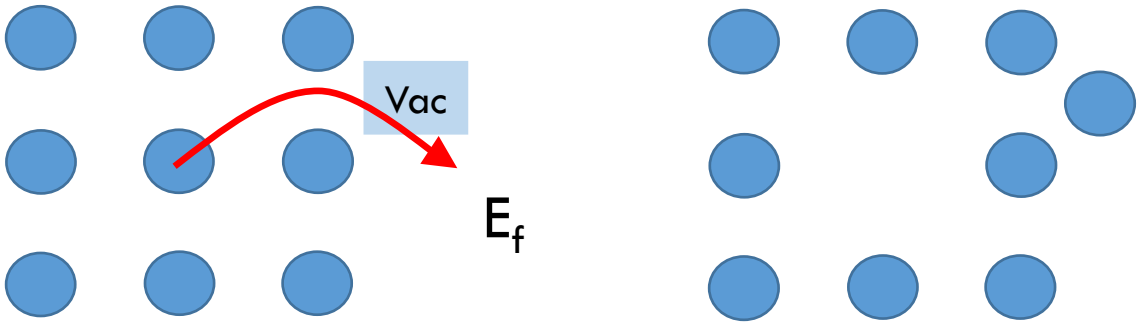
Cations are usually smaller, so they usually go into interstices more easily than anions (exceptions include CaF_2)

Mentimeter

Thermodynamics of intrinsic defects

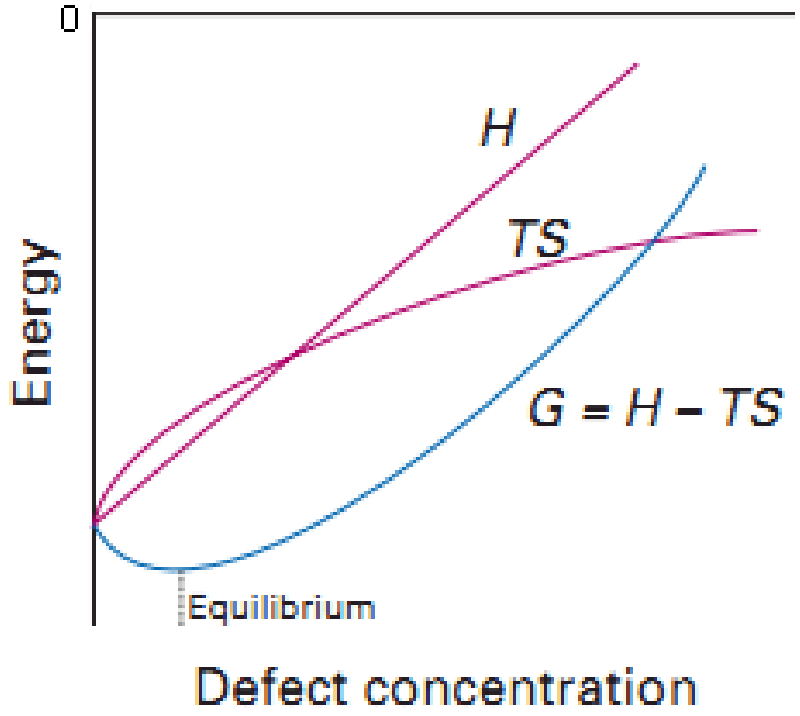
Creating a defect costs energy

Intrinsic defects form spontaneously because they increase entropy



Lower entropy

Higher entropy



Mentimeter

Thermodynamics of intrinsic defects

To estimate the entropy: How many ways are there to distribute n_d defects among N possible sites?

$$W = \frac{N!}{n_d!(N - n_d)!}$$

Calculate entropy using Stirling's approximation:

$$\Delta S = k \ln W \approx k \left(N \ln N - (N - n_d) \ln(N - n_d) - n_d \ln n_d \right)$$

Then the Gibbs free energy is

$$\Delta G = \Delta H - T\Delta S = n_d \Delta H_d - kT \left(N \ln N - (N - n_d) \ln(N - n_d) - n_d \ln n_d \right)$$

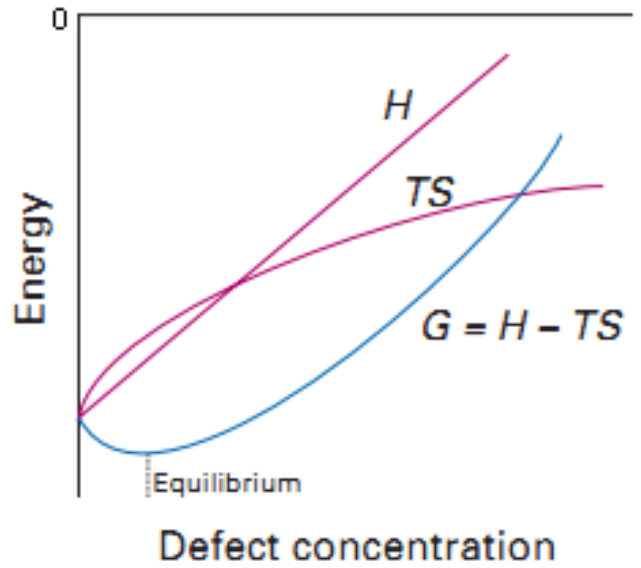
Thermodynamics of intrinsic defects

$$\Delta G = \Delta H - T\Delta S = n_d \Delta H_d - kT\left(N \ln N - (N - n_d)\ln(N - n_d) - n_d \ln n_d\right)$$

At equilibrium, $\dfrac{d\Delta G}{dn_d} = 0$

$$\Delta H_d - kT(\ln(N - n_d) - \ln n_d) = 0$$

$$\frac{n_d}{N - n_d} = \exp\left(-\frac{\Delta H_d}{kT}\right)$$

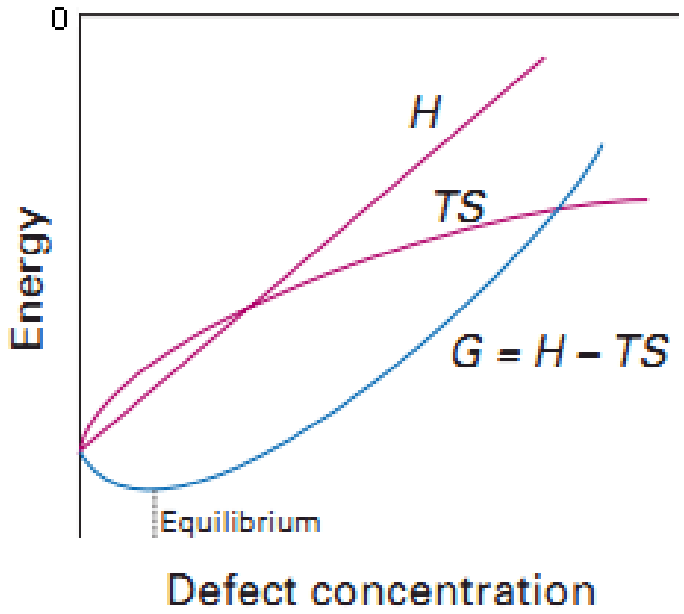


Since $N \gg n_d$, we can find the defect concentration:

$$\frac{n_d}{N} = \exp\left(-\frac{\Delta H_d}{kT}\right)$$

Thermodynamics of intrinsic defects

$$\frac{n_d}{N} = \exp\left(-\frac{\Delta H_d}{kT}\right)$$



Schottky Defects

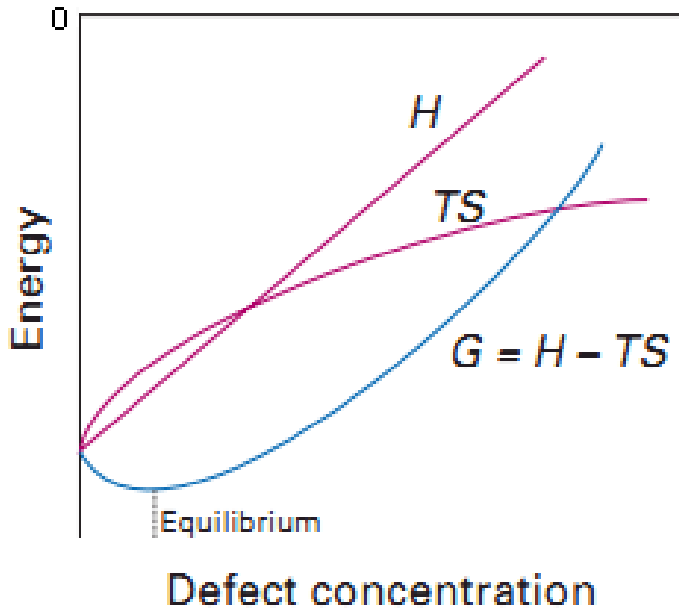
Compound	ΔH (10^{-19} J)	ΔH (eV)
MgO	10.57	6.60
CaO	9.77	6.10
LiF	3.75	2.34
LiCl	3.40	2.12
LiBr	2.88	1.80
LiI	2.08	1.30
NaCl	3.69	2.30
KCl	3.62	2.26

Frenkel Defects

Compound	ΔH (10^{-19} J)	ΔH (eV)
UO_2	5.45	3.40
ZrO_2	6.57	4.10
CaF_2	4.49	2.80
SrF_2	1.12	0.70
AgCl	2.56	1.60
AgBr	1.92	1.20
β-AgI	1.12	0.70

Thermodynamics of intrinsic defects

$$\frac{n_d}{N} = \exp\left(-\frac{\Delta H_d}{kT}\right)$$

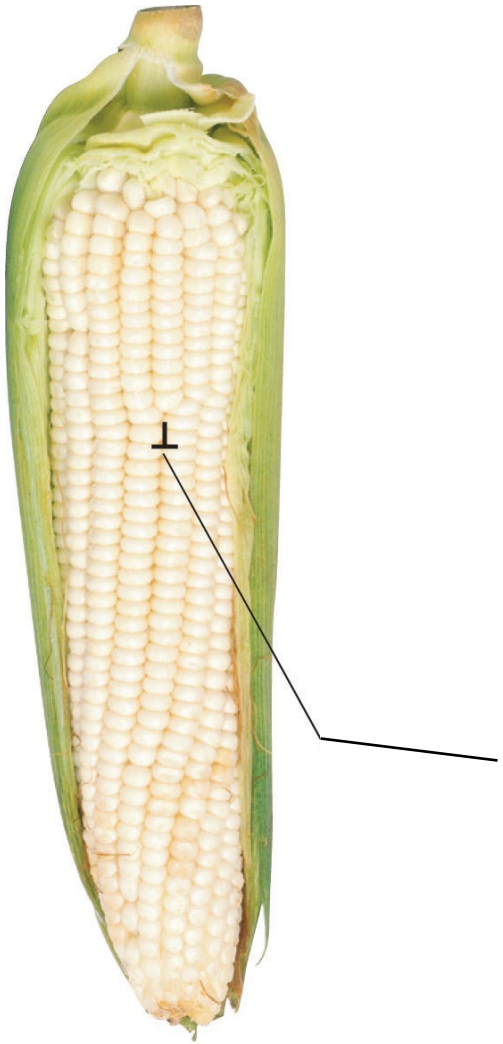


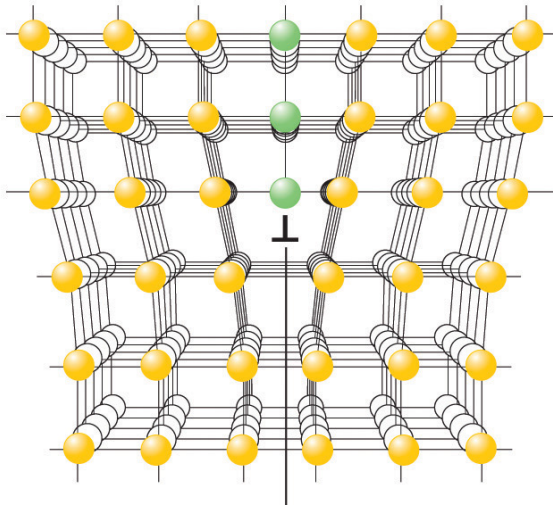
Taking $\Delta H_d = 1$ eV, the proportion of vacant sites at 300 K is 10^{-17}

At 1000 K, this increases to 10^{-7}

At room temperature, there are very few intrinsic defects, and even at 1000 K, it's only a few sites in tens of millions. Nevertheless, they are critical for certain material properties.

Linear defects: Edge dislocations

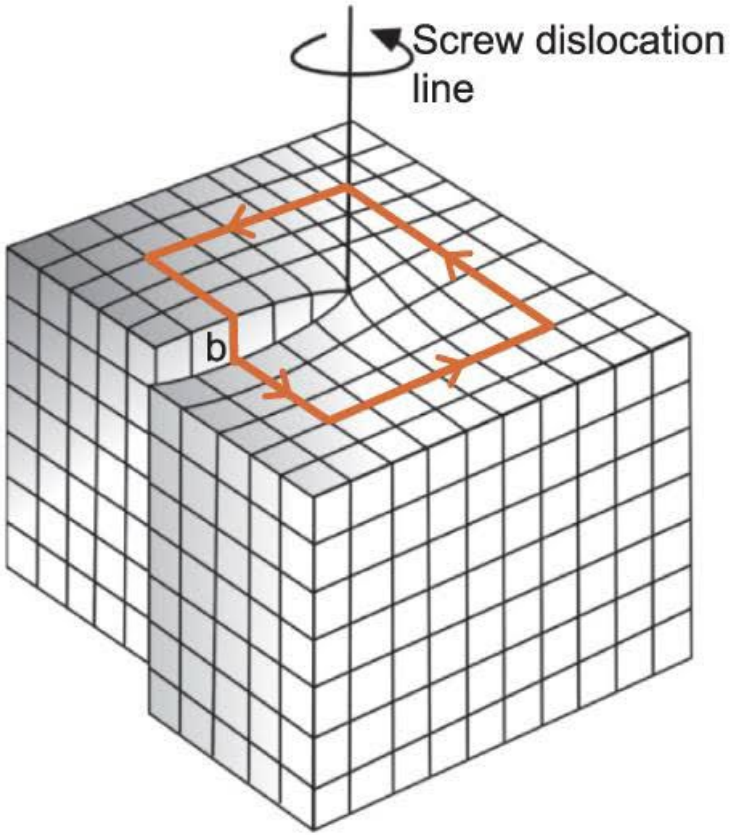




Edge dislocation

Edge dislocations can move ("slip") under shear, allowing for plastic or ductile deformation of the material

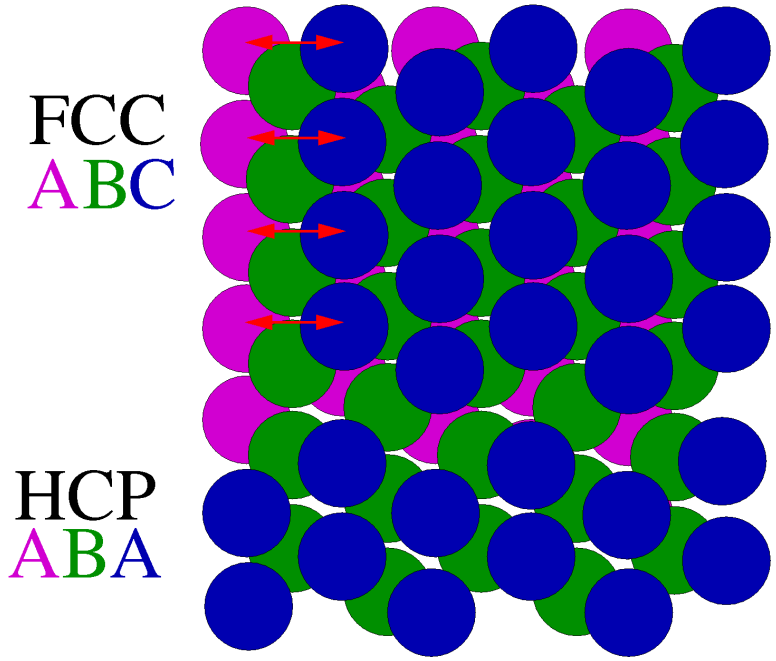
Linear defects: Screw dislocations

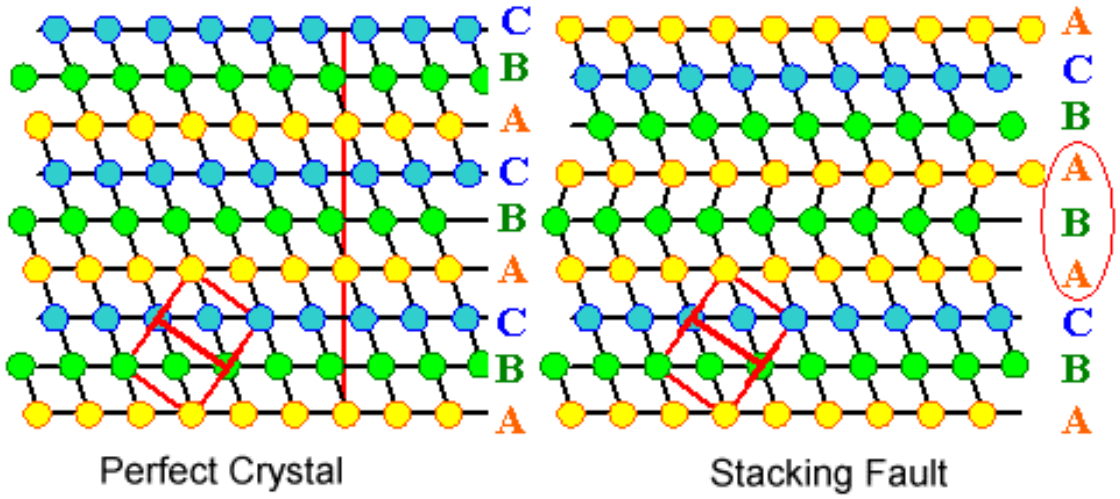


The atoms are arranged in a helical pattern around the screw line

Mentimeter

Planar defects: Stacking faults

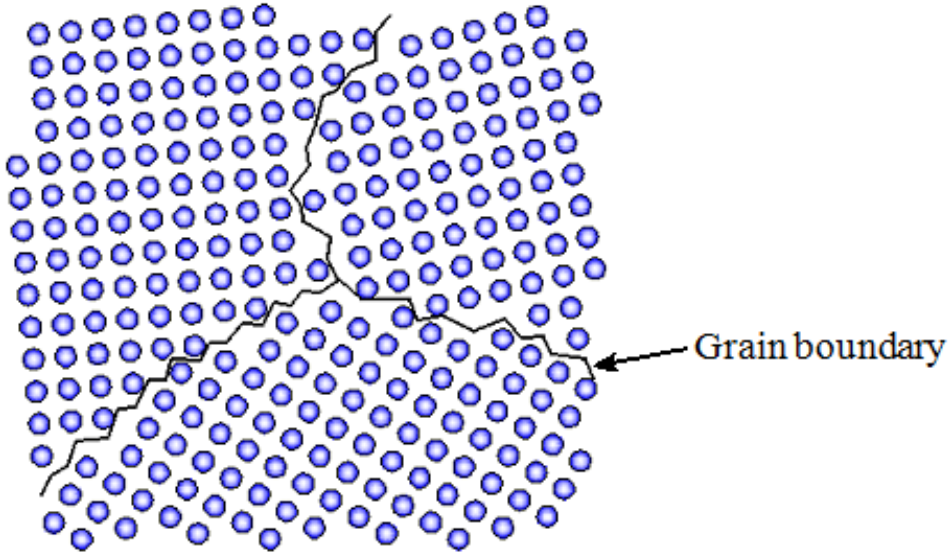


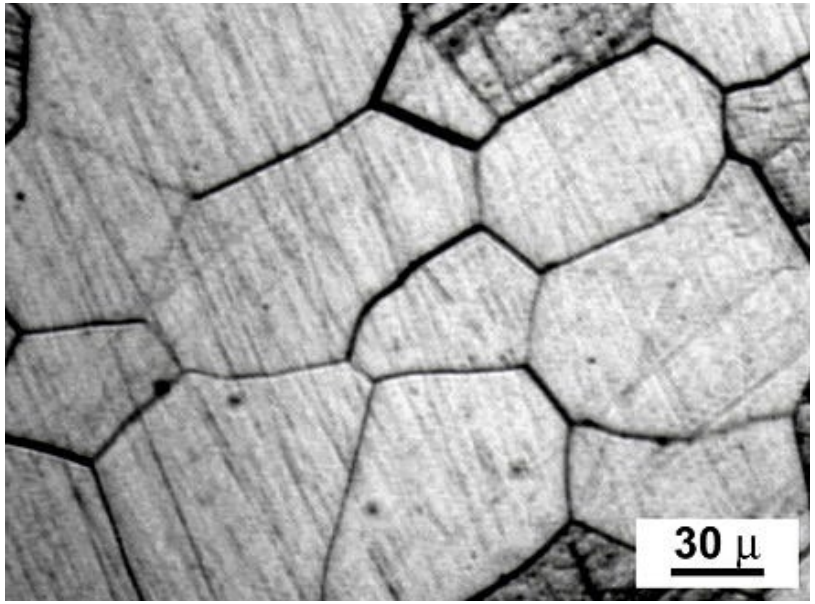


Planar defects: Grain boundaries

Grain boundaries are planes that that separate regions of different crystalline orientation ("grains") in a polycrystalline solid

Often result from non-uniform crystallization conditions, i.e., are extrinsic





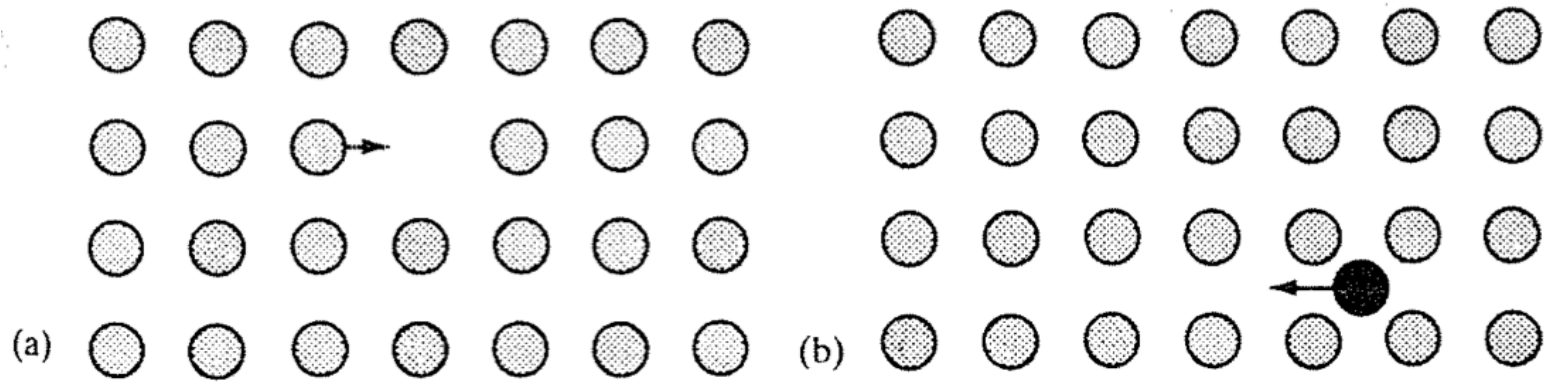
Mentimeter

Ionic conductivity

Atoms are generally trapped on their lattice sites (apart from thermal vibration), lacking the energy to move to another site

At high temperatures, atoms can move from one crystal site to another

Defects are what makes ionic conduction possible



Vacancy mechanism

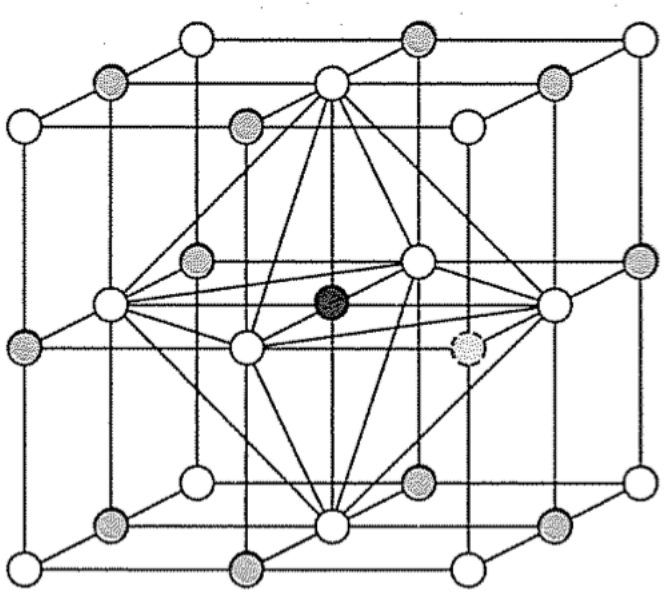
Interstitial mechanism

Ionic conductivity

	Material	**Conductivity / (S m^{-1})**
Ionic Conductors	Ionic crystals	$<10^{-16} – 10^{-2}$
	Solid electrolytes	$10^{-1} – 10^{3}$
	Strong (liquid) electrolytes	$10^{-1} – 10^{3}$
Electronic conductors	Metals	$10^{3} – 10^{7}$
	Semiconductors	$10^{-3} – 10^{4}$
	Insulators	$<10^{-10}$

Ionic conductivity

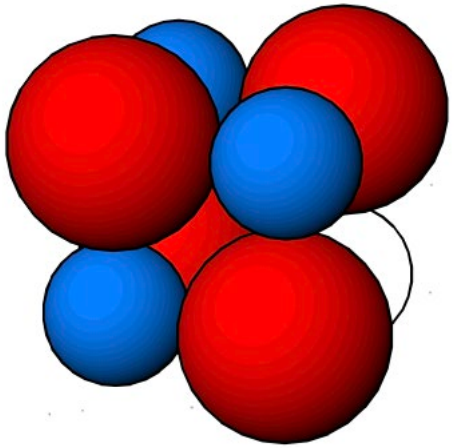
Example: Na^+ motion in NaCl

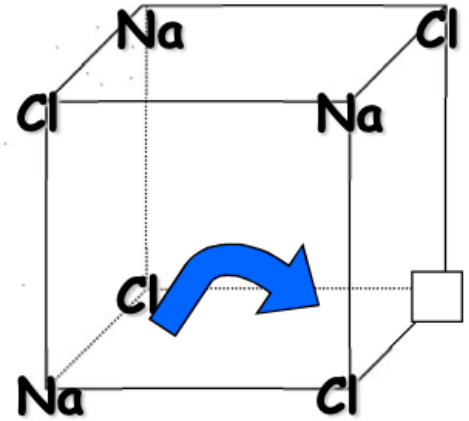


○ X^-

● M^+

◌ M^+ vacancy

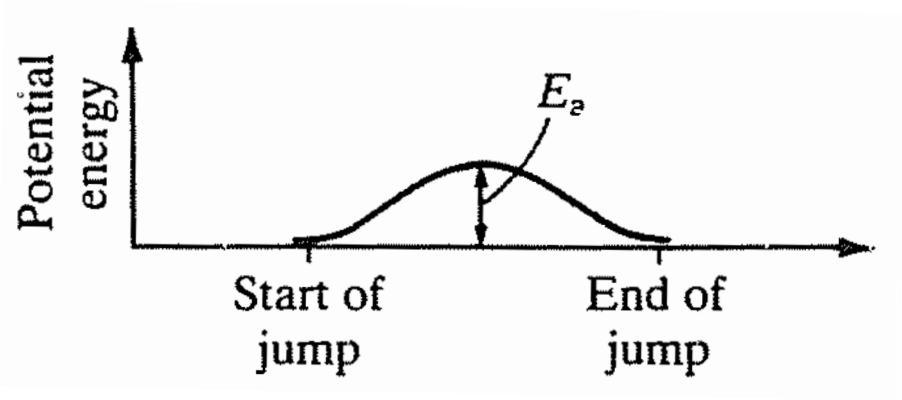


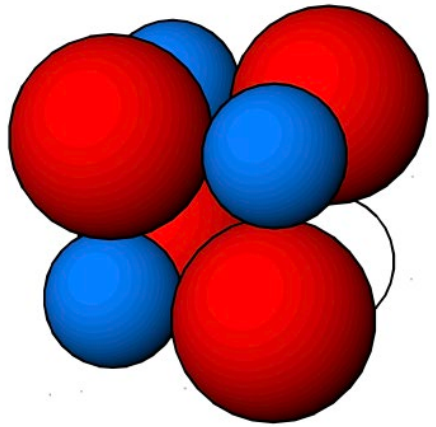


The ion experiences resistance from the crystal structure as it moves

Ionic conductivity

The energy needed to jump is the *activation energy*





Therefore, ionic conductivity usually obeys the Arrhenius equation

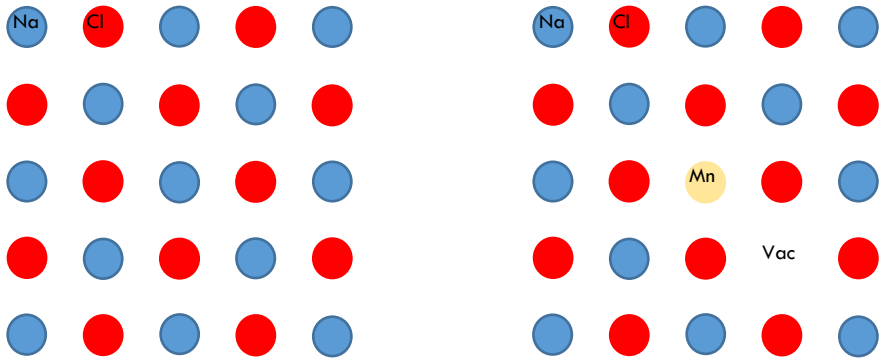
$$\sigma = \sigma_0 e^{-E_a/kT}$$

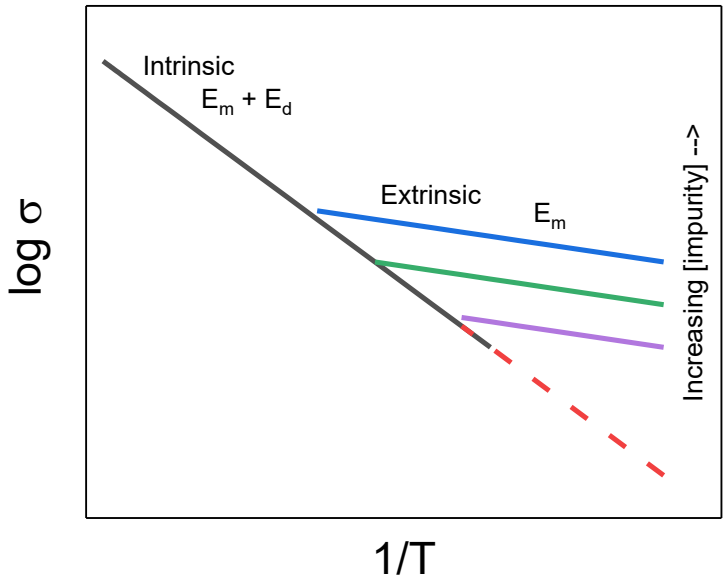
Extrinsic defects can increase conductivity

Conductivity can be increased by adding defects

Example: doping NaCl with $MnCl_2$ yields $Na_{1-2x}Mn_xV_xCl$

For each Mn cation added there is one associated cation vacancy.





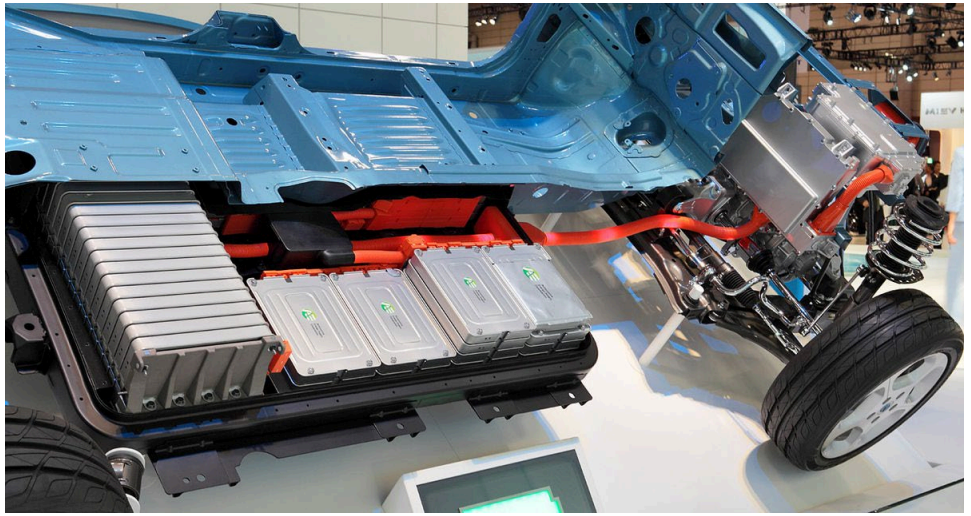
At low *T*, conductivity is dominated by the impurity concentration. At high *T*, intrinsic defects dominate.

How does this compare to the increased *electrical* conductivity when Si is doped?

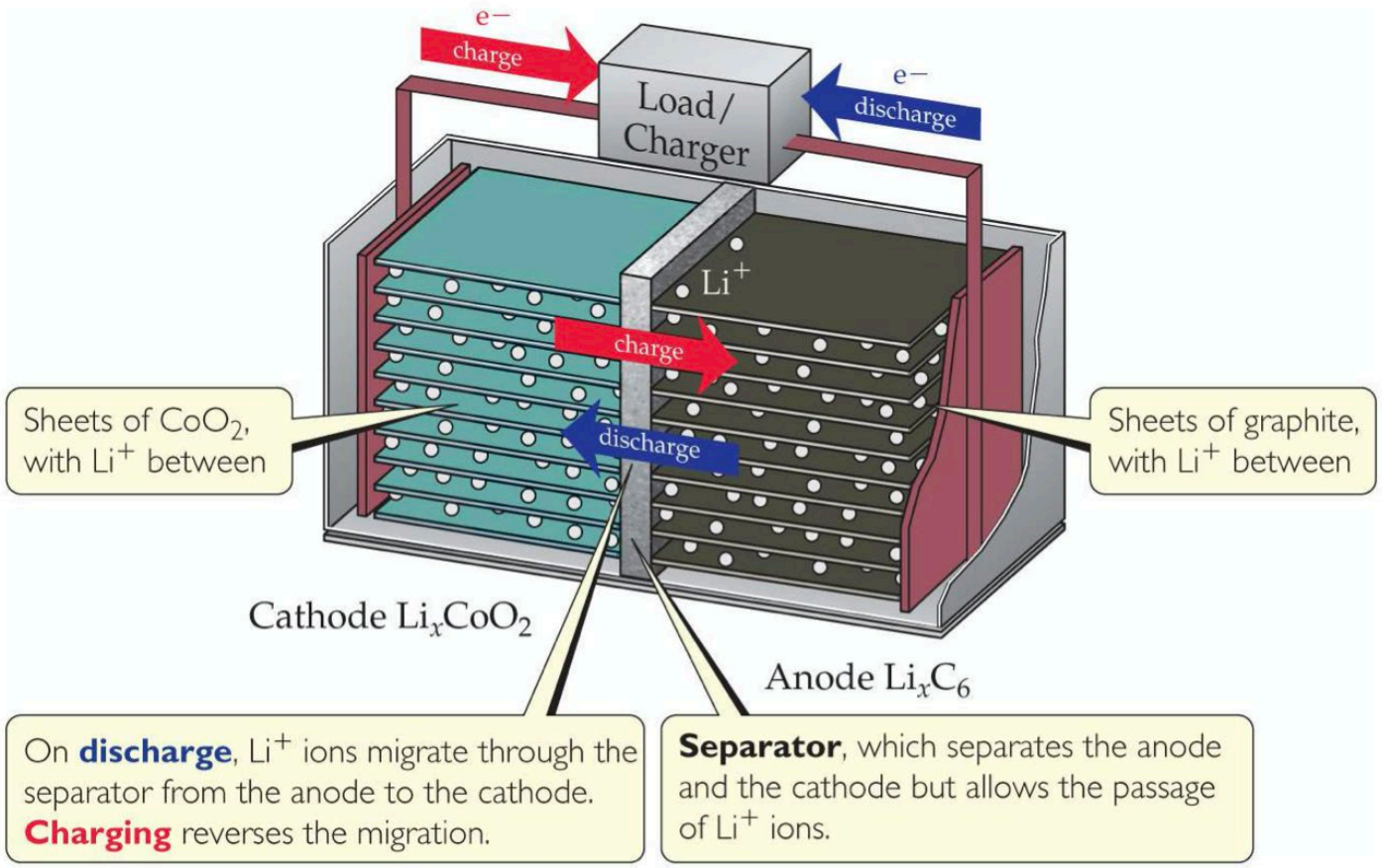
Applications of ionic conductivity

Ionic conductivity underpins several industrial applications:

- Batteries
- Solid-oxide fuel cells
- Halide-selective electrodes
- Membranes in separation processes



Lithium-ion batteries

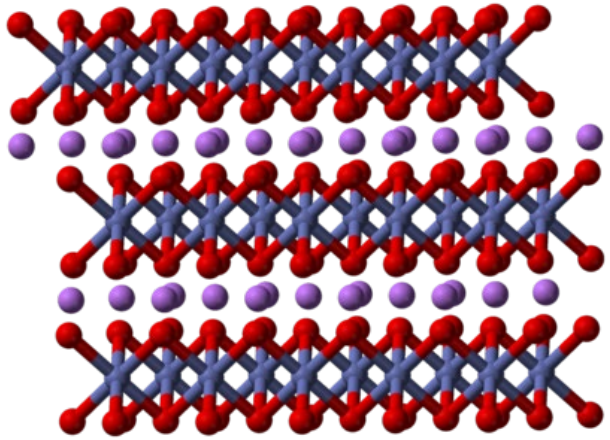


Anode reaction:

$LiC_6 \longrightarrow Li^+ + 6C + e^-$

Cathode reaction:

$Li^+ + CoO_2 + e^- \longrightarrow LiCoO_2$



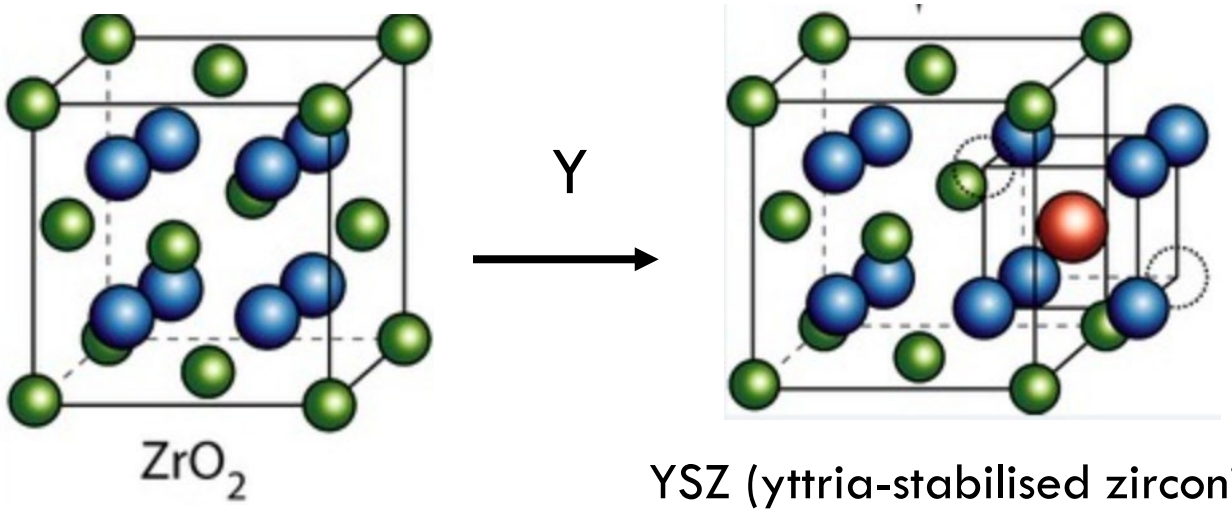
Solid-oxide fuel cells

Anode reaction:

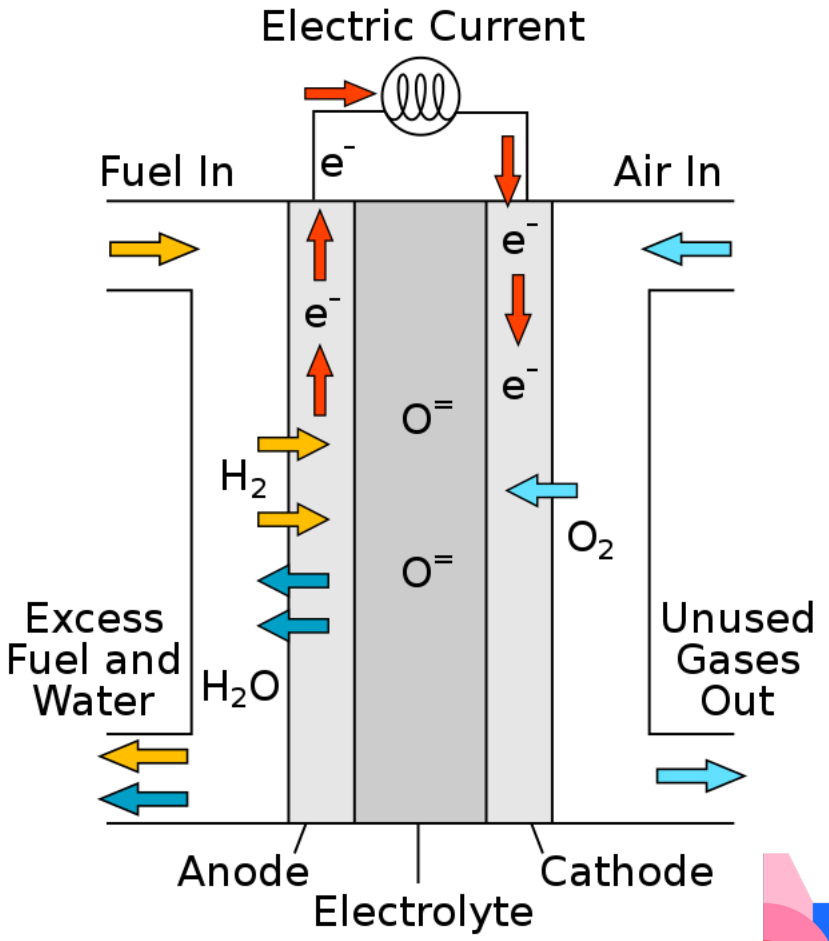
$2H_2 + 2O^{2-} \rightarrow 2H_2O + 4e^-$

Cathode reaction:

$O_2 + 4e^- \rightarrow 2O^{2-}$



YSZ (yttria-stabilised zirconia)



Mentimeter

Summary

Key points:

- Defects: point/line/plane
- Point defects can be intrinsic or extrinsic
- All solids contain intrinsic defects at non-zero temperature
- Defects blur x-ray diffraction
- Defects allow ionic conductivity
- Ionic conductivity has an activation barrier, and is described by an Arrhenius relationship
- Ionic conductivity underpins solid-state batteries

Next time

So far, we've only looked at the equilibrium of one kind of substance.

Sometimes, multiple phases of matter can coexist, and the transformation between them is the topic of phase transitions

We'll first look at some relatively simple examples, before moving on to explain common phase transitions like the boiling of a liquid