Inorganic Materials Chemistry and Nanomaterials

Core Module 9

Inorganic Materials Chemistry and Nanomaterials

8 lectures Module 9

Synopsis

1. Structural concepts: Dimensionality, defects and non-stoichiometry

2. Dynamics in solids: Batteries and dielectric materials

3. Magnetic Materials: Paramagnetism and Cooperative magnetism

4. Metals and Superconductivity: Electronic conduction.

5. Nanomaterials: Synthesis, characterisation and structure

6. Nanomaterials: Properties and applications

Bibliography:

H. M. Rosenberg	'The solid state'
A. R. West	'Solid state chemistry and its applications'
L. Smart and E. Moore	'Solid state chemistry. An introduction'
A. K. Cheetham and P. Day	'Solid state chemistry. Techniques'
M. T. Weller	'Inorganic materials chemistry'
Shriver and Atkins	'Inorganic Chemistry'

Associated Courses

AKD	Transition metals	1st year
MAB	Solid state structure	1st year
JML	Structure and bonding	1st year
RED	Metal-ligand bonding	2nd year
TD	Processes at solid surfaces	3rd year
NTH	Photochemistry	3rd year
KDC	Diffraction	3rd year

Learning Objectives: by the end of the course you should be able to

i) explain structure types and polymorphism.

ii) explain the main reasons for and types of defects in ionic solids.

iii) calculate the proportion of defects in a solid.

iv) explain what is meant by a non-stoichiometric solid and a solid solution.

v) understand the principles of a battery and calculate energetics

vi) describe the perovskite structure and its relation to ferroelectricity using the tolerance factor.

vii) describe the phenomenon of piezoelectricity and pyroelectricity.

viii) understand and explain the behaviour of a paramagnet, antiferromagnet, ferromagnet and ferrimagnet as a function of temperature.

ix) explain the effect of domain structure of ferro- and ferrimagnets.

x) explain the superexchange mechanism for rock salt metal oxides.

xi) describe the spinel structure and estimate the net magnetic moment of ferrimagnets.

xii) Understand basic models of electrical conductivity in metals and semiconductors, Fermi energy/level, density of states, and semiconductor doping.

xiii) describe the electric and magnetic properties of superconductors.

xiv) explain the structural characteristics of cuprates, fullerides and borides.

xv) qualitatively describe BCS theory of superconductivity and the relationship between T_c and atomic mass.

xvi) understand the structural differences between bulk materials and nanomaterials.

xvii) describe methods of synthesis of solid state compounds using examples.

xviii) understand the difference between synthesis and modification of materials.

xix) describe the use of diffraction, microscopy and spectroscopic methods used to characterise (nano)materials.

xx) understand the limitations of techniques for the analysis of (nano)materials.

xxi) understand the relationship between the size of nanoparticles and their physical properties.

Introduction

What is materials (solid state) chemistry?

Solid state chemistry is concerned with the synthesis, structure, properties and application of solids including inorganic and organic materials and their composites.

At the interface of chemistry, solid state physics, materials science, ceramics, mineralogy and metallurgy.

Why is materials (solid state) chemistry important?

Society and technology are underpinned by the solid state sciences. For example

Computing (data storage, CD lasers, batteries, metals, semiconductors)
Construction (concrete, steels)
Transport (catalytic converters, fuel cells, strong lightweight materials)
Chemicals (catalysts, sensors, coatings, additives)
Medicine (artificial joints, bones, and muscle)
Gems (jewellery, cutting tools, lasers)
Energy (Solar panels (metals and semiconductors), wind turbines, batteries, nuclear fission, and fusion containment)

The function of a material is dependent on the structure and composition

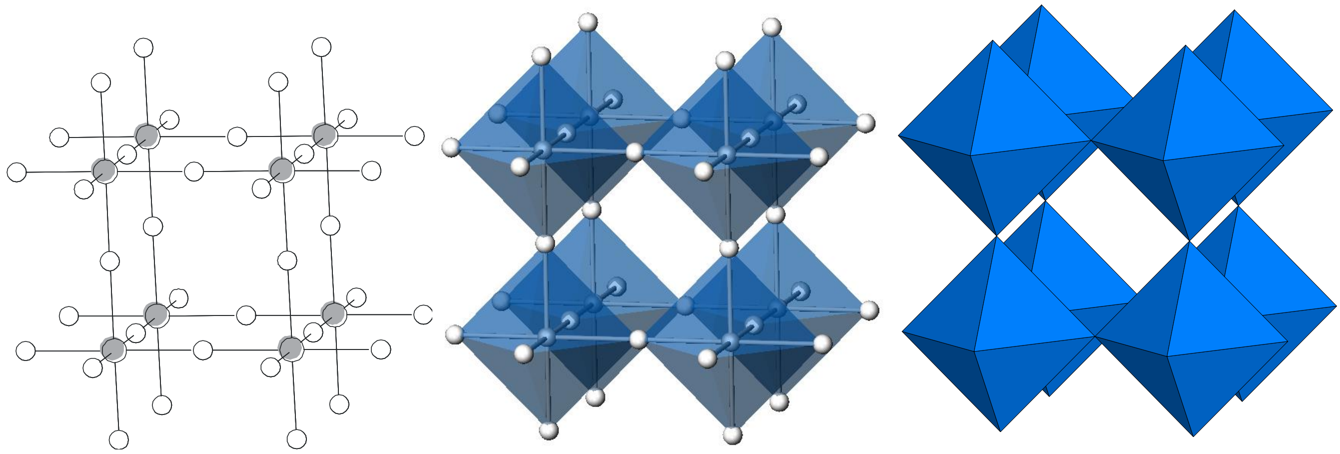
Structural Concepts

1. Crystallinity

Solids exhibit a continuum of order from perfect crystals to totally amorphous.
long range order = crystalline (e.g. SiO_2 as quartz)
short range order = amorphous (e.g. SiO_2 as glass).

Structure types

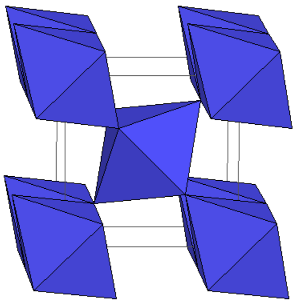
Structures of compounds can be divided into classes. Traditionally each class is named after an archetypal compound or mineral.



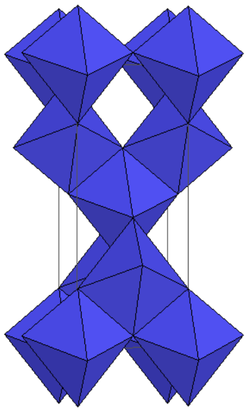
'ball and stick' and polyhedral representations of ReO_3 structure type

e.g.1 ReO_3 is built from vertex sharing ReO_6 octahedra. Any other compound that exhibits this type of structure (e.g. NbF_3) is called a *structure type*.
NbF_3 has the ReO_3 structure type.
e.g.2 The rock salts. These are simple cubic structures that many alkali metal halides adopt e.g. NaCl. NaCl has the rock salt structure type.

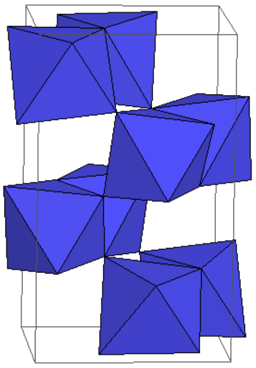
2. Polymorphism



Rutile



Anatase



Brookite

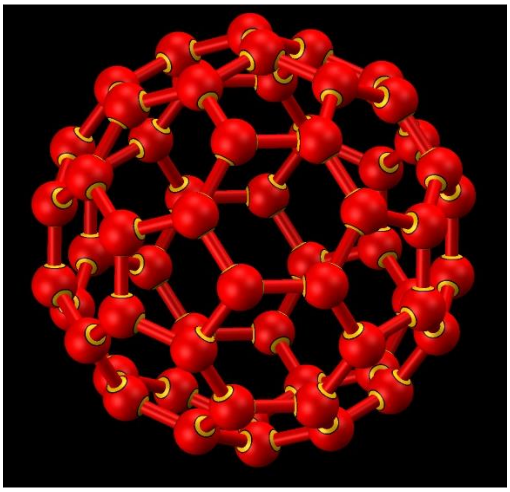
Some elements have allotropes e.g. C (graphite, diamond, fullerenes) and some molecular compounds have isomers e.g. (alkanes).

Some solid compounds can also have more than one crystalline structure for a single stoichiometry. This is called *polymorphism* and individual structures are called *polymorphs*. Rutile, anatase and brookite are all polymorphs of TiO_2. Individual polymorphs will be thermodynamic stability at a particular pressure and temperature, but other polymoprhs can have kinetic stability at the same pressure and temperatures

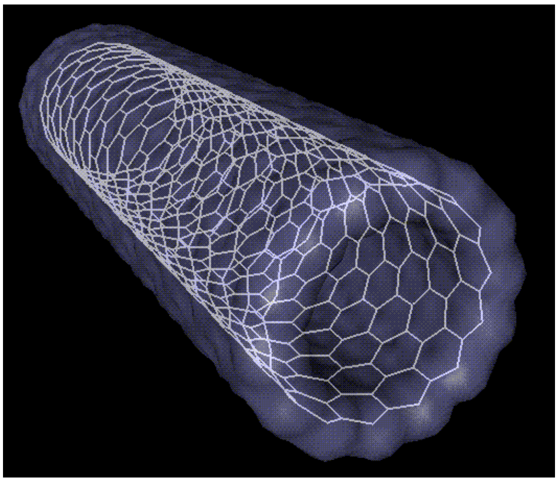
Often a solid having a particular crystalline structure and stoichiometry is referred to as a *phase*.

3. Dimensionality and porosity

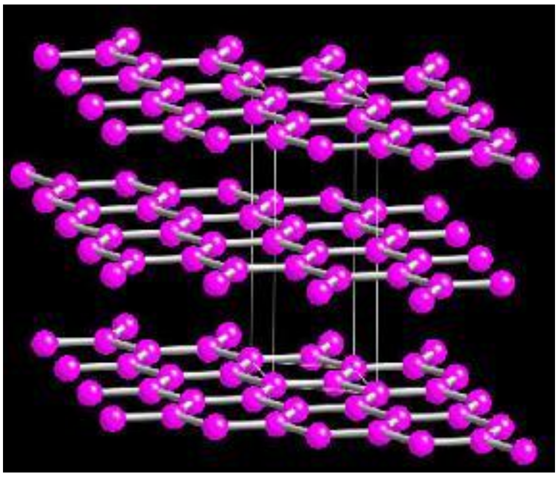
Dimensionality is important in understanding the properties of solids.
e.g. C_{60}, nanotubes, graphite and diamond.



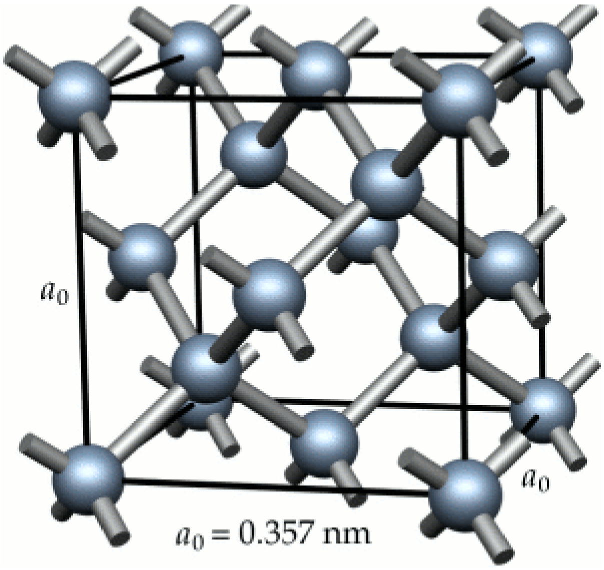
C_{60} (0-D). Soluble molecule.



Carbon nanotube (1-D). Semiconductors. Immense tensile strength.

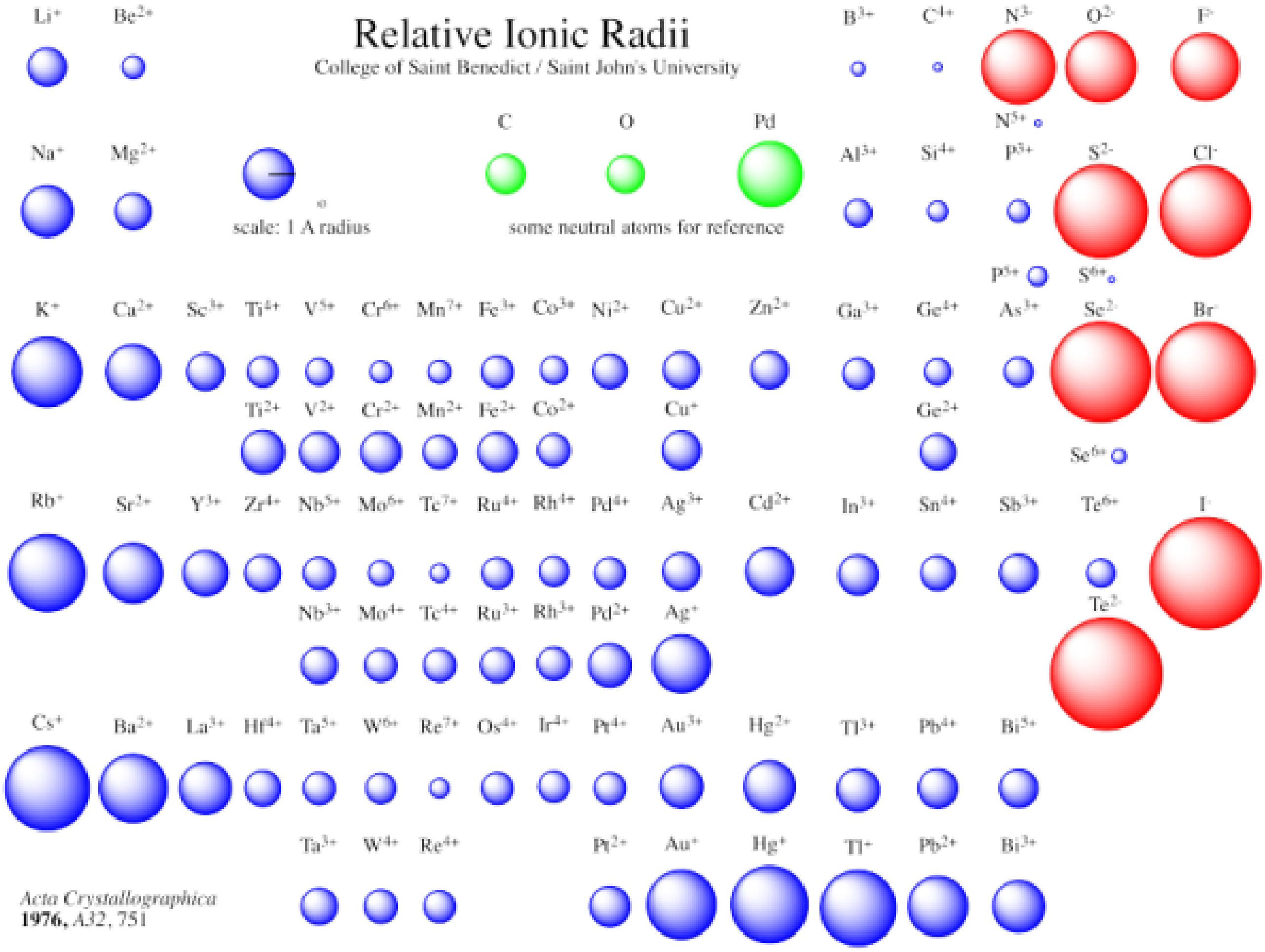


Graphite (2-D). Soft semimetal.



Diamond (3-D). Hard insulator.

Some general notes on structure



Acta Crystallographica
1976, *A32*, 751

1. For ionic structures (e.g. oxides, halides, silicates) the anions are much bigger than the cations. Therefore,

   the anions are close packed and the cations fit into the interstitial sites.

   the cations will be more mobile.

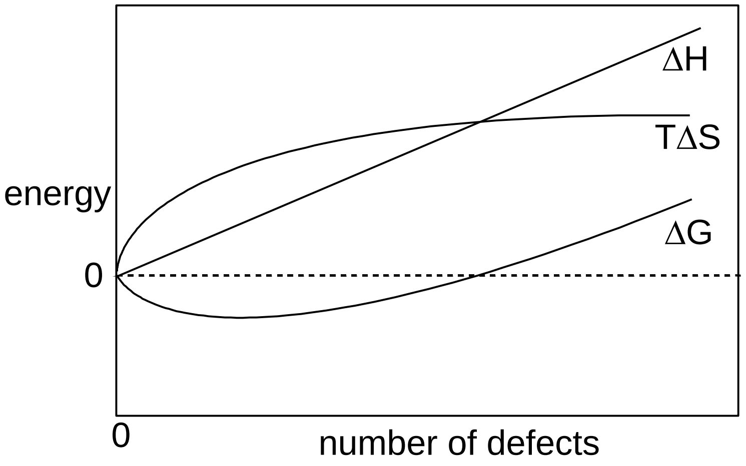
2. In drawings for solid structures lines between atoms do not always mean there is a localised bond. Particularly in ionic compounds the lines describe coordination (nearest neighbours). However, many ionic compounds do have some covalent character which can be used to understand properties.

3. The overall charge of a bulk solid will be zero. However, charge can be distributed heterogeneously (e.g. in a dielectric (see later))

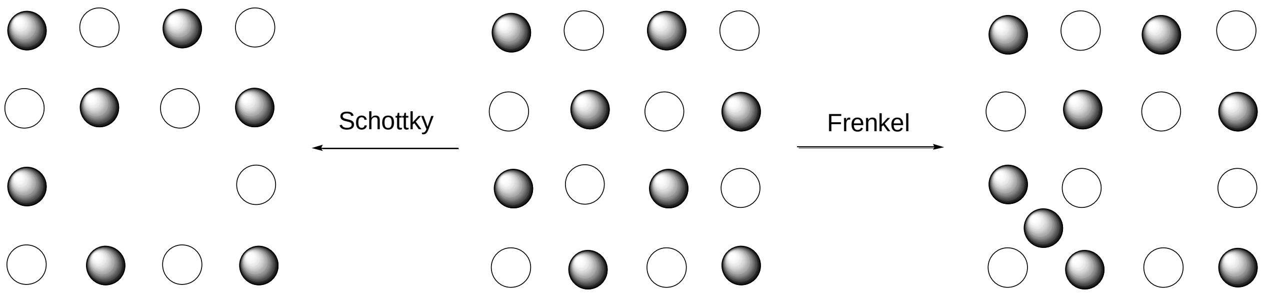
4. Defects and non-stoichiometry

Note: overall charge balance must be maintained.

Only at 0 K will an ionic crystal have a perfectly ordered array of atoms where every atomic lattice point contains an atom.
At > 0 K crystals contain defects. Defect formation requires energy and is always endothermic. However a structure with defects has higher entropy.
Increased entropy drives defect formation to $\Delta G = 0$ (equilibrium).
Remember $\Delta G = \Delta H - T\Delta S$. Strong temperature dependence on the number of defects.

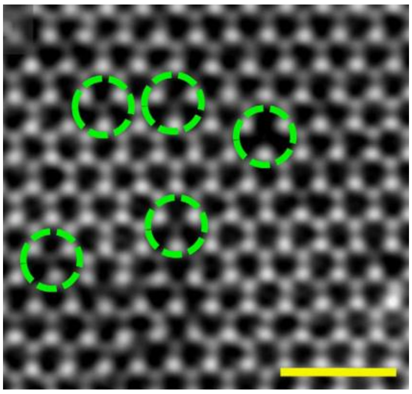


Point defects (intrinsic)
Vacancy: An ion is missing
Interstitial: an extra ion is present in an interstitial site
Schottky: a pair of vacancies are present in the lattice.
Frenkel: a defect pair is created by an ion (usually cation) moving into an interstitial site.
The lattice will distort at the vacancy site to minimise the loss in lattice energy. Vacancies or interstitial atoms do not have to be adjacent and can be mobile.



$$\text{Proportion of defects} \quad \frac{n_{S(F)}}{N} = \exp(-\Delta H_{S(F)}/2kT)$$

Where n_S (n_F) = Shottky (Frenkel) defects per unit volume, ΔH_S ((ΔH_F) = Shottky (Frenkel) enthalpy of formation, N = number of cation and anion sites per unit volume.



TEM of S vacancies in MoS_2 (scale bar 1 nm) (J. Hong et al, Nature Commun. **2015**, 6, 6293)

Temperature (K)	Compound (defect)	ΔH (10^{-19} J)	n/N
300	MgO (S)	10.57	3.62×10^{-56}
300	CaO (S)	9.77	5.69×10^{-52}
300	LiF (S)	3.75	2.14×10^{-20}
300	LiCl (S)	3.40	1.46×10^{-18}
300	LiBr (S)	2.88	7.83×10^{-16}
300	LiI (S)	2.08	1.23×10^{-11}

300	β–AgI (cation F)	1.12	1.33×10^{-6}

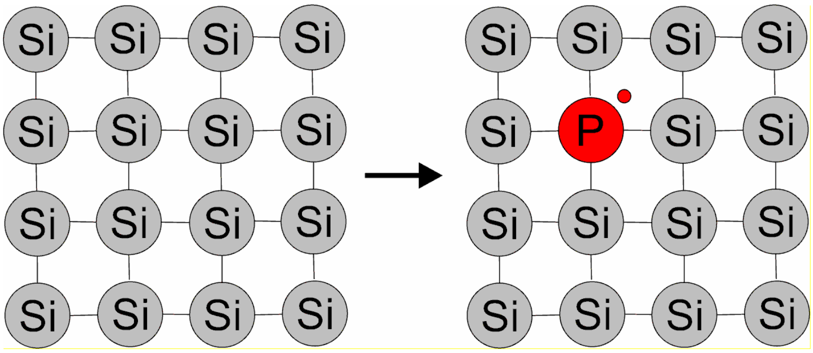
500	LiCl	3.40	1.99×10^{-11}
750	LiCl	3.40	7.35×10^{-8}
1000	LiCl	3.40	4.46×10^{-6}

The percentage of intrinsic point defects in most ionic compounds is small but they can have a significant effect on electrical, magnetic and optical properties. The smallest ΔH (ΔH_S or ΔH_F) will determine if Schottky or Frenkel defects dominate.

Point defects (extrinsic)

Introducing different ions into the structure. This is known as ***doping***.

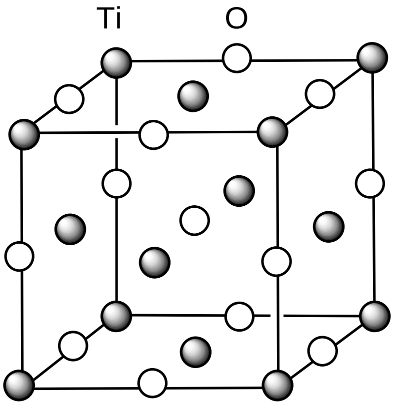
Silicon (group 14) is not a good conductor of electricity. If Si is doped with small amounts (1%) of P (group15) the conductivity increases significantly as an occupied state is introduced just below the Si conduction band. In effect after forming bonds to silicon the remaining electron from P acts as a conduction electron.

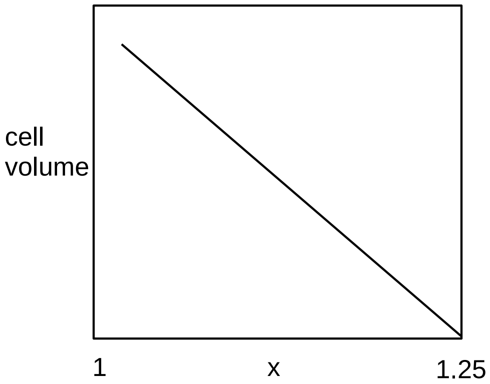


Non-stoichiometry and solid solutions

Defects and doping result in non-stoichiometric solids. e.g. $YBa_2Cu_3O_{7-x}$ (0<x<1). Non-stoichiometry is common for compounds of transition metals that can have variable oxidation state.

e.g. TiO is non-stoichiometric. It has the rock salt structure over the range TiO_x (where $0.7 < x < 1.25$).
Non-stoichiometric compounds are distinct from other compositions e.g. TiO_2 because they have a common structure.
However the lattice parameters (size of the unit cell) of the structure will change gradually as the ratio of elements changes.





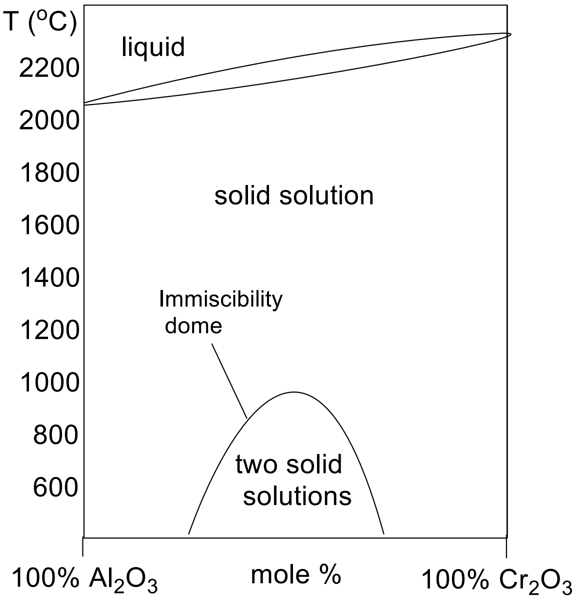
Consider that $TiO_{1.25}$ can be rewritten as $Ti_{0.8}O$. Is the non-stoichiometry due to extra oxygen present in interstitial sites or vacancies on the titanium site?

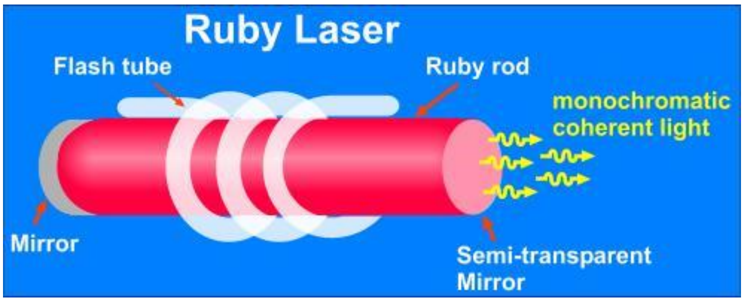
From experimental evidence
At $x < 1$ oxygen vacancies are present in the structure
At $x > 1$ titanium vacancies are present in the structure
TiO has both Ti and O vacancies!
What is the average oxidation state of Ti in $TiO_{1.25}$?
$Ti^{2.5+}$ = 50:50 mixture of Ti^{2+} and Ti^{3+}

Solid solutions are commonly observed in non-stoichiometric solids. A solid solution is a crystalline solid that can have continual variable composition for a given structure type. They are a useful method of discovering and fine-tuning properties. e.g. lasers and steel.

There are two types: *substitutional* where a new atom replaces an existing atom. e.g. by doping, and *interstitial* where an atom is added to an interstitial site.

Substitutional Al_2O_3 and Cr_2O_3 can form a solid solution over the compositional range $(Al_{2-x}Cr_x)O_3$ $0 < x < 2$. $x < 0.05$ (ruby)





Interstitial. e.g. C in Fe giving FeC_x $0 < x < 0.09$ (C atoms occupy the interstitial sites of Fe). (steel).

The Forth Bridge

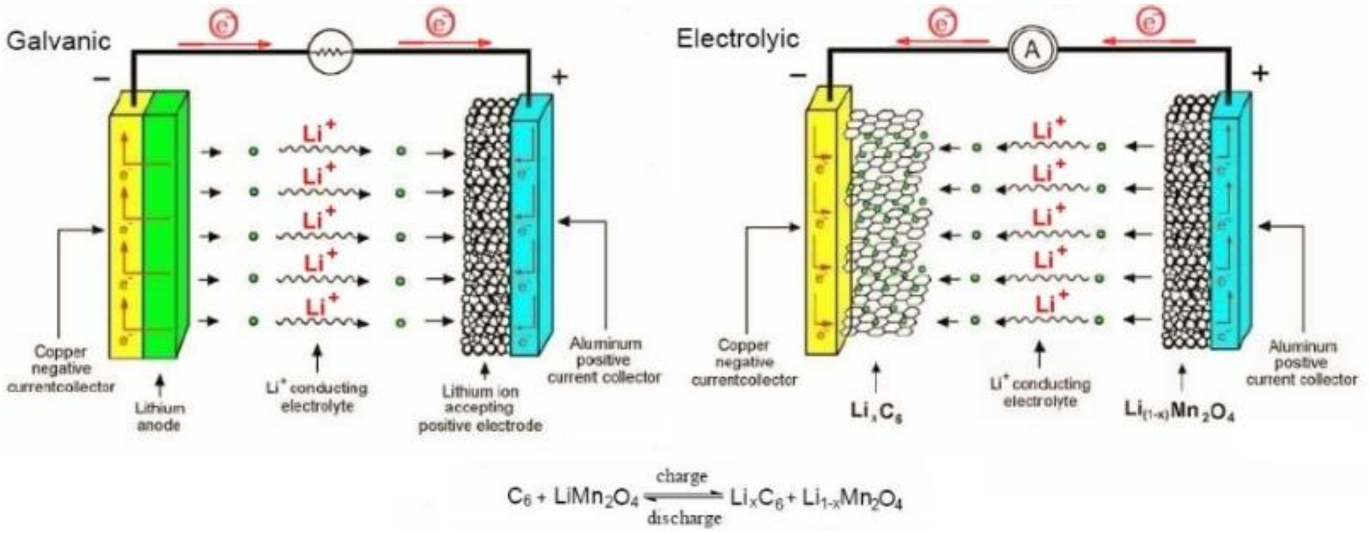
Dynamics in solids

Above 0 K, atoms and ions in compounds move and respond to external stimuli (e.g. magnetic and electric fields, pressure and temperature).

Long range movement of ions (μm-mm)

batteries and fuel cells

Lithium ion batteries (rechargeable) (Nobel Prize 2019)



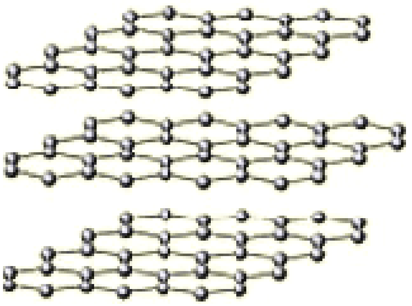
$$C_6 + LiMn_2O_4 \underset{\text{discharge}}{\overset{\text{charge}}{\rightleftharpoons}} Li_xC_6 + Li_{1-x}Mn_2O_4$$

Discharge Charge

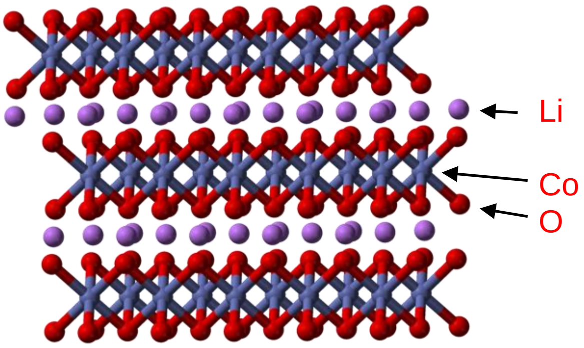
Batteries comprise two electrodes and an electrolyte (+membrane and connector-contacts). The Li^+ must be mobile in all the electrodes and electrolyte materials.

Intercalation/deintercalation

Species can be added/removed from a host structure. Needed for charge/discharge cycles. Important structural features: layers, channels or porosity provide space for Li^+ to move.



Graphite



$LiCoO_2$

$$xLi^0 + \text{graphite } (C_6) \xrightarrow{\text{intercalation}} Li_xC_6 \qquad 0 < x < 1$$

$$LiCoO_2 \xrightarrow{\text{deintercalation}} xLi^+ + e^- + Li_xCoO_2 \qquad 0 < x < 0.5$$

Energetics

E_{cell} (V) = $E_{cathode} - E_{anode}$

Power (W) = voltage (V) x current (A)

Charge (Ah) = current (A) x time (h) 1 Ah = 3600 C

Energy (Wh) = Power (W) x time (h) 1 Wh = 3600 J

Energy density = Energy stored per unit battery volume (Wh L^{-1})

Specific energy = Energy stored per unit battery weight (Wh kg^{-1})

Examples

AA battery (1.5V, 3 Ah) = 4.5 Wh

Lead Acid (12 V, 50 Ah) = 600 Wh

Lithium Ion battery laptop (10 V, 5 Ah) = 50 Wh

Toyota Prius battery (202 V, 6.5 Ah) = 1300 Wh

c.f. Tank of petrol = 600,000 Wh

e.g. For a lithium battery during discharge

$$LiC_6 \longrightarrow e^- + Li^+ + \text{graphite } (C_6)$$

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

$$e^- + Li^+ + CoO_2 \longrightarrow LiCoO_2 \qquad E^o \sim +1\text{ V}$$

$$e^- + Li^+ + \text{graphite } (C_6) \longrightarrow LiC_6 \qquad E^o = -3\text{ V}$$

E_{cell} = 1 - (-3) = 4V

$\Delta G = -nFE$ (F = 96500 C mol^{-1}) = -386000 J mol^{-1} = -107.2 Wh mol^{-1}

LiC_6 = 79 g mol^{-1}, CoO_2 = 91 g mol^{-1}

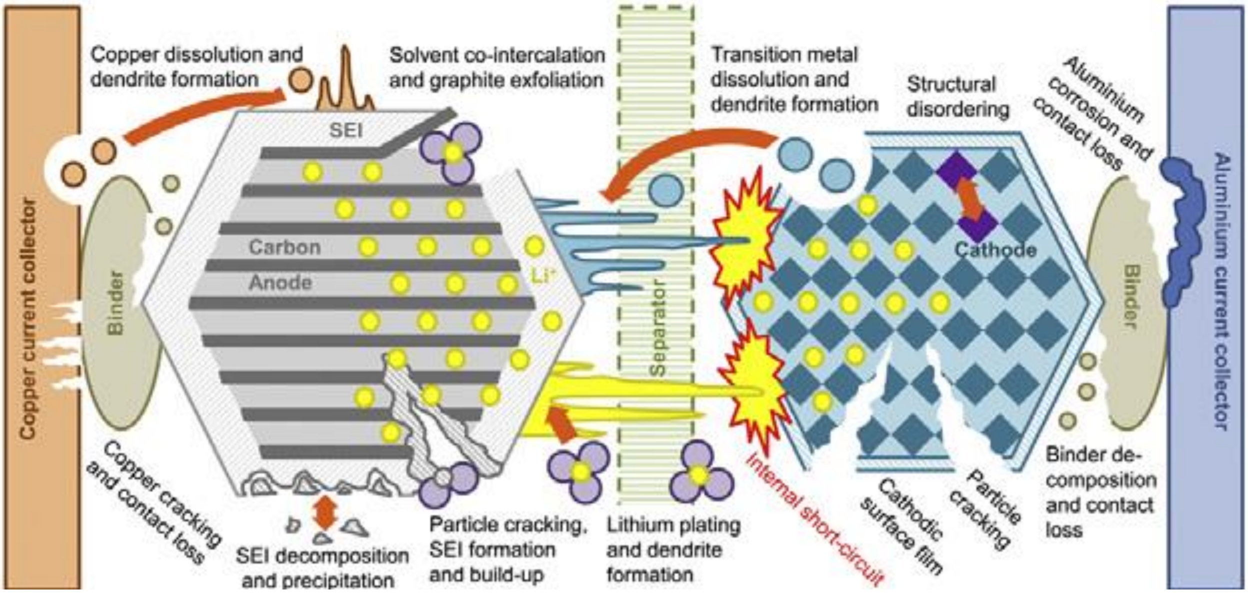
Theoretical specific Energy = -107.2/0.170 = 630.6 Wh kg^{-1}

In reality about 30% is achieved ~ 190 Wh kg^{-1} because of resistivity losses and the extra weight of terminals, case, separators etc.

Challenges

Battery science is a complicated chemical and engineering problem

Goals
Maximise energy density and/or specific energy with long life
Cheap manufacturing/recycling using sustainable elements



Potential Problems (*Journal of Power Sources* **2017,** *341*, 373 – 386)

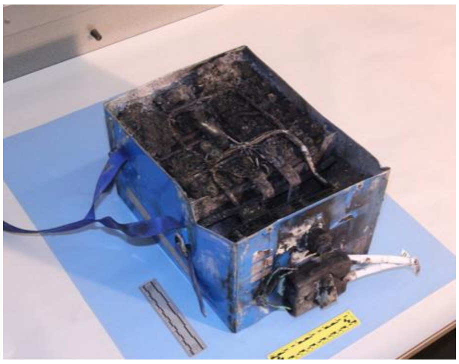
Intercalation/deintercalation should not result in big structural changes
leads to mechanical stress, fracture and performance loss

Avoid uncontrolled Li metal growth (dendrites)
leads to shorting and probable ignition of the flammable electrolyte.

Interfaces between electrodes and electrolyte are critical. (solid electrolyte interface (SEI))
growth of secondary layer on electrodes usually helps to prevent degradation of electrolyte on contact with strongly reducing and oxidizing electrodes and growth of Li dendrites.

Kinetics of charge and discharge are also critical (fast charge/discharge)
But not too fast!

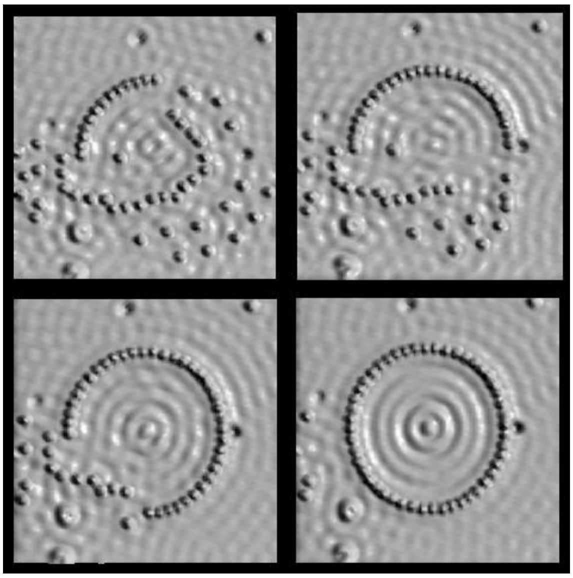
Boeing Dreamliner 787



Battery Fires in 2012

Localised movement of ions (pm)

electronics
(capacitors (in all electronic devices), switching, radio, radar)
transducers
(sound generation (sonar and ultrasound), measurement (e.g. light and pressure sensors), time keeping)
Many scientific instruments
(spectrometers, microbalances, electron microscopy and atom manipulation)

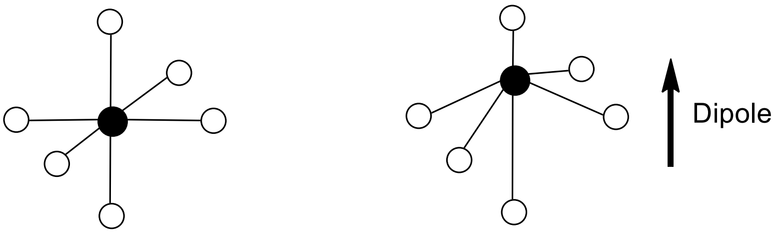


‘Quantum coral’ 48 Fe atoms positioned on a Cu(111) surface.
Crommie et al, *Science*, 1993, 262, 218

How is it possible to manipulate individual atoms with pm precision?
Piezolelectric materials (also used to generate ultra sound)

Ultrasound Scan (Douthwaite et al, 2014)

When an ion is in an asymmetric site there will be a local dipole moment.

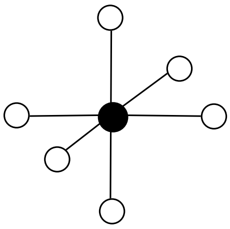


To obtain a bulk polarisation (*P*) the material must have a non-centrosymmetric crystal structure otherwise the local dipoles cancel out.

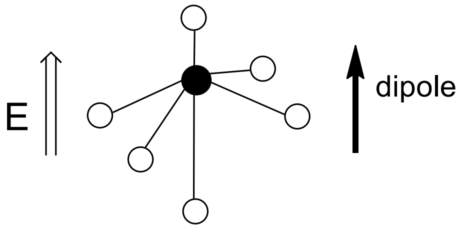
Any process that changes the relative position of ions will change the polarisation.

Ferroelectrics-dipoles respond to an electric field (energy storage (electrical potential))
Piezoelectrics-dipoles respond to pressure (convert kinetic to electrical potential and vice versa)
Pyroelectrics-the dipoles respond to heat (photons) (convert heat to electrical potential)

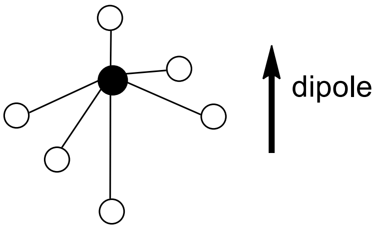
Ferroelectrics can retain polarisation (*P*) after the electric field has been removed and have a very high dielectric *permittivity*, ε_r.



Symmetric electric field
No dipole moment,I *P* = 0



Apply electric field (*E*) displaces ion
dipole moment, *P* > 0



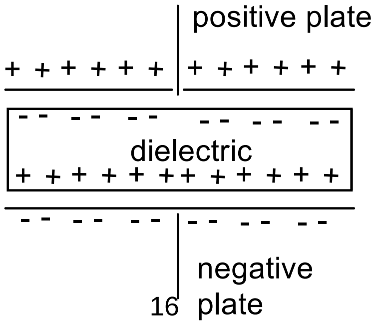
Remove field (*E*)
P > 0

A good dielectric material should have high *dielectric strength* (not breakdown at high voltages and become electron or ion conducting) and have low dielectric loss (not lose electrical energy as heat in an alternating electric field).

The stored charge can be measured in a parallel plate capacitor and the dielectric permittivity (ε_r) determined.

$Q = C V$

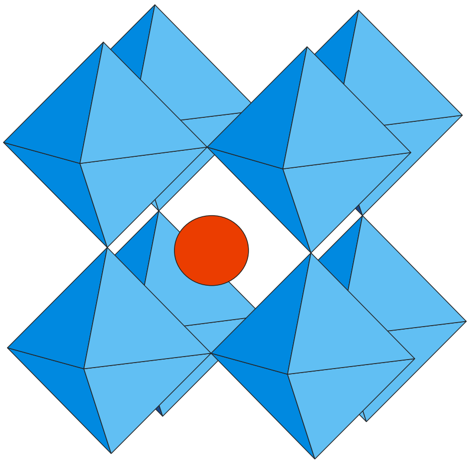
where V = potential difference
Q = stored charge
C = capacitance

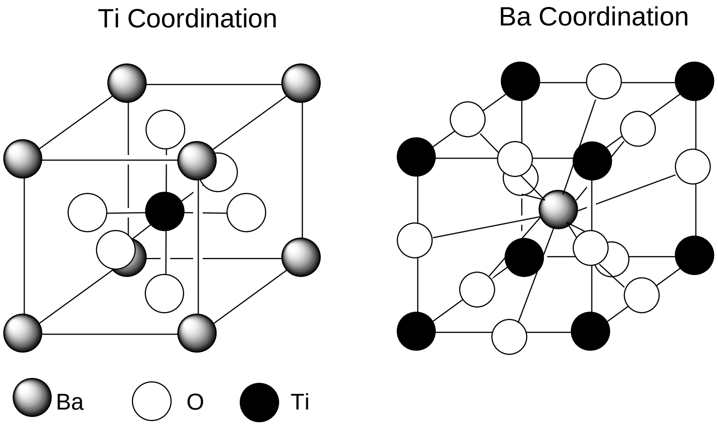


$$\varepsilon_r = \frac{C_{dielectric}}{C_{vacuum}}$$

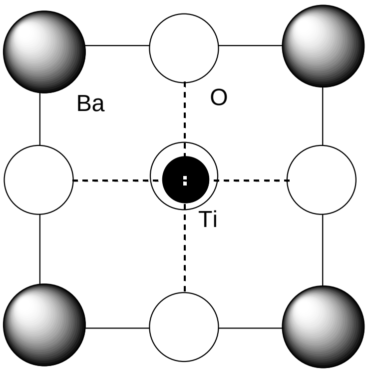
An example of a ferroelectric is $BaTiO_3$ that has the perovskite ABO_3 structure (related to ReO_3).

ε_r $BaTiO_3 = 10^2 - 10^4$



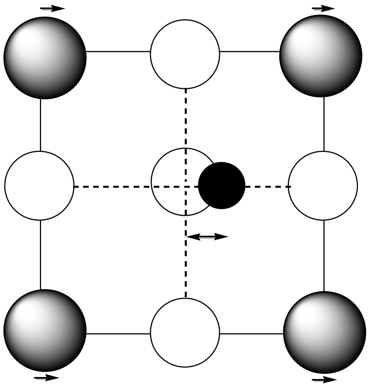


At temperatures above 120°C the Ti atoms are in a symmetric octahedral TiO_6 site (cubic $BaTiO_3$ (centrosymmetric)).
Between 5 - 120°C the Ti atoms are displaced along one of the axis of the octahedron (by 0.1 Å) and polarisation results (tetragonal $BaTiO_3$ (non-centrosymmetric)).



cubic

T > 120°C



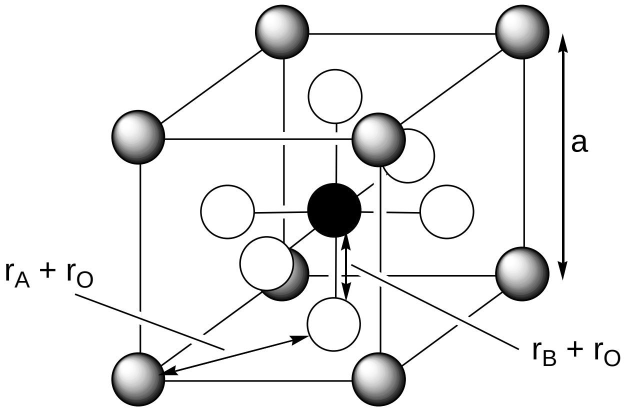
tetragonal

5 < T < 120°C

Why does the structure distort?
The structure of a compound is dependent on the size, charge and preferred coordination number/geometry of the constituent ions.
For compounds that contain several elements the ideal preferences for each ion may not be accommodated and strain may be present. Significant strain will result in a structural distortion.

For transition metal oxides distortions can be estimated using a *tolerance factor*.

Consider the perovskite ABO_3 structure.



From the diagram it can be seen that

$$a = 2 (r_B + r_O) \text{ and } a = \sqrt{2} (r_A + r_O)$$

Therefore to obtain ideal contact between A, B and O

$$2 (r_B + r_O) = \sqrt{2} (r_A + r_O)$$

Some deviation from this ideal can be included by introduction of a *tolerance factor* t.

$$t\, 2(r_B + r_O) = \sqrt{2} (r_A + r_O)$$

For the ideal structure t = 1. As t deviates from 1 strain is introduced due to one or both of the cations not fitting properly. $0.85 < t < 1.06$ gives a distorted perovskite. Outside this range a non-perovskite structure is usually adopted.

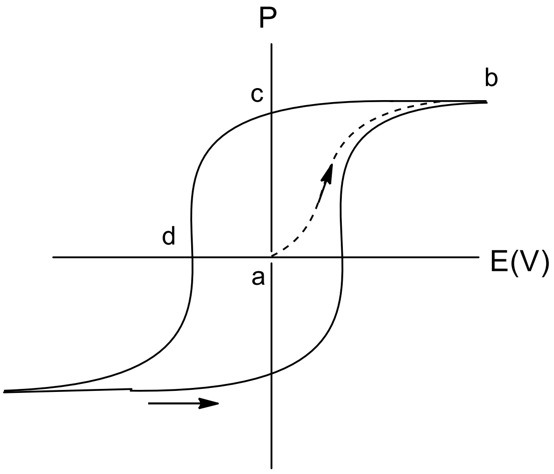
e.g. $SrTiO_3$ Sr^{2+} (r = 158 pm), Ti^{4+}(r = 74.5 pm), O^{2-} (r = 126pm) t = 1.002 (good fit, almost ideal)

$BaTiO_3$ Ba^{2+} (r = 175 pm), t = 1.06 (Ti ion is occupying a site larger than it would prefer, strain)

At T > 120°C the thermal motion of the Ti atom creates enough chemical pressure to retain the ideal cubic perovskite structure.
At 5 < T < 120°C the thermal motion no longer compensates for the strain and the structure distorts.

The polarisation can be removed and reversed by application of an opposing electric field. Ferroelectrics exhibit hysteresis which allows charge to be stored and their use in capacitors.

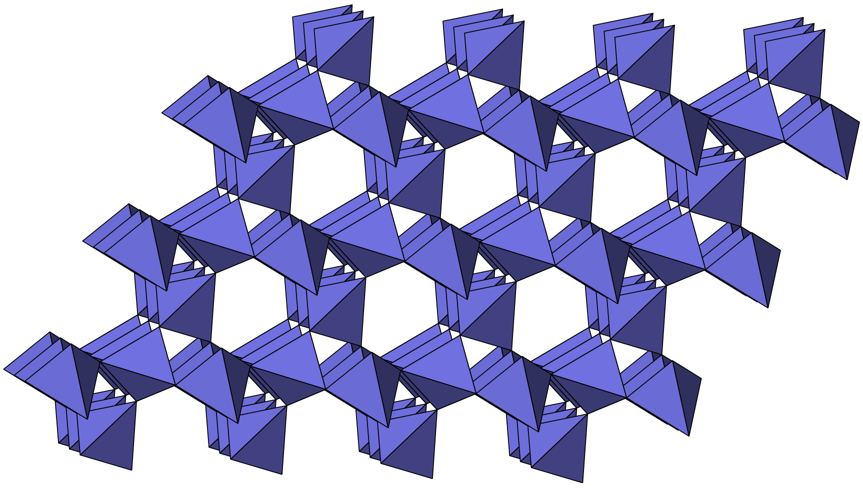
Capacitor



a to b. Apply electric field and individual dipoles are aligned. At b the sample has reached *saturation polarisation*.
b to c. Electric field is returned to 0 but the sample remains polarised this is known as the *remanent polarisation*.
c to d In order to depolarise the sample a field in the opposite direction is required. This is the *coercive field*.

Piezoelectrics polarise under the action of mechanical stress and develop electrical charges on opposite crystal faces (i.e. a voltage difference). Conversely when an electric field is placed across a piezoelectric crystal it develops strain.

Many compounds composed of tetrahedral groups distort under stress and are peizoelectric. Also tetrahedra do not have a centre of symmetry and often lead to non-centrosymmetric structures. An example is α-quartz.

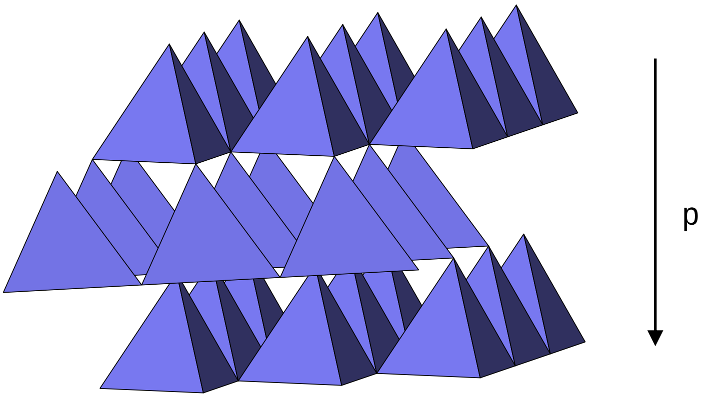


Piezoelectrics are used extensively as transducers for loudspeakers, earphones, inkjet printers, STM (see later), cigarette lighters etc
If an alternating electric field is applied to a piezoelectric the crystal will vibrate. Resonance occurs if the vibration corresponds to a fundamental mode of the crystal. This oscillation is the basis of using quartz for timekeeping.

Lighter watch (two piezoelecrics in action!)

Pyroelectrics exhibit a net bulk spontaneous polarisation that is temperature dependent. Thermal expansion or contraction of the lattice changes the size of the dipoles.

An example of a pyroelectric material is ZnO that has the wurtzite structure.



The ZnO_4 tetrahedra (dipoles) point in the same direction, giving rise to a net bulk polarisation. In contrast to ferroelectrics the polarisation of pyroelectrics cannot usually be reversed by the action of an electric (coercive) field.

Pyroelectrics are used in systems where an electrical response to temperature is useful. e.g. infrared radiation detectors (night vision and PIR (passive infra-red) motion sensors), spectrometers and temperature sensors.

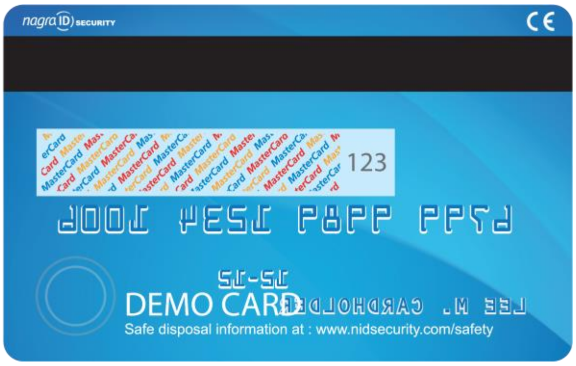
Security PIR sensor

Magnetic Materials

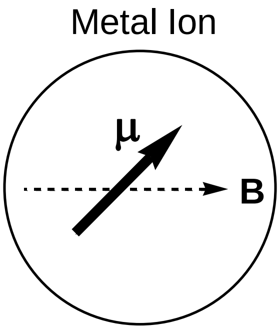
Transition metals and lanthanides can have partially filled valence orbitals that result in unpaired electrons and magnetism. For materials, the collective interaction of the ions is key. The strength and direction of the interaction will depend on the spatial relationship (crystal structure) between the ions and the mechanism for magnetic exchange (exchange interaction). The angular momentum (J) of unpaired electrons gives rise to magnetic behaviour. Magnetic behaviour is a quantum mechanical phenomenon.

Nobel Prize (1970, 1977, 1982, 2007)

Magnetic memory
(security strips, hard drives)
Power generation
(transformer cores, motors)
Sound generation
(loudspeakers, microphones)



Magnetism of individual ions



(**B** = magnetic field experienced by the ion)

On the microscopic level individual ions with unpaired electrons have a magnetic dipole moment μ (sometimes called spin). The size of μ depends on the spin and orbital angular moments. (see *f*-elements course)

$$\boxed{\mu_S = g\sqrt{(S(S+1))}}$$

Spin only formula

$$\boxed{\mu_{S+L} = \sqrt{(4S(S+1) + L(L+1))}}$$

Includes spin orbit coupling (Russell-Sanders coupling)

S = total spin angular momentum (No. electrons/2), L = total orbital angular momentum, g = g-factor (free electron value ~2 can be used when L = 0)

ion	Unpaired electrons	μ_S (calc)	μ_{S+L} (calc)	μ_{eff} (observed)
V^{4+}	1	1.73	3.00	~ 1.8
V^{3+}	2	2.83	4.47	~ 2.8
Cr^{3+}	3	3.87	5.20	~ 3.8
Mn^{2+}	5 (high spin)	5.92	5.92	~5.9
Fe^{2+}	4 (high spin)	4.90	5.48	5.1 – 5.5
Co^{2+}	3 (high spin)	3.87	5.20	4.1 – 5.2
Ni^{2+}	2	2.83	4.47	2.8 – 4.0
Cu^{2+}	1	1.73	3.00	1.7 – 2.2

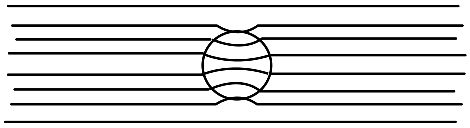
The orbital angular momentum is due to the motion of the electron about the nucleus. In many compounds (particularly the first row) the orbital angular momentum is almost entirely quenched because the *d*-orbitals are no longer degenerate.

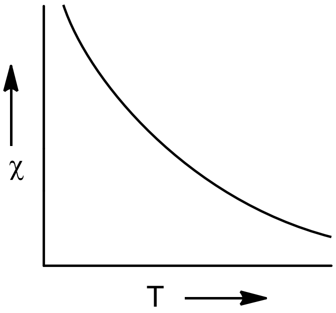
For heavier transition metals and the actinides the spin-orbit coupling is large and Russell-Sanders coupling inappropriate. Use j-j coupling scheme instead. Large spin-orbit coupling can give rise to very large moments. We shall not consider j-j coupling any further.

Collective (bulk) magnetism

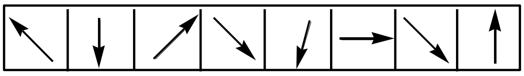
The magnetic susceptibility χ is a measure of how magnetic a material is.
χ varies with temperature (and applied external magnetic field) for different types of magnetism. (basis of technological applications of magnets)

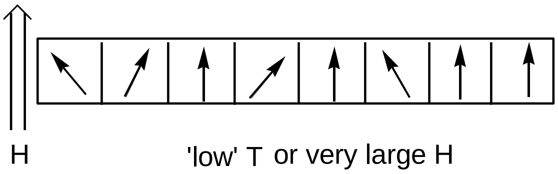
Paramagnetism is observed for compounds that contain unpaired electrons and *where the magnetic dipoles do not interact with each other*. A paramagnet is attracted to an external magnetic field.





As the temperature decreases the dipoles can begin to align (order) parallel (lowest energy configuration) to an external field.

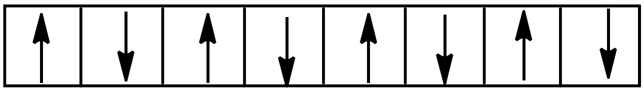

'high' T, no H

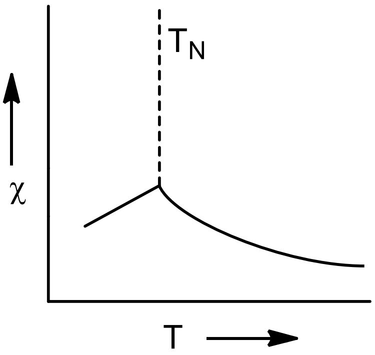


'low' T or very large H

Paramagnetism is temperature dependent.

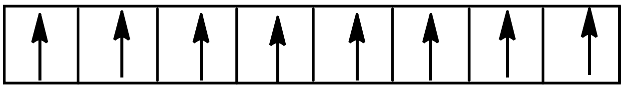
Antiferromagnetism is an example of cooperative magnetism where no applied field is necessary to align dipoles (spins) anti-parallel.

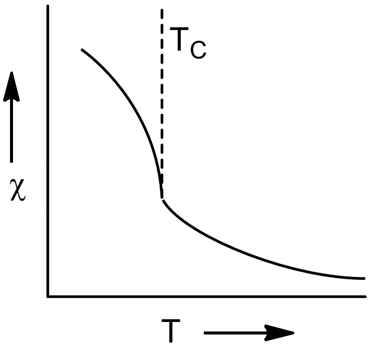




T_N is the Néel temperature (antiferromagnetic-paramagnetic transition temperature)

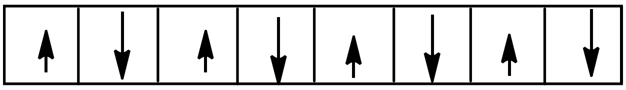
Ferromagnetism is an example of cooperative magnetism where no applied field is necessary to align spins parallel.

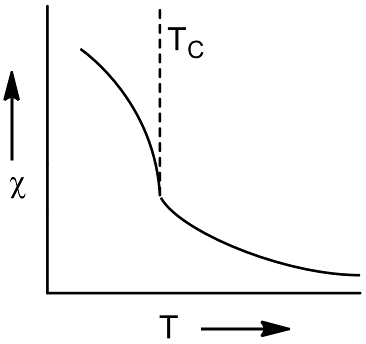




T_C is the Curie temperature (ferromagnetic-paramagnetic transition temperature).

Ferrimagnetism is an example of cooperative magnetism where no applied field is necessary to align spins. The alignment is essentially non-parallel giving partial cancellation of ‘up’ and ‘down’ spins.





ferromagnet

The Exchange Interaction

Ferromagnetism

Is usually associated with metals that have an electronic band structure.

There are only a few elements that are ferromagnetic Fe, Co, Ni, Gd and Tb.

We will not consider the magnetism of metals

Antiferromagnetism and Ferrimagnetism

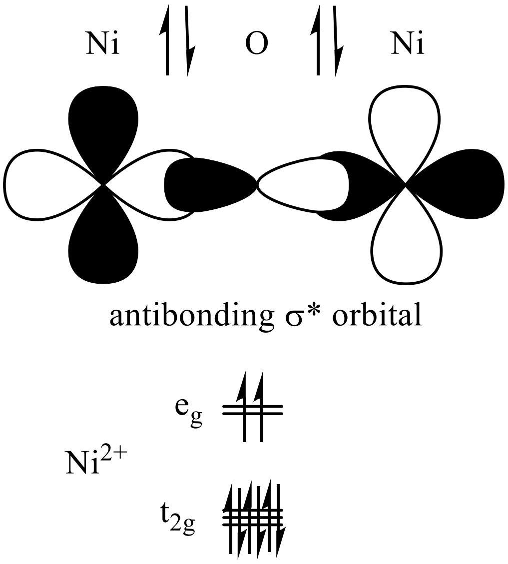
Superexchange

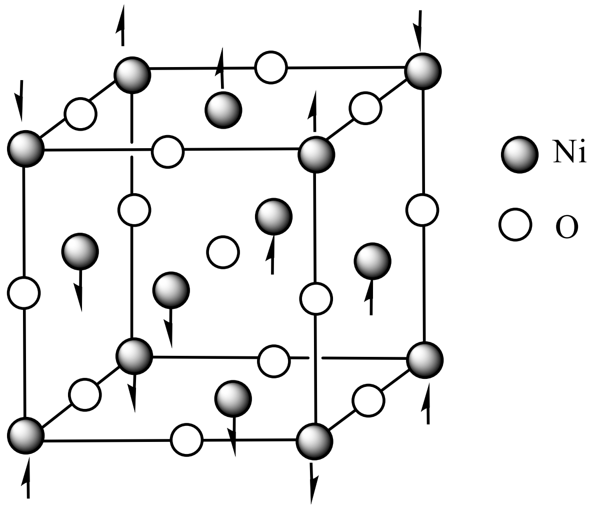
Superexchange is where anions mediate magnetic exchange between metal cations. Anions can be sulfur and fluorine but more commonly oxygen.

Superexchange occurs via overlap of atomic orbitals of the oxygen (*p*) and metal (*d*) atoms.

Superexchange leading to Antiferromagentism

e.g. First row transition metal monoxides such as NiO and MnO adopt the rock salt structure where the metal and oxygen are in octahedral sites.





Two e_g (d_{x2-y2} or d_{z^2}) orbitals containing an unpaired electron overlap with an O^{2-} *p* orbital that contains two oppositely aligned electrons. The spins align themselves to be antiparallel giving an overall antiferromagnetic exchange coupling.

Effectively there are two Ni lattices that contain Ni spins ‘up’ and one ‘down’. Each of these is know as a sublattice. Below T_N the sublattice structure of NiO can be determined experimentally using neutron diffraction (see later).

Above T_N thermal energy is greater than the superexchange interaction and the spins no longer align giving paramagnetic behaviour.

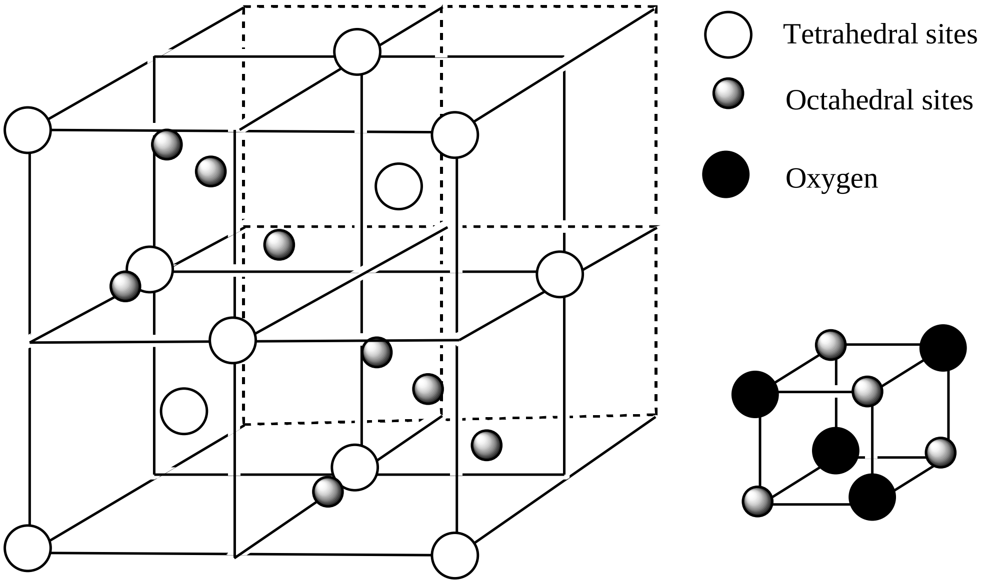
Superexchange leading to Ferrimagnetism

We need a structure that can have at least two types of ions, either different elements or oxidation states that that have different magnetic moments and can occupy unique crystallographic sites. Consider an antiferromagnet that has two unique sublattices but where the magnetic moment of one sublattice is greater than the other.

Ferrimagnets are very important industrial materials because they have similar properties to ferromagnets, but are electrically insulating.

A crystal structure is required that has two different metal sites. This is found in the spinel and inverse spinel structure type.

Spinel is the name given to a structure type of the formula AB_2X_4 e.g. $MgAl_2O_4$.



The structure is based on a cubic close packed array of anion atoms.

The spinels and inverse spinels are then constructed by filling 1/8 of the tetrahedral and ½ of the octahedral sites in an ordered manner.

spinel	Inverse spinel
$[A^{2+}]^{tet}\,[B^{3+}]^{oct}$	$[B^{3+}]^{tet}\,[A^{2+}, B^{3+}]^{oct}$
$MgAl_2O_4$	$CoFe_2O_4$
$BaFe_2O_4$ (credit card strips, speakers	$NiFe_2O_4$
Mn_3O_4	Fe_3O_4 (magnetite) (loadstone)

Not all spinels have clear preference of metal ions for particular coordination sites. Many examples contain mixed metal sites. e.g. $MnFe_2O_4$ contains 80% normal and 20% inverse.

The preference for normal or inverse spinel is due to several factors.

1. From electrostatics M^{3+} should prefer the octahedral site and M^{2+} the tetrahedral site.
2. The smaller cation would generally go in the smaller tetrahedral site
3. Crystal field stabilisation energies (CFSE). Which ion prefers the Oh site?

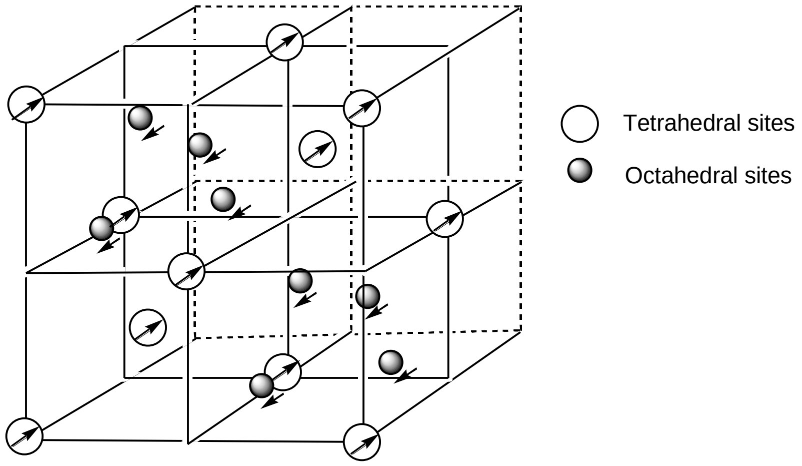
e.g. $NiFe_2O_4$
Oxide lattice provides a weak field for the metal atoms.
Must be 1 x Ni(II) and 2 x Fe(III). Fe(III) d^5 are high spin. No preference for Oh or Td based on CFSE. CFSE for Ni in octahedral > tetrahedral. Therefore Ni goes in octahedral site to give the inverse spinel structure.

Estimation of the magnetic moment of ferrimagnets

Using $\mu = gS$ as a rough estimate (instead of $\mu_s = g\sqrt{(S(S+1))}$) we can calculate the magnetic moment μ for each ion. The saturation (maximum) magnetic moment (μ_{sat}) for a ferrimagnet is then a vector sum of the individual ion moments.

We need to know how the spins couple with respect to each other.

1) The coupling between octahedral site ions is weak. Between tetrahedral sites also weak.
2) Superexchange between the octahedral and tetrahedral ions is strong giving antiferromagnetic alignment.
Therefore all A moments in same direction and all B moment in same direction (but opposite to A)



e.g. $NiFe_2O_4$ (inverse spinel)

ion	$[Ni^{2+}]^{oct}$, d^8	$[Fe^{3+}]^{oct}$, d^5	$[Fe^{3+}]^{tet}$, d^5	μ_{tot}
No. unpaired electrons	2	5	5	
μ_{ion}	2	5	5	2 + 5 – 5 = 2

Comparison of estimation and experimental data for $M^{II}Fe^{III}_2O_4$

M(II)	S	$\mu_{sat\ calc}$	$\mu_{sat\ expt}$	T_N	Discrepancy
Mn	5/2	5	4.55	573	90% normal
Fe	2	4	4.1	858	s.o. coupling
Co	3/2	3	3.94	793	s.o. coupling
Ni	1	2	2.3	858	s.o. coupling
Cu	1/2	1	1.3	726	s.o. coupling
Mg	0	0	1.1	713	90% inverse

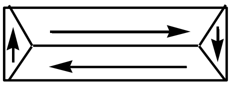
Domains

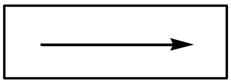
Fe has a T_C of 1043K. Why are not all Fe objects magnetic at room temperature?
Why does placing a magnet next to Fe magnetise it?
How can $BaFe_2O_4$ be used to store magnetic data?

Below T_C magnet materials are divided into *domains*.

Each domain has ions aligned in parallel, but in the absence of an external magnetic field the domains are not parallel to each other. Entropy drives the formation of domains.

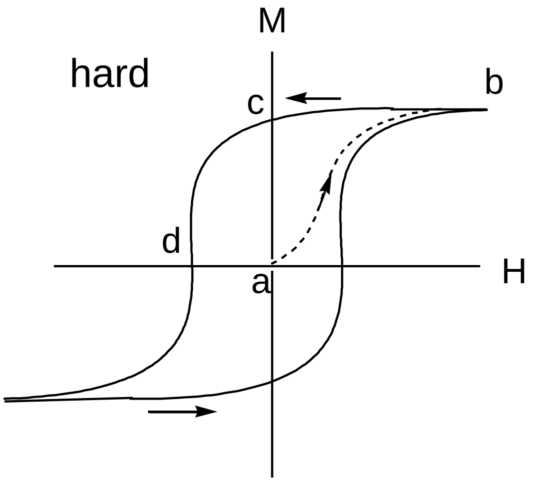
On the application of an external magnetic field (H) the domains align in the same direction as the field.

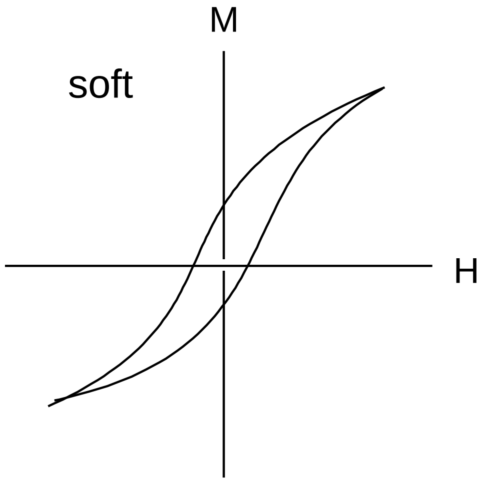




When all the domains are parallel the magnetisation M is at a maximum (*saturation magnetisation*). M is the magnetic dipole moment per unit volume.

These M vs H diagrams are known as hysterisis curves





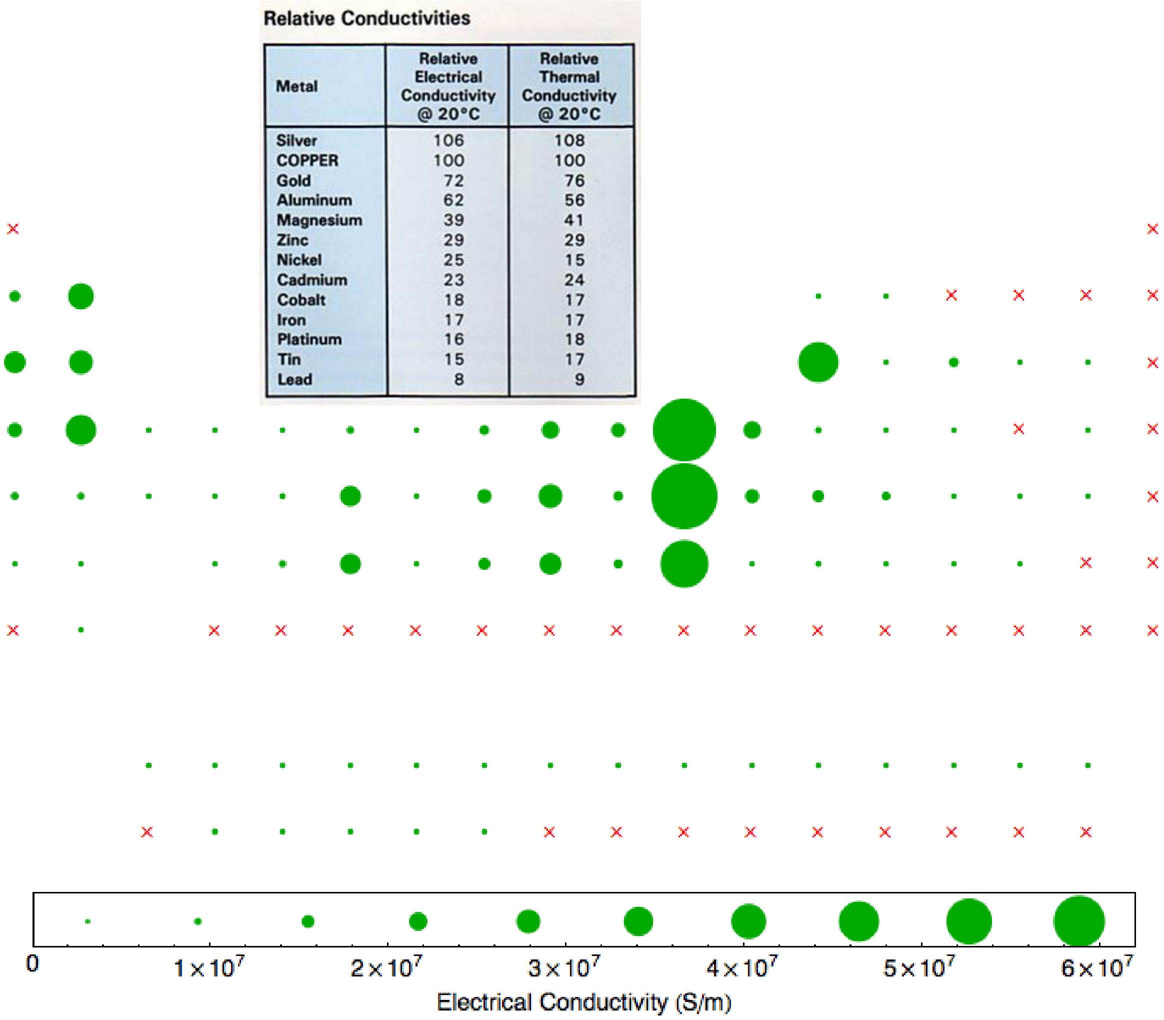
The domains can be aligned in any direction by changing the direction of the external field. Aligning and changing the direction of domains requires energy.

a to b. The domains of a sample are aligned in a magnetic field. At b the sample has reached *saturation magnetisation*.
b to c. The field is returned to 0 but the sample remains magnetised this is known as the *remanent magnetisation*.
c to d In order to demagnetise the sample a field in the opposite direction is required. This is called the *coercive field*.

A hard magnet has a large remanent magnetisation and large coercive field: used as permanent magnets and magnetic memory ($BaFe_2O_4$).
A soft magnet has a small remanent magentisation and a small coercive field: used as transformer cores (Si doped Fe).

Electrical Conductivity

All materials can be classified with respect to their electrical conductivity.

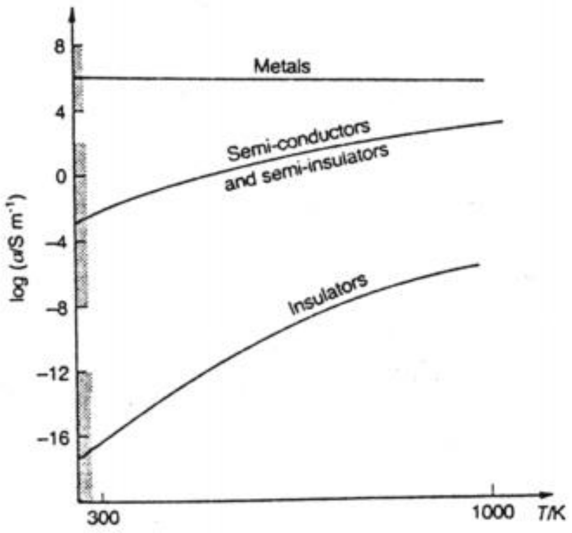


Relative Conductivities

Metal	Relative Electrical Conductivity @ 20°C	Relative Thermal Conductivity @ 20°C
Silver	106	108
COPPER	100	100
Gold	72	76
Aluminum	62	56
Magnesium	39	41
Zinc	29	29
Nickel	25	15
Cadmium	23	24
Cobalt	18	17
Iron	17	17
Platinum	16	18
Tin	15	17
Lead	8	9

Conductivity (σ) as a function of temperature

Note the log scale



Insulator: $\sigma < 10^{-9}$ Sm^{-1}.
Conductivity increases with Temp.

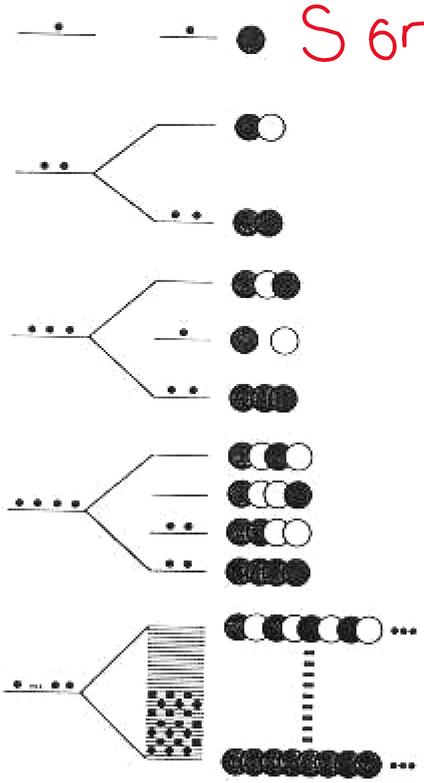
Semiconductor: $\sigma = 10^{-3} - 10^{3}$ Sm^{-1}
Conductivity increases with Temp.

Metal: $\sigma > 10^{7}$ Sm^{-1}
Conductivity decreases with Temp.

Can we explain the trends in conductivity?

Band Theory

(Overlap of large numbers of atomic orbitals. Extension of LCAO-MO theory)



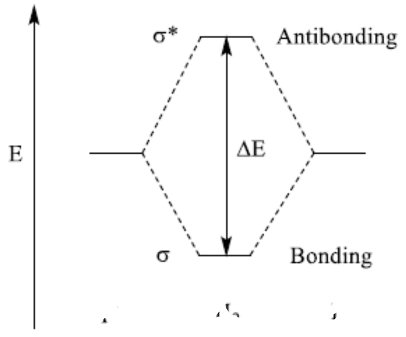
S orbital

antibonding

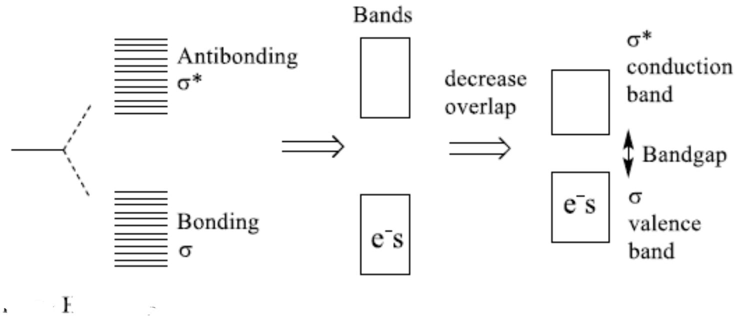
bonding

Band orbitals are not distributed evenly in a band. There are fewer at the band edges. The number of orbitals (states) per unit energy is called the density of states N(E). The density of states is lower at the band edges.

For some materials the bonding and antibonding bands split (like in a molecule) giving an energy gap (band gap)

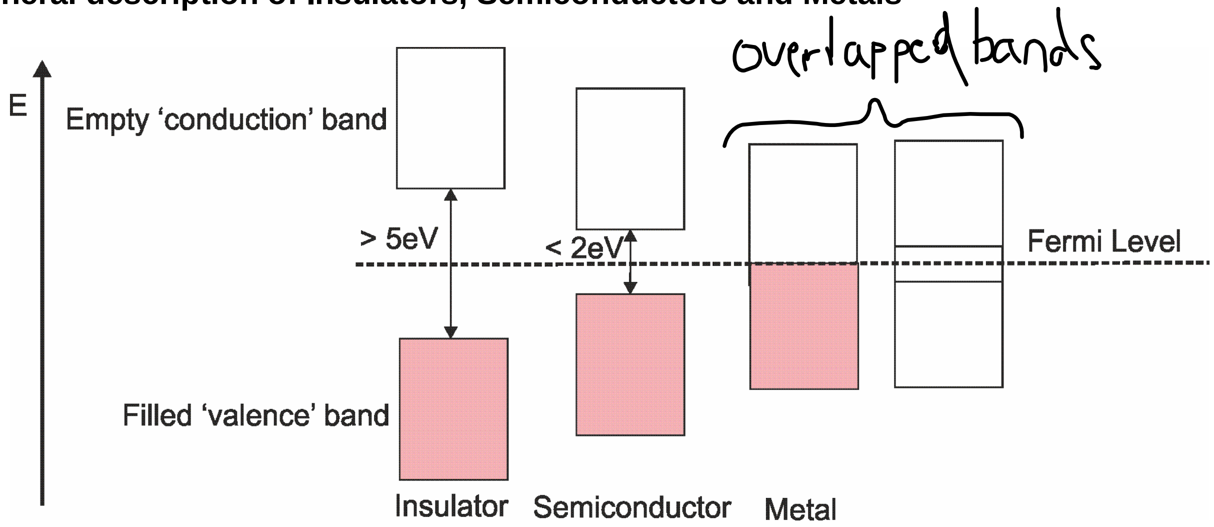


ΔE increases with greater overlap



The band width (energy range), band structure (distribution of orbitals), and band gap will depend on the orbitals, structure and bonding (e.g. metallic, ionic, or covalent). A key parameter is orbital overlap, which can be interpreted very similarly to metal-ligand bonding in metal complex coordination chemistry (see yr 2 course M-L bonding).

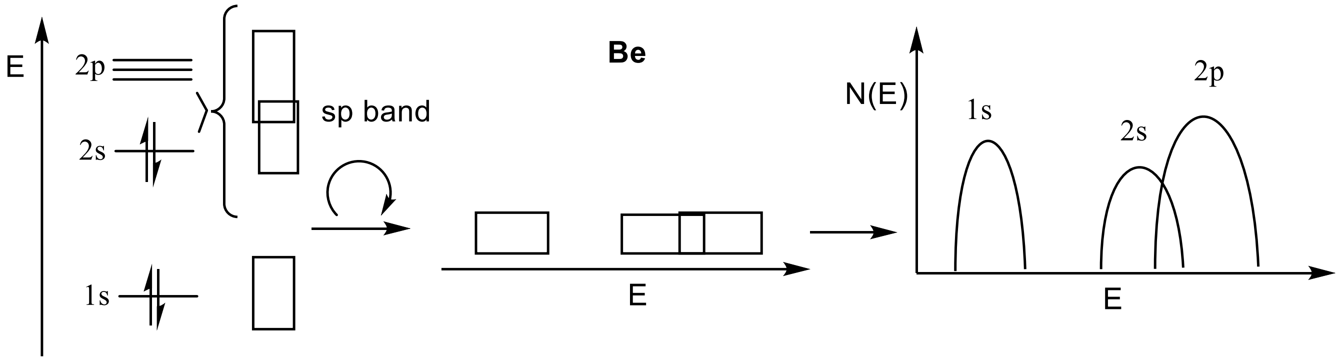
General description of Insulators, Semiconductors and Metals



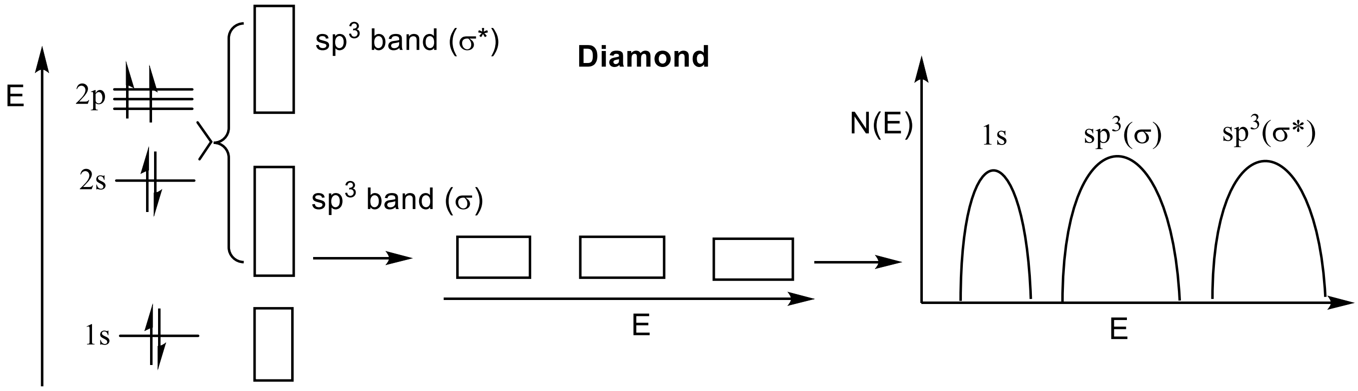
Fermi level is the energy with a 50% probability of electron occupation under any conditions. Very important concept (see below).

Bands from s, p and d-orbitals

e.g. Be (hcp structure) vs C (diamond structure)

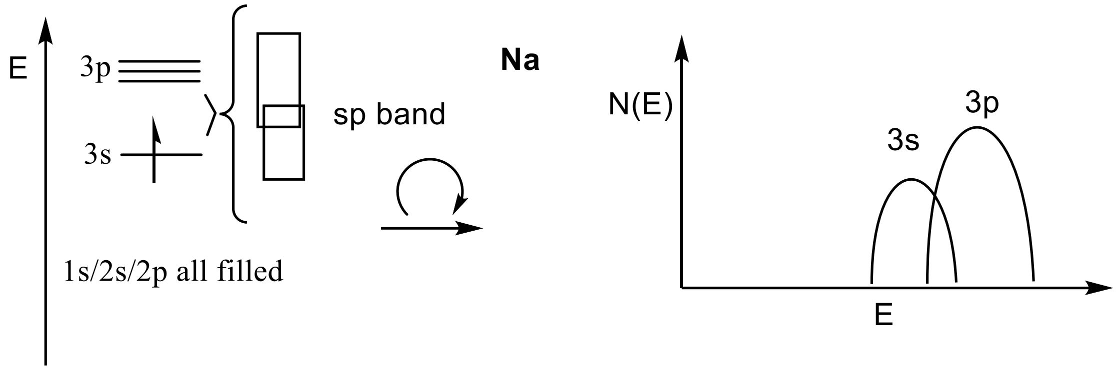


Overlap of 2s and 2p valence orbitals gives a single band.
The band is partially filled with electrons.
Be is a metal.

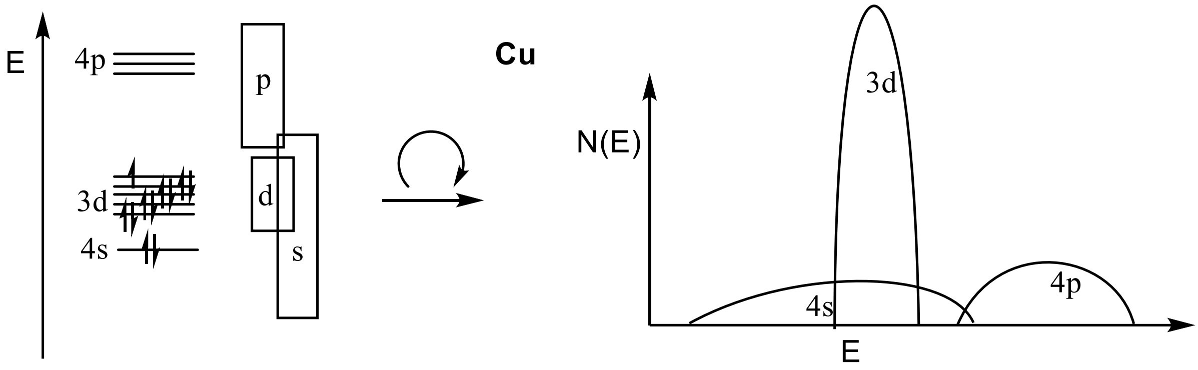


Overlap of 2s and 2p valance orbitals gives two bands (sp^3 bonding and antibonding bands).
The lower band is completely filled with electrons.
Diamond is an insulator

Na (bcc structure) vs Cu (fcc structure)



Essentially a half filled 3s band
Na is a metal.

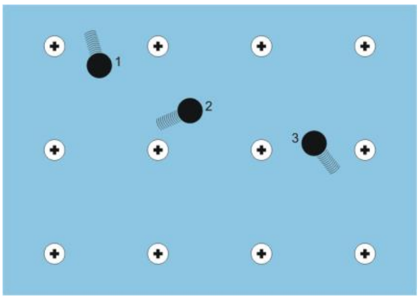


d-band is very narrow and has a high density of states (lots of orbitals and electrons).
For Cu electron filling at 3d/4s boundary. Other transition metals will be filled within the d-band (< group 11) or sp band (> group 11).
Cu is a better conductor than Na.

Orbital dependence on conductivity

Electron delocalisation increases conductivity
Orbital overlap, energy and shape are key (cf molecular bonding)
s-orbitals are isotropic = good delocalisation.
Heating a metal reduces orbital overlap and the ions vibrate more (decrease conductivity)

Simple free electron model for a metal



Similar to ideal gas. Electrons are able to move without interacting with the positive lattice or each other (Fermi gas).
This model can be used to estimate the Fermi Energy (E_F)

$$E_F = \frac{\hbar^2}{2m_e}\left(\frac{3\pi^2 N}{V}\right)^{2/3}$$

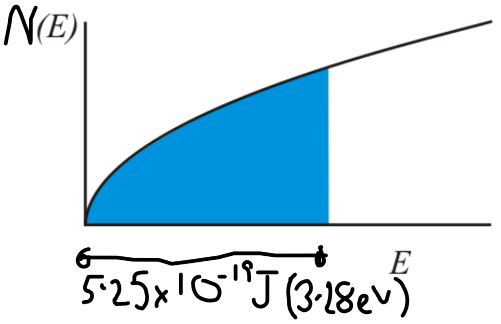
Where m_e = electron mass, h = planc's constant, N = number of unpaired electrons per unit volume, V = volume

e.g. for Na (1 unpaired electron per atom, lattice parameter of 4.2 Å, 2 atoms per unit cell)

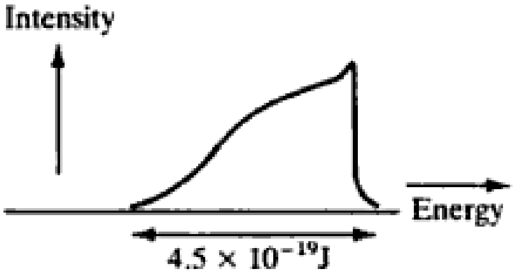
$$E_F = \frac{\hbar^2}{2m_e}\left(\frac{3\pi^2 N}{V}\right)^{2/3} = \frac{(1.0546\times10^{-34}\,\mathrm{Js})^2}{(2\times9.1095\times10^{-31}\,\mathrm{kg})}\left(\frac{3\times3.141592^{\,2}\times2}{(4.2\times10^{-10}\,\mathrm{m})^3}\right)^{2/3}$$

$$= 5.2576\times10^{-19}\,\mathrm{J}$$

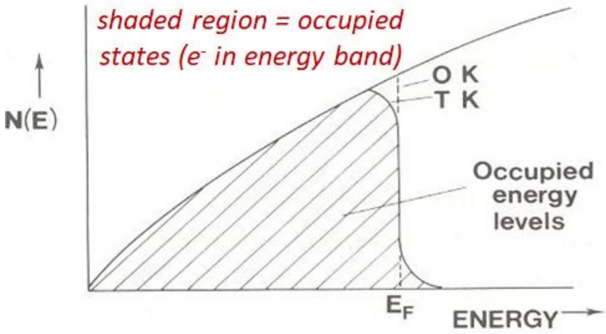
$$= 3.28\,\mathrm{eV}$$



Free electron density of states



Experimental x-ray emission spectroscopy



At 0 K electrons 'paired' in band orbitals (very low conductivity). The highest filled energy at 0 K is called the Fermi Energy. Above 0 K the energy with a 50% probability of occupation is called the Fermi Level (these terms are often used interchangeably which can be confusing).

Above 0 K electrons are promoted by heat to higher energy orbitals (increases conductivity).

kT at room temperature = 4.14×10^{-21} J (0.0258) eV

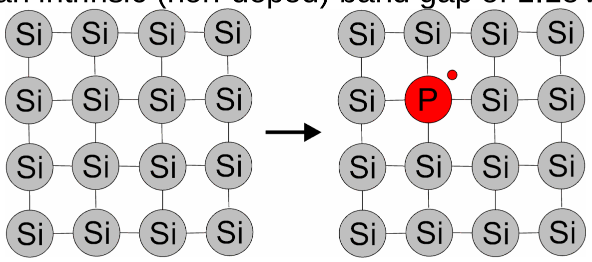
Relatively few electrons are promoted into unoccupied orbitals

If there is a large N(E) more orbitals with unpaired electrons (increases conductivity)

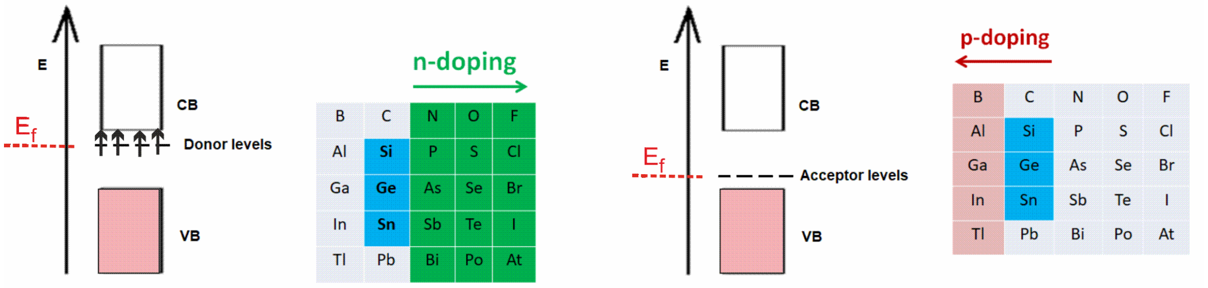
e.g. Na vs Cu

Semiconductor Doping and Applications

Semiconductor doping modifies the conductivity and position of the Fermi level. A good example is Si which has an intrinsic (non-doped) band gap of 1.1eV.



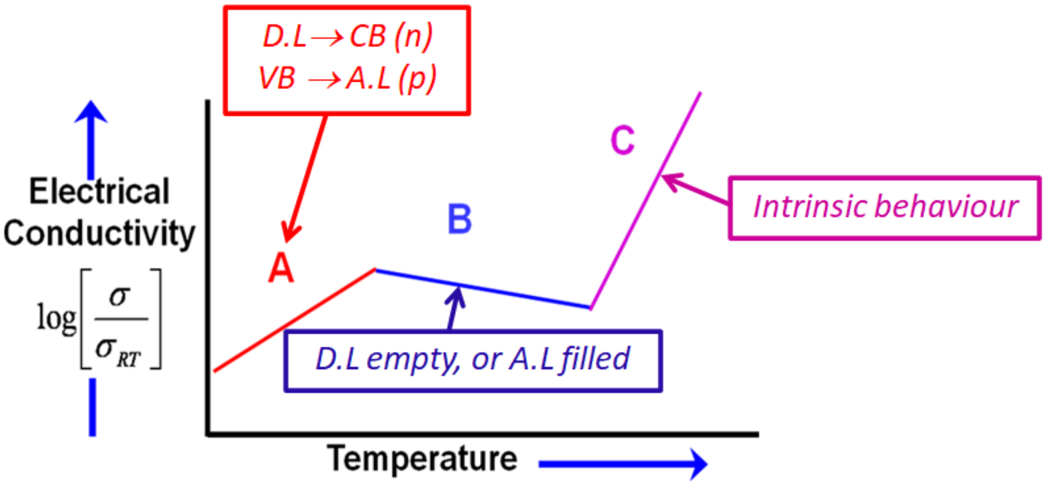
Doping with a group 15 element gives an extra electron in an orbital with an energy within the band gap (n-doping).
Doping with a group 13 element gives one fewer electron in an orbital with an energy within the band gap (p-doping).



B	C	N	O	F
Al	Si	P	S	Cl
Ga	Ge	As	Se	Br
In	Sn	Sb	Te	I
Tl	Pb	Bi	Po	At

B	C	N	O	F
Al	Si	P	S	Cl
Ga	Ge	As	Se	Br
In	Sn	Sb	Te	I
Tl	Pb	Bi	Po	At

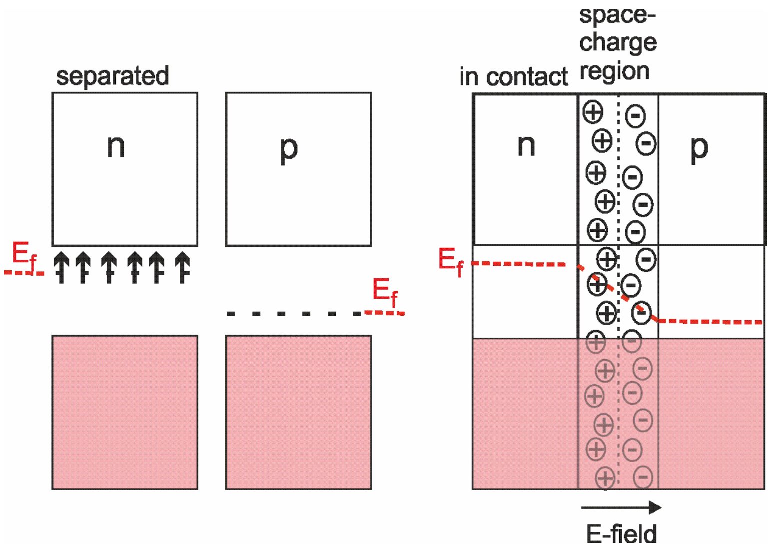
Temperature depdendent conductivity



Fermi Levels

At the interface of ***any*** two substances the Fermi levels will equilibrate (electrons are transferred). This concept is the basis of all interfacial science, phenomena and reliant technology e.g. adhesion, corrosion, sensors, transistors, LED lighting + many, many more.

Another example **p-n junction** (solar cells and LED's)



At interface of p-n junction charge is transferred (from n-p) to equilibrate the fermi levels. Charge transfer causes generation of a field in a region close to the interface (space charge region).

Solar cells (light to electricity)
Illumination of the space charge region causes excitation of an electron from the valence to conduction band.
The field separates the electron and hole inducing an electrical current.

LED's and electroluminescence (electricity to light)
Inject an electron and hole into the space charge region.
Recombination causes emission of a photon.

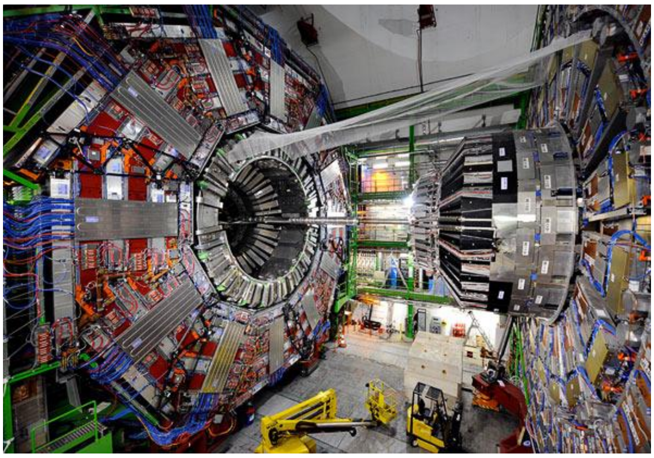
Superconductivity

Superconductors exhibit two remarkable properties
Zero electrical resistance and the Meissner effect (an external magnetic field is ejected)

Nobel Prize (1972, 1973, 1987, 2003)

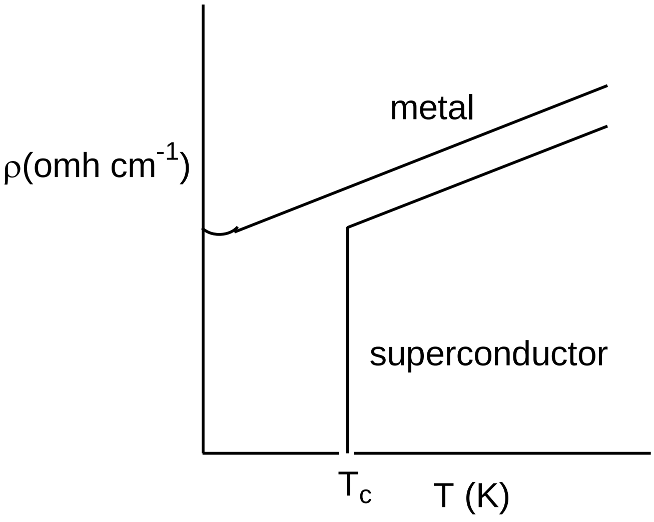
MRI

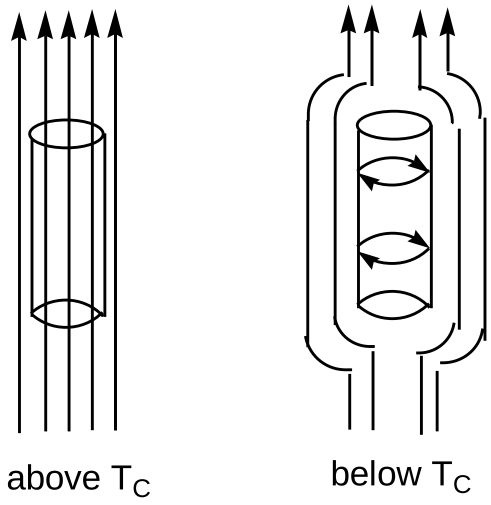
NMR



Large Hadron Collider

Maglev Train





1. Below a critical temperature T_C zero electrical resistance is observed.
2. Below T_C magnetic flux is expelled B = 0 (Meissner effect). $\chi = -1$

Superconductors are used for the generation of large magnetic fields (such as NMR and MRI) because they can support very large currents without resistive heating.
If the T_C could be increased to > 300K many technologies (e.g. transport and power generation) would be revolutionised.

Superconductivity was discovered by Onnes in 1911 for Hg (T_C = 4.2K) and many examples of superconductors have since been investigated. However until 1986 the highest known T_C's were approximately 25K.

H. K. Onnes (1911). "The resistance of pure mercury at helium temperatures". *Commun. Phys. Lab. Univ. Leiden* 12: 120.

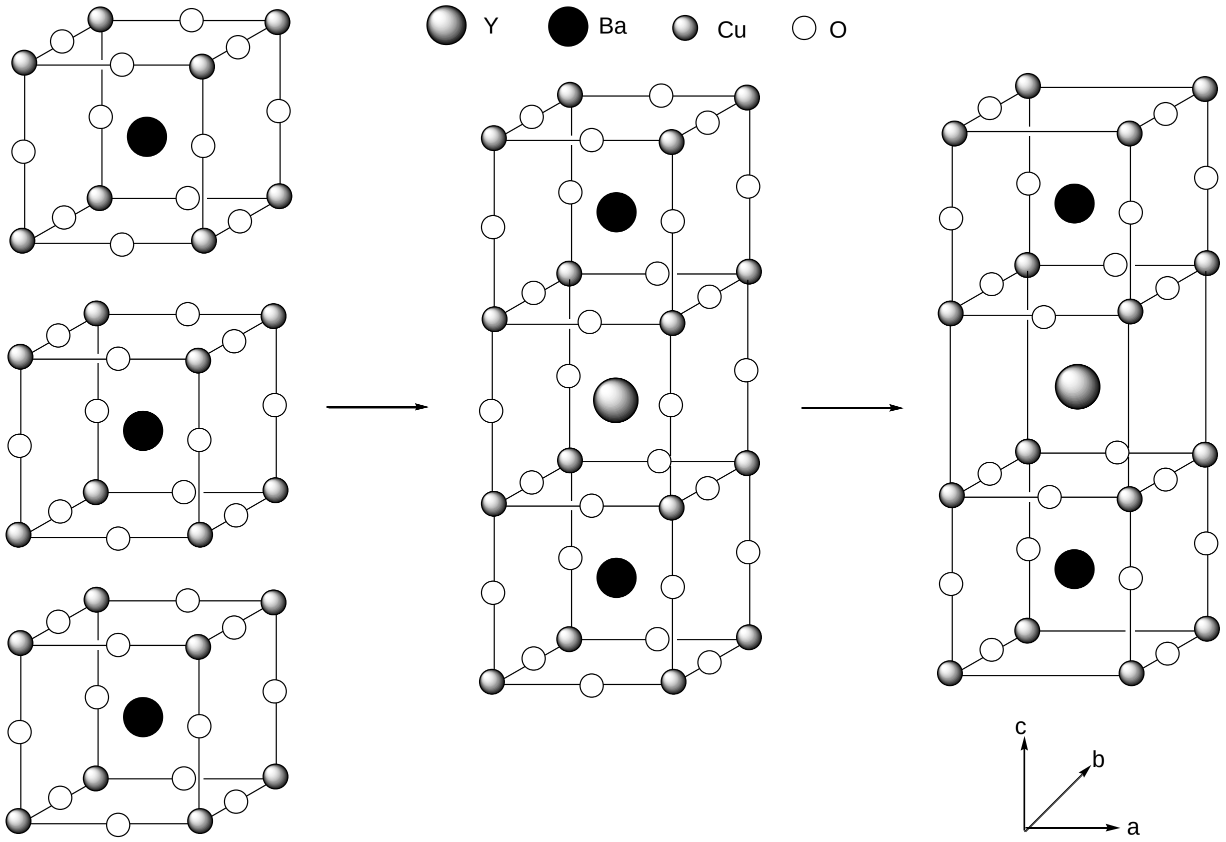
Cuprates (high T_C superconductors)

In 1986 the compound $La_{1.8}Ba_{0.2}CuO_4$ was reported to have a T_C of 35K. This compound has the K_2NiF_4 type structure that is related to the perovskites. Later the phases $YBa_2Cu_3O_{7-x}$ 0<x<1 were investigated and the T_C raised to 93K. The highest T_C to date is about 160K for $HgBa_2Ca_2Cu_3O_{10}$ under pressure. (but there are higher claims based on hydrides)

J. G. Bednorz and K. A. Müller (1986). "Possible high T_c superconductivity in the Ba−La−Cu−O system". *Z. Physik, B* **64** (1): 189–193.

M. K. Wu et al. (1987). "Superconductivity at 93 K in a New Mixed-Phase Y-Ba-Cu-O Compound System at Ambient Pressure". *Physical Review Letters* **58** (9): 908–910.

Structure of Cuprates



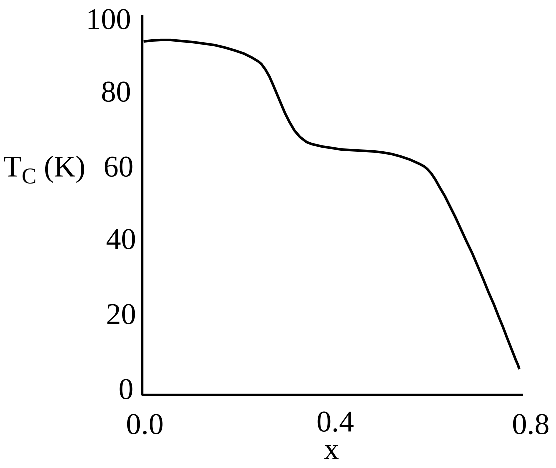
Perovskite cubes

Hypothetical $YBa_2Cu_3O_9$

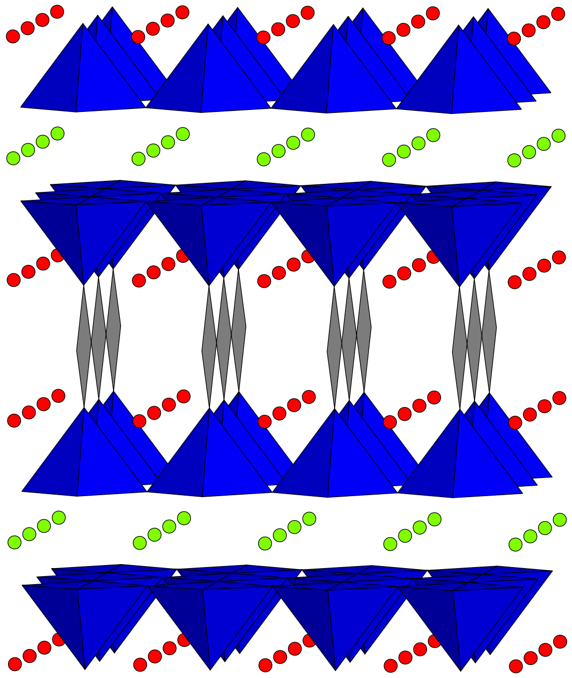
$YBa_2Cu_3O_7$

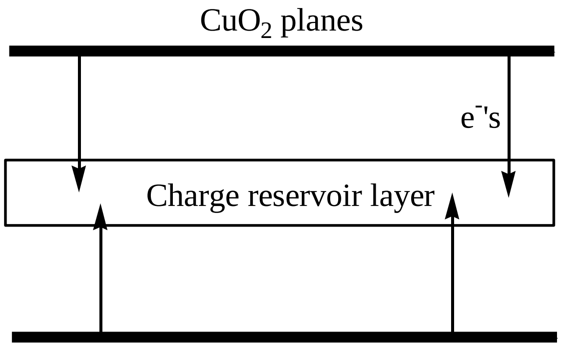
There are two copper sites: A distorted square pyramid of Jahn-teller distorted Cu^{2+} (that form CuO_2 layers) and square planar geometry (that link the layers). Oxygen is removed from the basal planes (0, ½, 0) for the compositions $YBa_2Cu_3O_{7-x}$ leading to linear geometry for the Cu atoms linking the CuO_2 layers. The structure is orthorhombic $a \neq b \neq c$.

The average oxidation state for Cu in $YBa_2Cu_3O_{7-x}$ $0<x<1$ ranges from 2.33 (Cu^{3+}/Cu^{2+}) to 1.66 (Cu^{2+}/Cu^{+}). T_C is very dependent on the Cu oxidation state and hence the oxygen content. For Cu^{2+}/Cu^{+} $YBa_2Cu_3O_{6.0-6.5}$ antiferromagnetism is observed and superconductivity is suppressed. For Cu^{3+}/Cu^{2+} $YBa_2Cu_3O_{6.5-7.0}$ T_C increases with increasing oxygen content.



Studies indicate that the important structural features are CuO_2 square planar layers separated by ‘charge reservoir layers’ that control the average Cu oxidation state in the CuO_2 layers. The average Cu oxidation state should also be > 2+. For $YBa_2Cu_3O_7$ the charge reservoir layers are CuO chains.



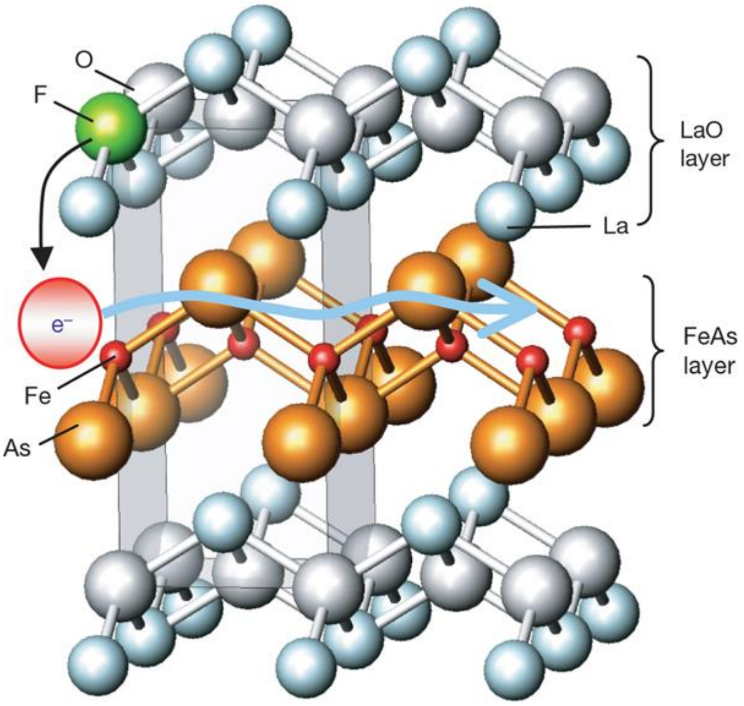


FeAs

2008 a new family of superconductors based on FeAs layers separated by LaO layers. cf. the structure of cuprates.

e.g. $LaO_{1-x}F_xFeAs$

Hideo Hosono et al (2008). "Superconductivity at 43 K in an iron-based layered compound $LaO_{1-x}F_xFeAs$". _Nature_ **453**, 376.

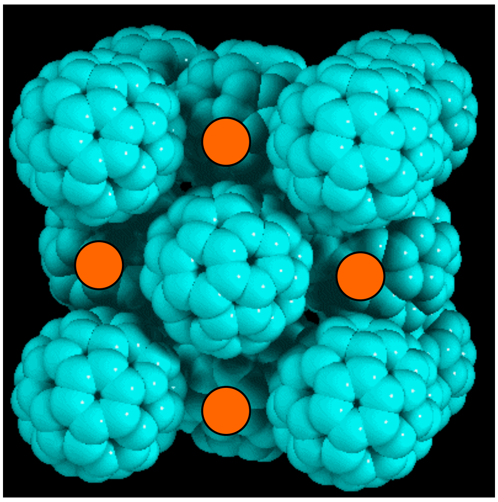


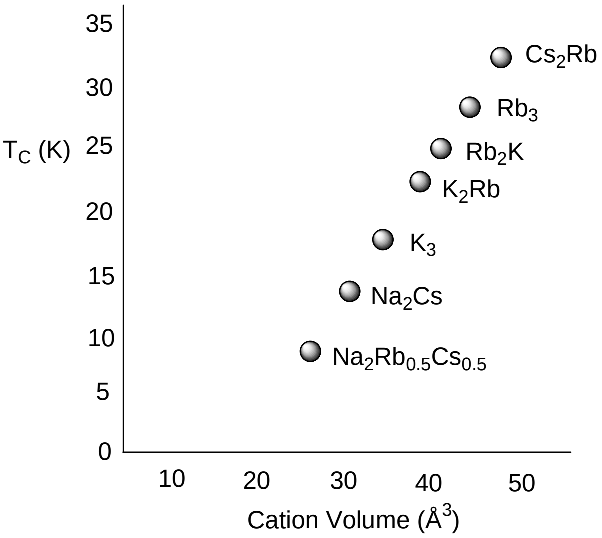
Fullerides

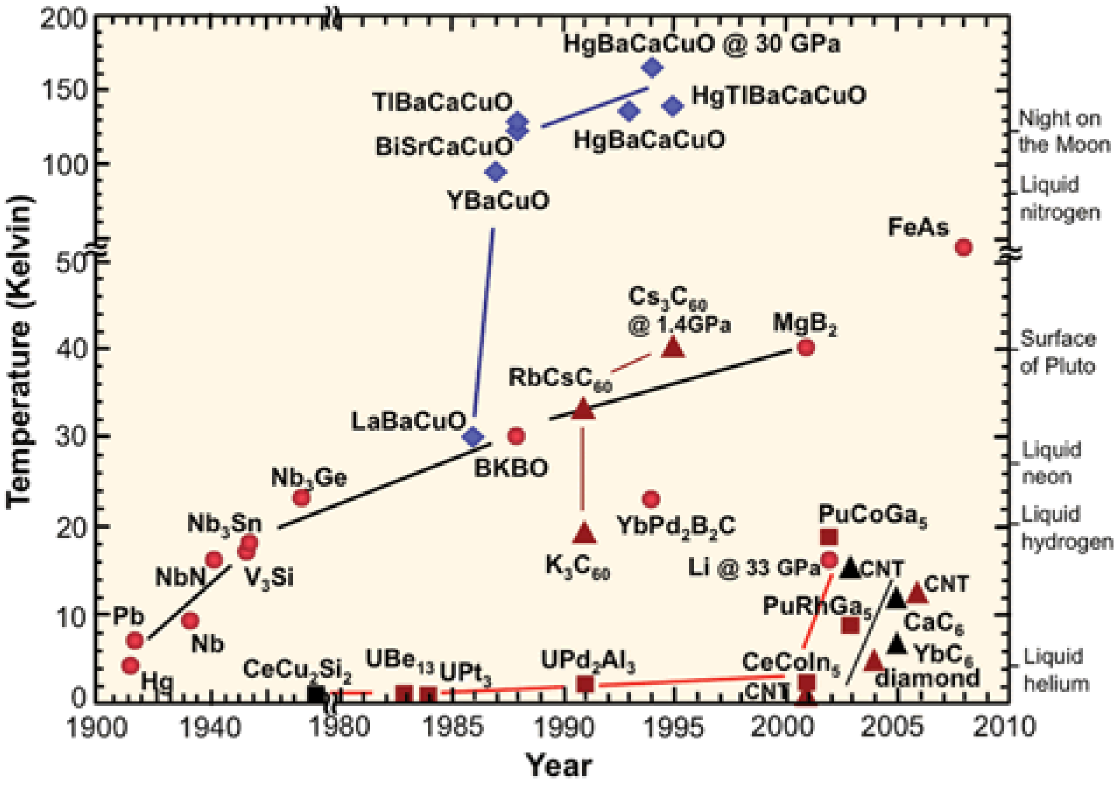
Synthesised by intercalation of electropositive metals into the C_{60} lattice.

Electron transfer from the metal to C_{60} gives C_{60}^{n-} anions (fullerides). The orbitals of neighbouring C_{60} molecules overlap forming bands and the electrons are able to move throughout the solid i.e metallic. T_C high for molecular based solid.

For the superconducting A_3C_{60} (A = alkali metal) that have a cubic structure, all the tetrahedral and octahedral interstitial sites are filled. T_C is proportional to the average cation volume (the distance between C_{60} molecules).







Theory of superconductivity (conventional superconductivity)

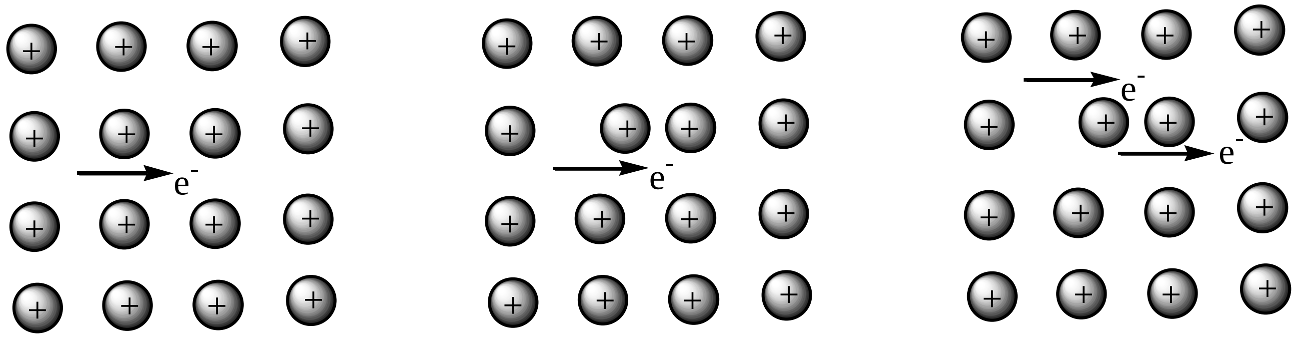
J. Bardeen, L. N. Cooper and J. R. Schrieffer (1957). "Microscopic Theory of Superconductivity". *Physical Review* **106** (1): 162–164.

The theory(ies) of superconductivity are mathematically very complicated however a qualitative picture of one (BCS theory) can be given.

BCS (Bardeen, Cooper, and Schrieffer) theory describes the mutual attraction of two conduction electrons mediated by lattice vibrations.

In the same way electromagnetic waves can be quantised as photons, the frequencies of lattice vibrations can also be quantised as *phonons*. Electron-phonon coupling is the mechanism by which electrons can be attracted to each other. The two electrons are known collectively as a *Cooper pair*.

The two electrons do not have to be close to each other and can be many thousands of atomic spacings apart.



Electron-phonon coupling

The importance of phonons can be demonstrated experimentally by the use of isotopes. T_C is inversely proportional to $\sqrt{M}$ where M is the mass of a lattice ion.

Except for at very low temperatures the resistance of metals is due to the scattering of electrons by phonons, which is one reason why the resistance of metals increases with increasing temperature. (more phonons at higher temperature). For superconductors Cooper pairs are not scattered and therefore have zero resistance.

There is of course a repulsive electrostatic interaction between two electrons. Electron-phonon coupling must be strong for the Copper pair to remain intact and it must be greater than electron-electron repulsion. The binding energy of Cooper pairs is usually weak and this is why T_C is usually low.

Nanomaterials

Have been known for millennia but have hit the headlines more recently because of their remarkable properties and the development of synthetic and analytical tools to characterise and manipulate them. (mainly metals and metal oxides, but more recently carbon based e.g. carbon nanotubes and graphene)

Many properties have size dependence. Nanomaterials are focused mainly on structures with a dimension between 1 – 100 nm, bridging the gap between molecules (0.1 -10 nm) and traditional solid state compounds > 100 nm.

Size Dependent Properties

e.g.

Optical
Magnetic
Electronic
Catalytic
Mechanical

Nanotechnology Applications

Technological

Colour (colloids, quantum dots)

Computing (Magnetic memory, spintronics)

Strong and dense materials (reduce brittleness and fatigue)

Catalysis (Car converters, fuel cells, chemicals)

Energy Conversion (solar, electromechanical)

Health

Imaging (microscopy, MRI)

Drug Delivery (needleless injection)

Magnetic heating (anti-cancer)

Protection (sunscreen)

Food

Additives

Nanoparticles

How many atoms are in e.g. a 2 nm diameter silver nanoparticle?
Assume a sphere, Ag atom radius = 172 pm

$V_{Ag} = \frac{4\pi r^3}{3} = 0.0213\ nm^3$ $\qquad V_{np} = 4.18\ nm^3$ 74% packing efficiency ca. 145 Ag atoms

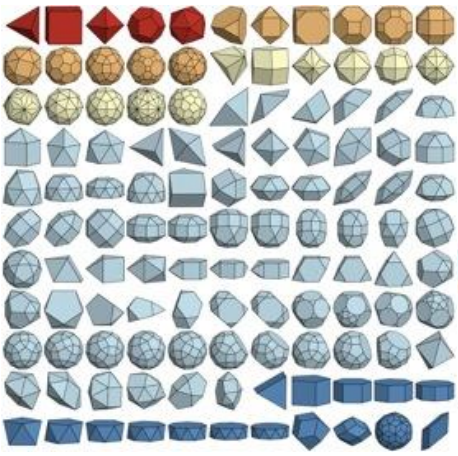
$A_{Ag} = \pi r^2 = 0.093\ nm^2$ $\qquad A_{np} = 4\pi r^2 = 12.56\ nm^2$ 90% packing efficiency ca. 120 Ag atoms

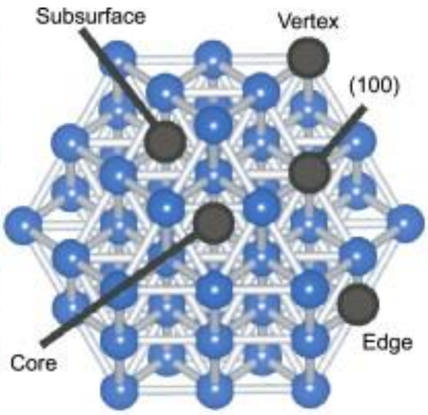
footprint on surface

i.e. A lot of the nanoparticle atoms will be at the surface.

Shapes of nanoparticles

But nanoparticles are not spherical. Exhibit a range of shapes. Each shape and surface has unique energy and electronic structure. Certain shapes preferred thermodynamically. Surface can have many defects.



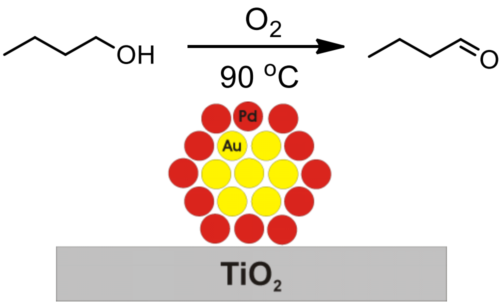


site	coordination number
vertex	5
edge	7
(100)	8
subsurface	12
core	12

Cubeoctahedron is very common shape. Surfaces with low miller indices generally have lower surface energy. All this leads to chemistry that may be very different from the bulk material and is sensitive to the surface structure and number and type of defects. e.g. in catalysis and sensing.

e.g. gold is generally considered inert, but as nanoparticles it is a good oxidation catalyst. When mixed with other metals, alloys are formed.

2.5% Au/Pd supported on TiO_2. No stoichiometric oxidant required (Cr, Mn, peroxides etc). Oxidation with air at low T. Alloy nanoparticle is core shell Au@Pd.



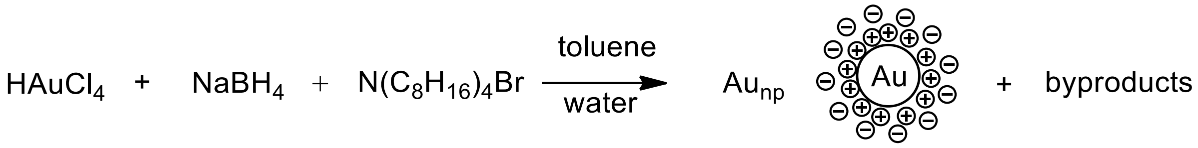
How can shape be controlled?

Wet chemical methods

Used to prepare soluble nanoparticles. Need to prevent aggregation which causes precipitation. Need to coat the nanoparticle surface.

Ligands can form a steric barrier or cause electrostatic repulsion between particles. Steric barrier most common. Can use many long chain ‘fatty’ acids, amines, thiols, phosphines which covalently bind to the metal or metal compound surface.

e.g. Reduction of metal salts or compounds to make metal nanoparticles

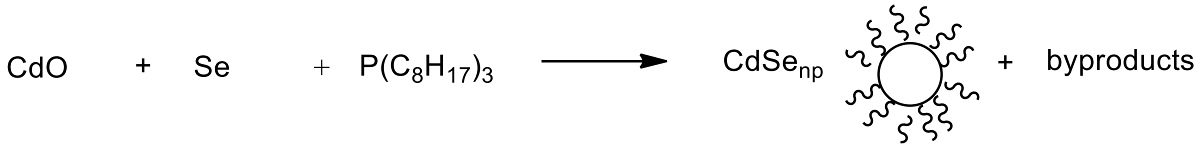


$$HAuCl_4 + NaBH_4 + N(C_8H_{16})_4Br \xrightarrow[\text{water}]{\text{toluene}} Au_{np} + \text{byproducts}$$

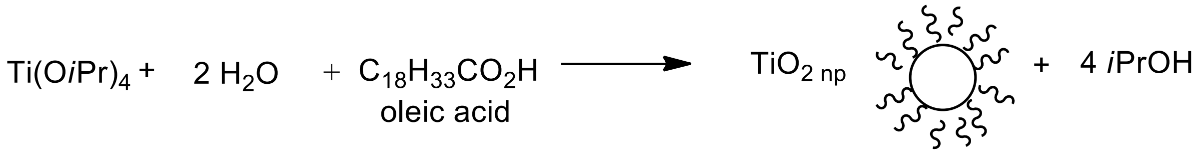
Electrostatic stabilisation of the gold. The ammonium ions are not covalently bound to the metal surface. Can add thiols to bind strongly and increase stabilisation.

Metal oxides and other semiconductors prepared by hydrolysis or decomposition of a metal compound or complex in the presence of a ligand that binds covalently to the surface.

e.g.



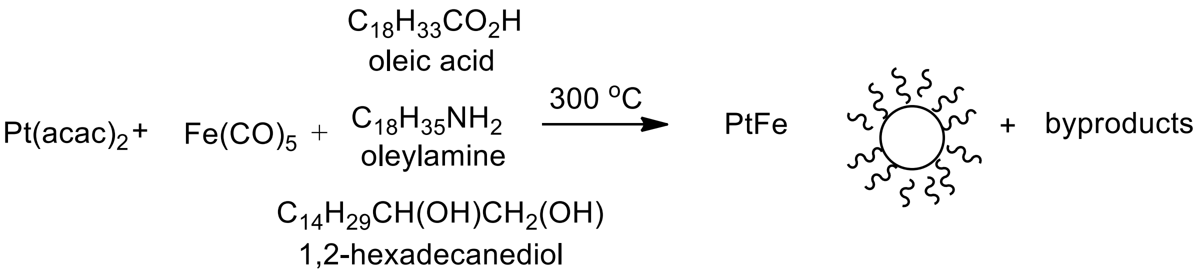
$$CdO + Se + P(C_8H_{17})_3 \longrightarrow CdSe_{np} + \text{byproducts}$$



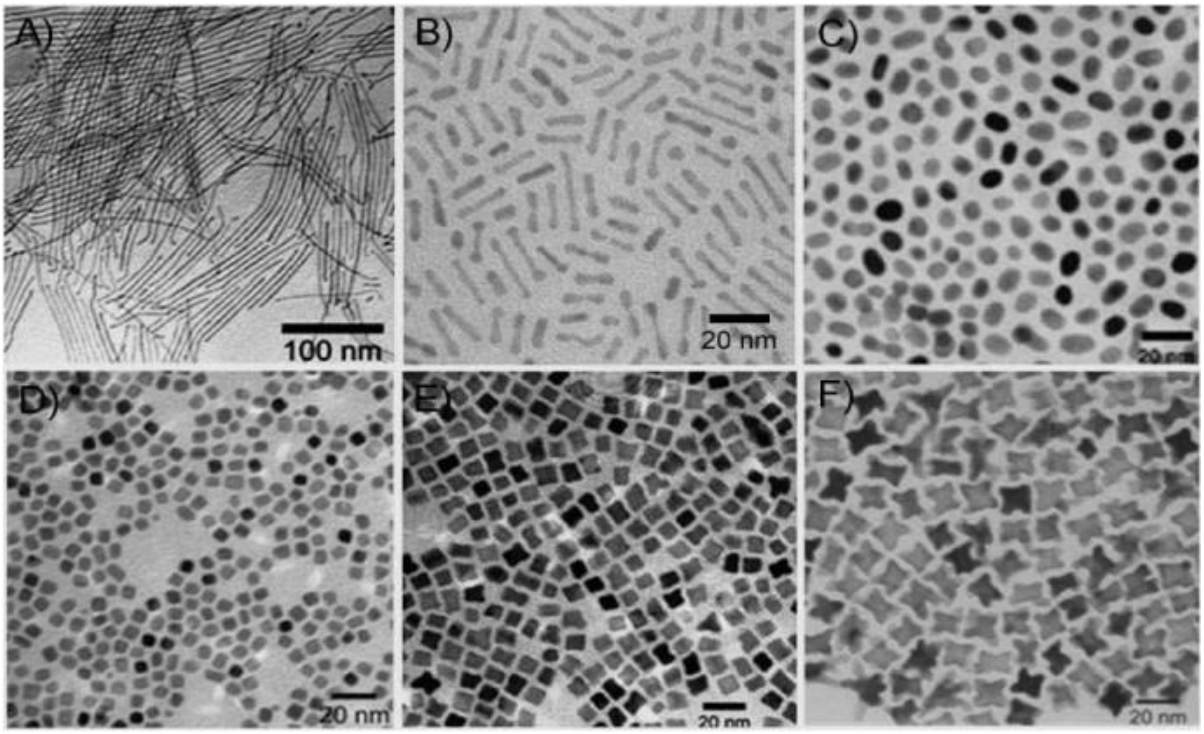
$$Ti(O\mathit{i}Pr)_4 + 2\,H_2O + \underset{\text{oleic acid}}{C_{18}H_{33}CO_2H} \longrightarrow TiO_{2\,np} + 4\,\mathit{i}PrOH$$

Size and shape of the nanoparticles can be controlled by synthesis temperature, time and relative concentrations of ligand and metal precursor.

e.g. FePt nanocrystals



$$Pt(acac)_2 + Fe(CO)_5 + \begin{matrix} \underset{\text{oleic acid}}{C_{18}H_{33}CO_2H} \\ \underset{\text{oleylamine}}{C_{18}H_{35}NH_2} \\ \underset{\text{1,2-hexadecanediol}}{C_{14}H_{29}CH(OH)CH_2(OH)} \end{matrix} \xrightarrow{300\ ^{o}C} PtFe + \text{byproducts}$$



FePt nanocrystals Narayan Poudyal, J. Appl. Phys. 2009, 105, 07A749

Varying the ligand concentrations and temperature changes the shape. The ligands will bind preferentially to specific surfaces (e.g. 001) and prevent growth in this direction.

Solubility allows use in solution chemistry (e.g. biological applications) and processing to make materials containing isolated nanoparticles e.g. for catalysis.

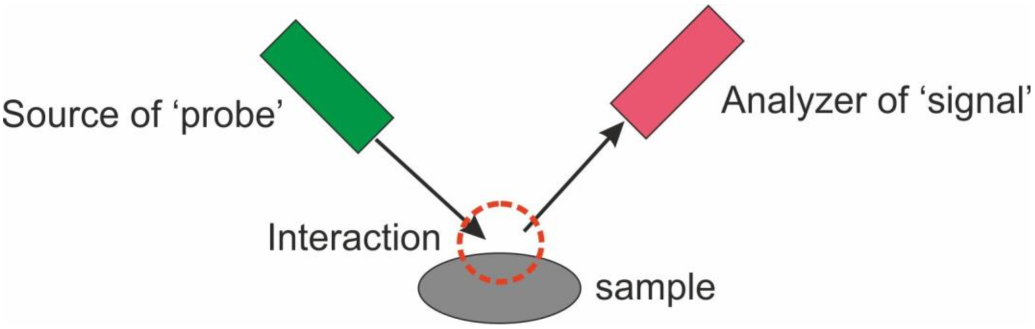
Characterisation of Nanoparticles

Development of analytical tools has revolutionized materials (nano)science

What would we like to know?

These include
1. Composition: stoichiometry(elemental analysis) and particle homogeneity
2. Structure: internal bulk, surface, defects
3. Morphology and particle size: shape and size distribution of particles
4. Properties (e.g. magnetic, electrical, dielectric, optical, catalytic, dynamic)

Analysis



Probe: photons, electrons, neutrons, ions

Interaction: absorption, absorption-emission, reflection, refraction, diffraction, scattering.

Signal: photons, electrons, neutrons, ions

Can perform measurements as a function of time, temperature, pressure, and field (electric and magnetic).

Considerations
1. Probe size (spatial resolution). Is the probe 'local' with high spatial resolution or will the signal be averaged over a larger interaction volume.
2. Timescale (temporal resolution). Are the timescales of the source and analyser fast compared to the phenomenon of interest.

Common analytical techniques for structure and composition

Diffraction Methods: Single crystal if lucky but often powders.

X-ray Diffraction (Nobel Prize 1914, 1915, 1985): Maps electron density giving the relative atomic positions.

Neutron Diffraction (Nobel Prize 1994): Based on scattering length and cross section of individual isotopes (not related to electron density e.g ^{2}H gives large response). Neutrons also have a magnetic moment allowing the magnetic structure to be determined.

Electron Diffraction (Nobel Prize 1937). Most often used in conjunction with electron microscopy (see below). Sensitive to electron density similar to x-ray diffraction. Can be used on individual nanocrystals.

Note that the structures obtained are an average structure.

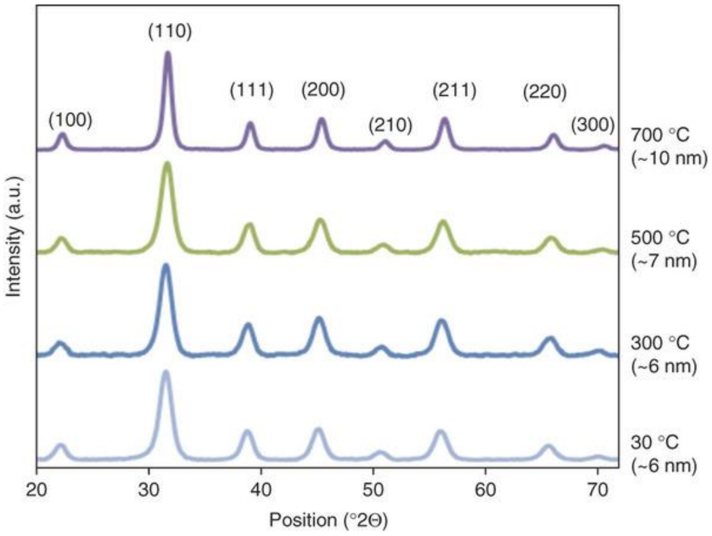
Particle Size from X-ray Diffraction

The width of diffraction peaks increase as the size decreases and is described by the Scherrer equation. Applicable to particles <100 nm.

$$\tau = \frac{\kappa\lambda}{\beta\cos\theta}$$

Where τ = particle size, κ = shape factor, λ = x-ray wavelength, β = full width half maximum (fwhm) in radians (1 degree = $\pi/180$ radians), θ = Bragg angle.

e.g. $BaTiO_3$ nanoparticles. Synthesised at 500 °C, the 111 reflection measured using Cu X-rays (1.5418 Å), at 39.45° 2θ, has a fwhm of 1.20° (0.0210 radians). Assume a shape factor of 0.9, τ = 7 nm.

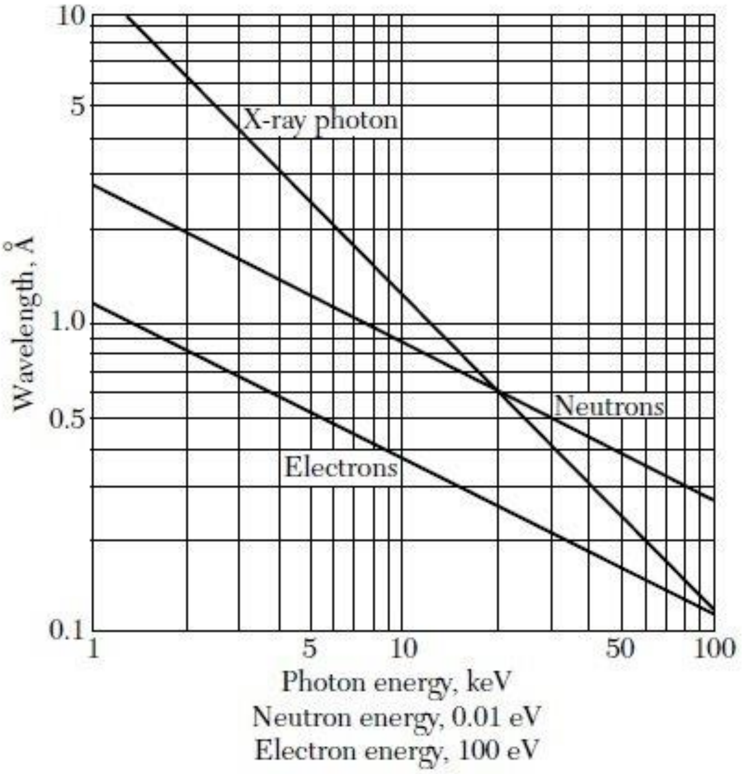


The calculated value does not include other effects of broadening so is often an underestimation.

For $BiTiO_3$ the particles are growing (sintering) with heating because larger particles have lower surface area and hence surface energy.

Electron microscopy and scanning probe microscopy (Nobel Prize 1928, 1929, 1986)

Why do we need electron microscopy?



Two distinguish two positions you need sufficient resolving power
For standard optics the minimum distance that can be resolved is described by The Abbe diffraction limit.

$$d = \frac{\lambda}{2n \sin\theta}$$

Where d (minimum resolvable distance), λ (wavelength), n (refractive index), θ (half angle light is converging to).

Shorter wavelength = smaller distance that can be resolved.

Wave-particle duality. All moving matter has wave properties.

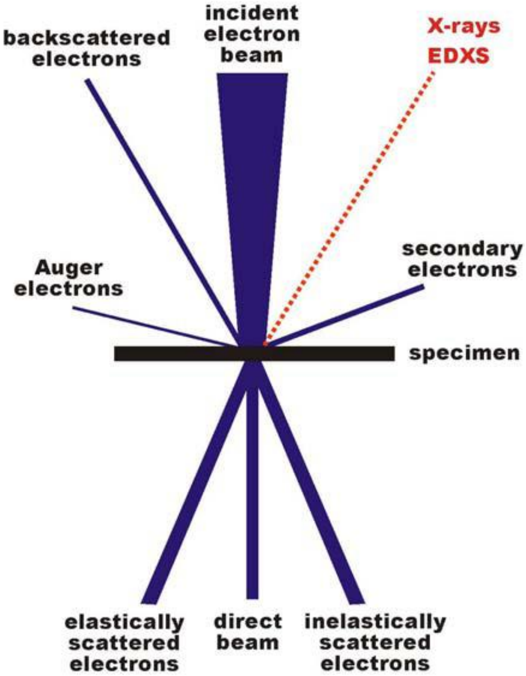
$$\lambda = h/p = h/mv$$

(h = Planck constant; *p = momentum;* m = mass; v = velocity)

Wavelength of Photons	**Wavelengths of electrons**
Visible light: 2000 Å	0.035 Å at 120kV
X-rays: 1.5 Å for Cu Kα	0.020 Å at 300 kV

Therefore a high energy collimated electron beam can be used to image very small distances

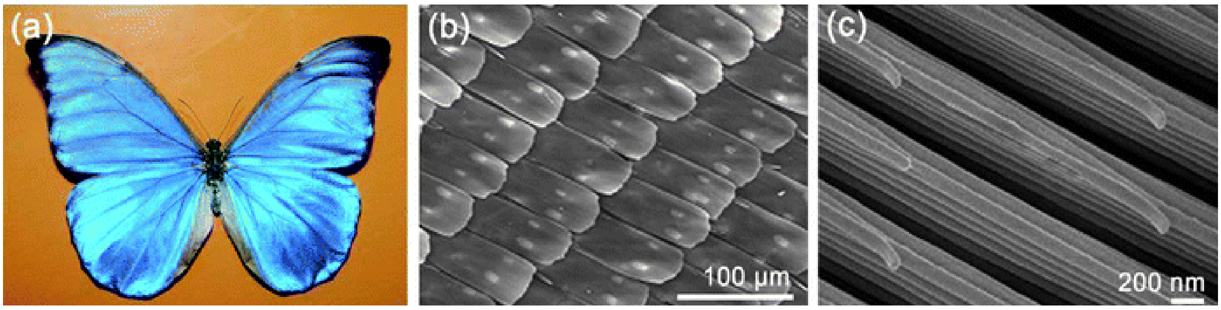
Electron Microscopy: Usually performed in vacuum to reduce electron scattering



Electron beams can interact (elastically and inelastically) with solids in many ways, which can be used to probe the structure and properties of materials. Needs fancy electron 'optics' to focus the beam = £££.

SEM (scanning electron microscopy): Back scattered and secondary electrons give morphology and particle size distribution. Resolution 10 nm -10 μm.

Energy Dispersive Spectroscopy (EDS, EDXS, EDX): Used with SEM. Electrons used to excite inner electrons of atoms and then emit a characteristic photon giving an element map.



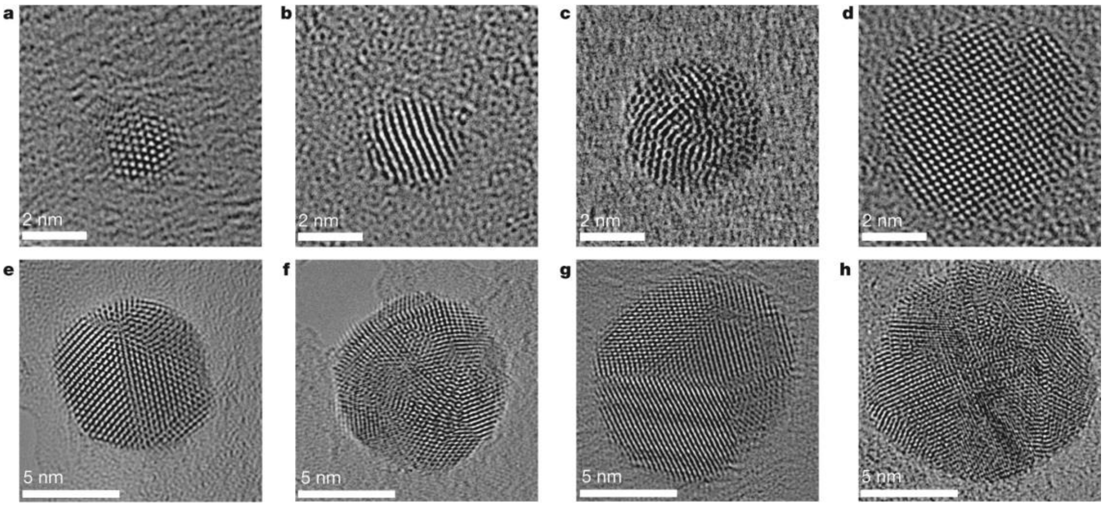
Butterfly wings at increasing magnification

TEM and STEM ((scanning) transmission electron microscopy): requires thin sample so electrons pass through and uses scattered electrons to image. Resolution Atomic - 100 nm. Also usually fitted with EDS

Other modes:

Electron diffraction also gives information about the crystal structure of individual particles including defects.

Electron energy loss spectroscopy (EELS): Similar in principle to EDS but better for lighter elements and can probe valence electrons and chemical bonding. Can generate element maps with atomic resolution.

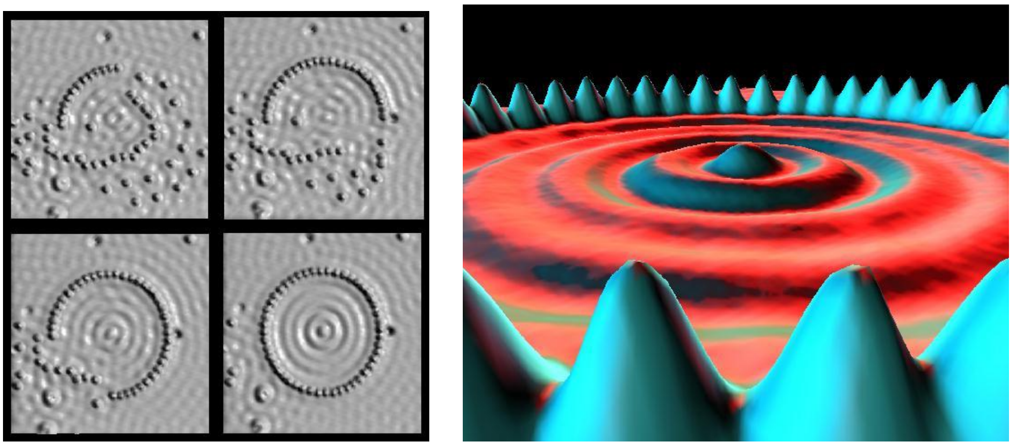


STEM of Ag nanoparticle

Scanning probe microscopy (SPM): Used in vacuum or in liquids

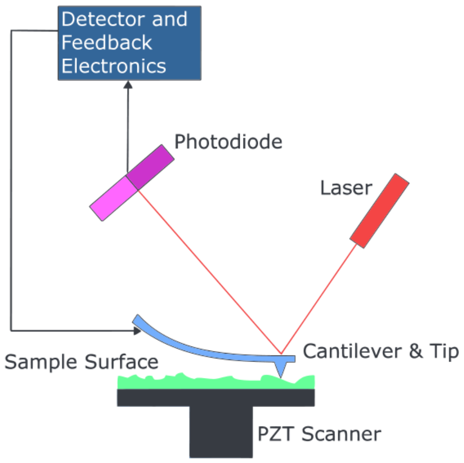
Used for surface characterisation to map structure but also function (e.g. magnetic and electrical properties)

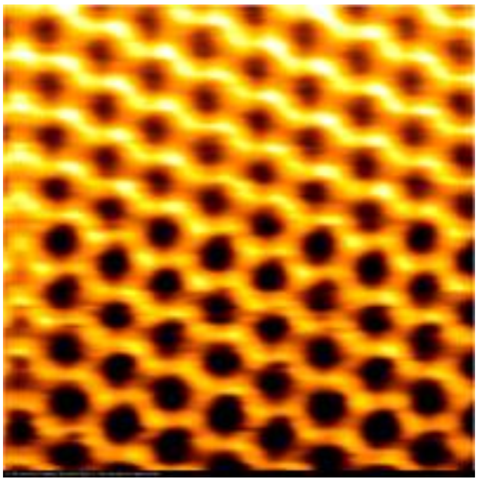
STM (scanning tunnelling microscopy): Atomic resolution imaging and atom manipulation. Uses piezoelectric crystals to maintain a current between the tip and sample.



Quantum corral ‘particle in a box’

Atomic Force Microscopy (AFM): Measures deflection of a tip as it is scanned across the surface of a material. Sub nm resolution now possible. Can be used for direct imaging but also many other functional modes (e.g. electrochemistry).





AFM of graphite

Other common spectroscopic techniques

Using electrons

X-ray fluorescence spectroscopy (XRF) (Nobel Prize 1924): Quick method to determine elemental analysis of a solid. Very similar to EDS and EELS but at much lower resolution (μm-mm)

X-ray photoelectron spectroscopy (XPS) (Nobel Prize 1981): surface composition and oxidation states

Using photons

Solid state NMR spectroscopy: Local structure and dynamics (need active nuclei)

Electron spin resonance (EPR): Local structure and defects

Uv-Vis spectroscopy: Band gap of semiconductors

Raman spectroscopy: Vibrations (phonons) in crystals

Summary

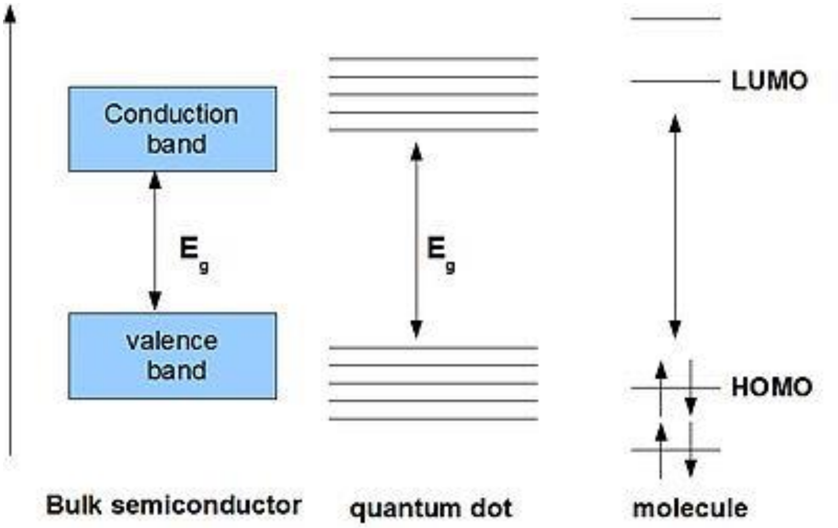
	X-ray/Neut. diffraction	**SEM**	**TEM**	**STM**	**AFM**	**NMR and ESR**	**XPS**
Bulk elemental composition	X	X	X				
Crystal structure	X		X				
Local structure	X		X			X	
Defects			X			X	
Morphology		X	X				
Surface structure				X	X		
Surface composition				X	X		X
Oxidation state			X				X

Electronic structure and Optical properties of Nanoparticles

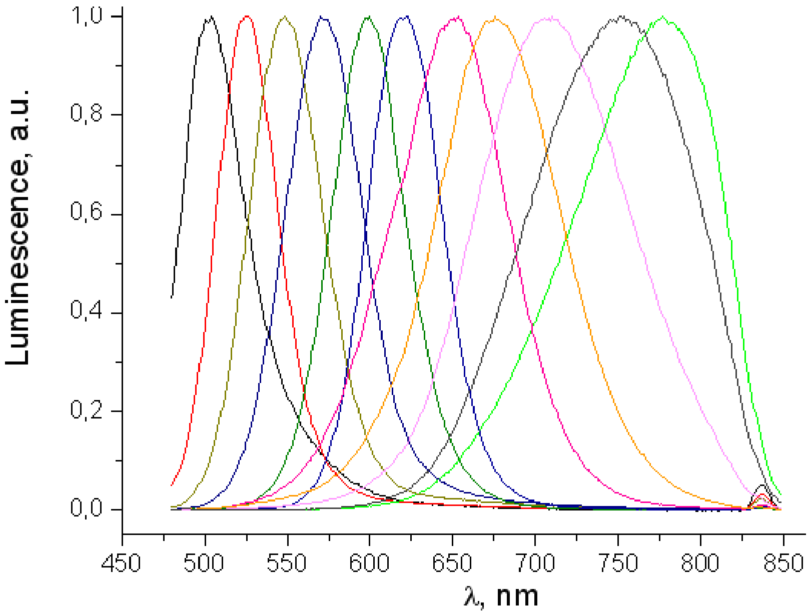
Differences between metals and semiconductors.

Semiconductors

As the number of atoms and size reduces the band structure tends toward that of a molecule.



When a photon is absorbed an exited state (electron-hole pair) called an exciton is generated. Relaxation can lead to luminescence (fluorescence) which is size dependent. Nanoparticles in this size regime are called quantum dots. The band gap (Eg) will increase with decreasing size.



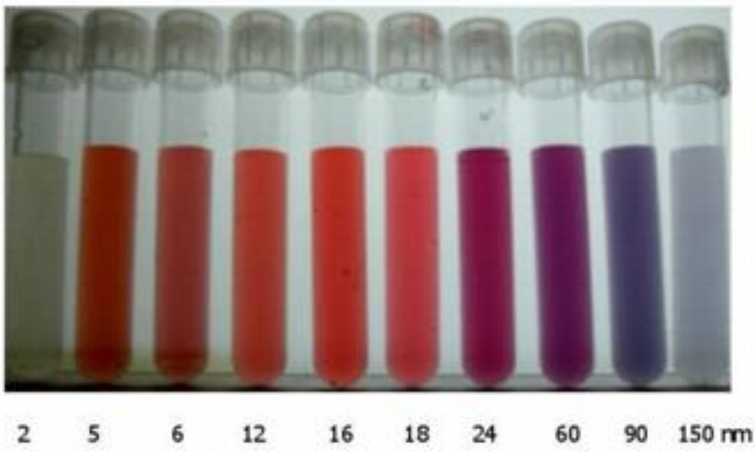
CdTe nanoparticles fluoresce in the visible region (size increases left to right).

Can be used as sensors and tags in biology (more inert than organic dyes). Solar energy conversion. Light emitting diodes.

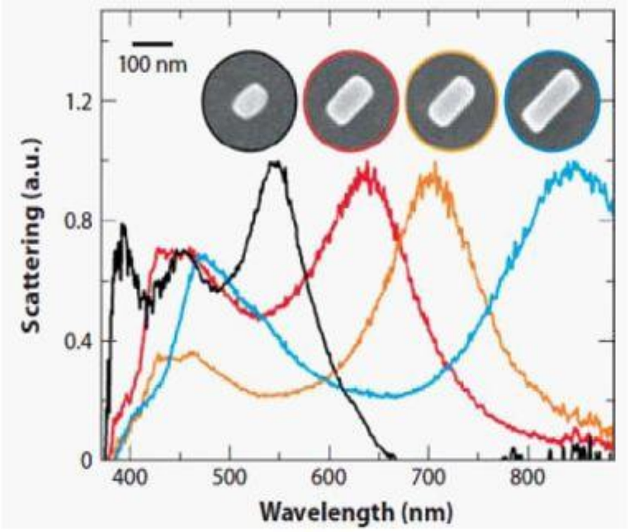
Metals

In metals the conduction band is retained until very small particle size (ca. 2 nm). The conduction electrons can absorb light leading to a collective excitation. This excitation is called Surface Plasmon Resonance (SPR). For some metals SPR is in the visible region (gold, silver and copper) leading to colour. The SPR is dependent on a number of factors including size and shape.

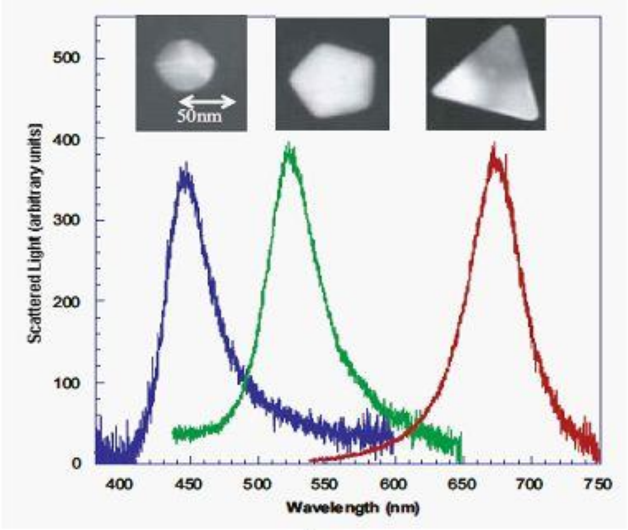
e.g. gold nanoparticles have size and shape dependent colours.



colourless red purple blue colourless

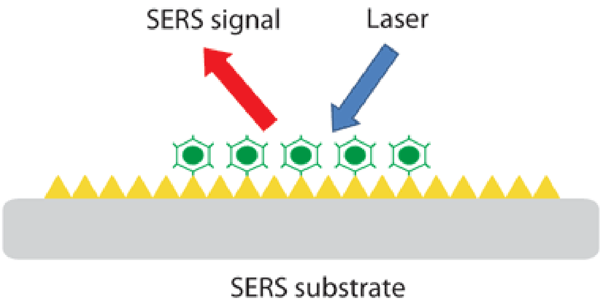


(a)



(b)

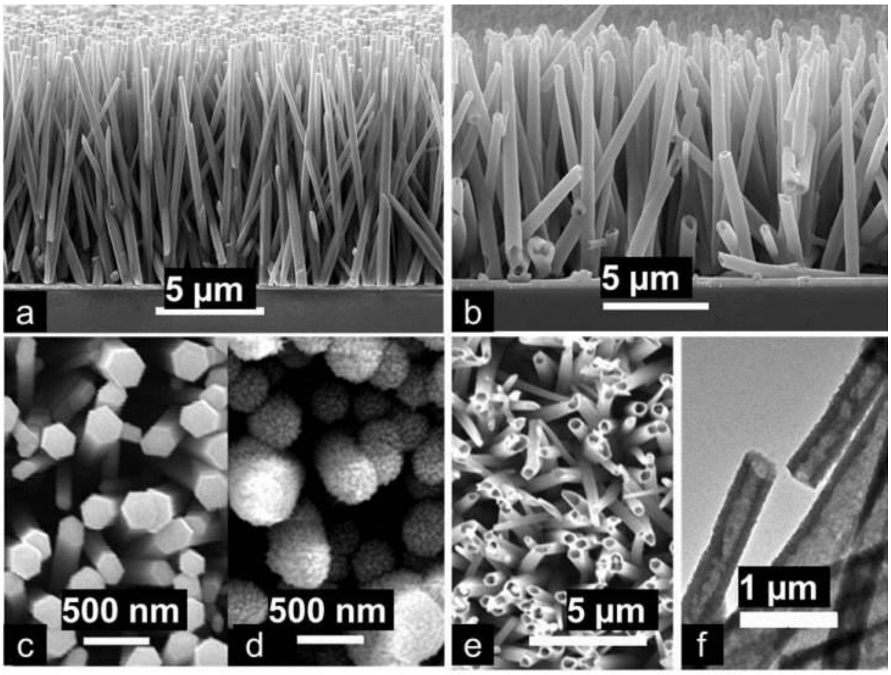
Used for centuries to stain glass, also more recently in medicine, but most commonly now in very sensitive sensors (surface enhanced Raman spectroscopy (SERS)) as the plasmon is very sensitive to surface species.



Other uses of nanostructured materials

Nanotubes

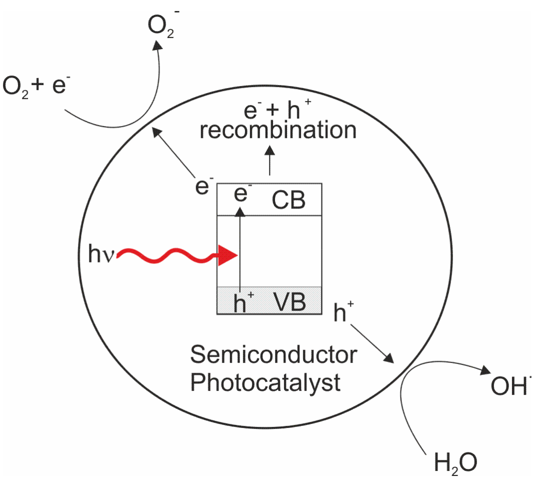
e.g. TiO_2 nanotubes formed electrochemically by etching Ti metal foil with HF.



Nanotube structure changes the surface energy preventing wetting, which reduces the growth of bacteria. Used as antibacterial surfaces e.g. for metal surgical implants.

Photocatalysts

e.g. TiO_2 nanoparticles

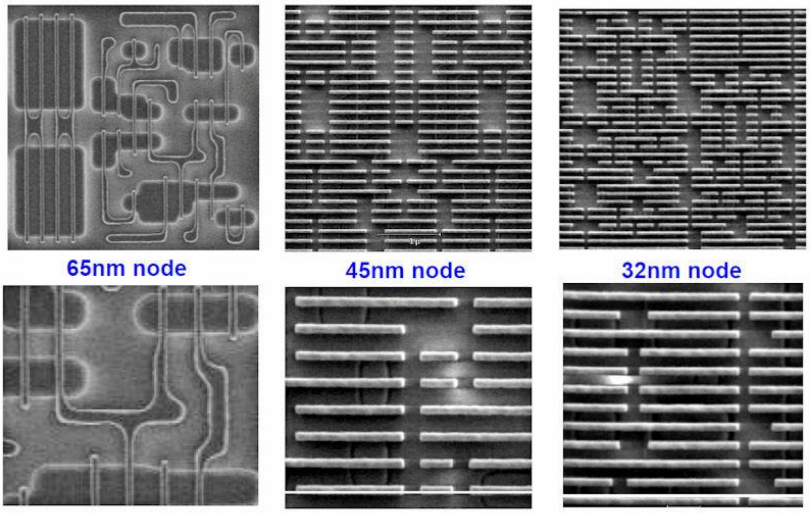


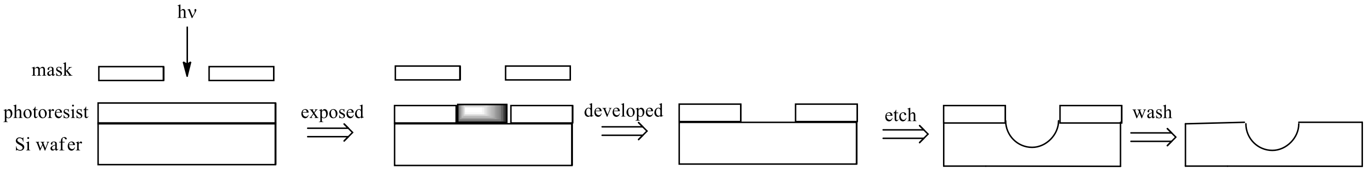
Jubilee Church in Rome

$OH^{\cdot}$ and O_2^- are strong oxidizing agents and will degrade organic compounds to CO_2 and H_2O. TiO_2 (titania) is used to clean surfaces, reduce air pollution and clean drinking water. Can add to materials including plastics, glasses and concrete.

Integrated circuits

Based on silicon with <100 nm features are prepared using photolithography.





The size of the features largely determines the computing power. The photoresist is usually a polysilane. The etching step can be an acid or usually a plasma. Can also add dopants onto the exposed wafer.

Current state-of-the-art 10 nm feature size (25 million transistors per mm^2)

Additives

One of the biggest markets for inorganic (nano)materials are in additives used for a very wide range of products including coatings (e.g. paint) for protection and colour. Some applications are in direct contact with humans including food, cosmetics and suncreams. *Environ. Sci.: Nano*, **2019**, 6, 1549.

e.g. TiO_2 (E171) used to whiten sweets, ice-cream, icing, chewing gum, bread, pastries + lots of other products.

Current controversy over safety and some countries have recently banned its use.

A selection of other food additives and their uses

Colours		
E171	Titanium Dioxide	White
E172	Iron oxides and iron hydroxides	Brown
E173	Aluminium	Silver/Grey
E174	Silver	Silver
E175	Gold	Gold
Additives		
E518	Magnesium sulfate (Epsom salts), (acidity regulator)	firming agent
E519	Copper(II) sulfate	preservative
E520	Aluminium sulfate	firming agent
E521	Aluminium sodium sulfate	firming agent
E522	Aluminium potassium sulfate	acidity regulator
E523	Aluminium ammonium sulfate	acidity regulator
E524	Sodium hydroxide	acidity regulator
E525	Potassium hydroxide	acidity regulator
E526	Calcium hydroxide (acidity regulator)	firming agent
E527	Ammonium hydroxide	acidity regulator
E528	Magnesium hydroxide	acidity regulator
E529	Calcium oxide (acidity regulator)	improving agent
E530	Magnesium oxide (acidity regulator)	anti-caking agent
E535	Sodium ferrocyanide (acidity regulator)	anti-caking agent
E536	Potassium ferrocyanide	anti-caking agent
E537	Ferrous hexacyanomanganate	anti-caking agent
E538	Calcium ferrocyanide	anti-caking agent
E539	Sodium thiosulfate	antioxidant
E540	Dicalcium diphosphate[citation needed] (acidity regulator)	emulsifier
E541	Sodium aluminium phosphate (i) Acidic (ii) Basic	emulsifier
E542	Bone phosphate (Essentiale Calcium Phosphate, Tribasic)	anti-caking agent
E543	Calcium sodium polyphosphate	emulsifier
E544	Calcium polyphosphate	emulsifier
E545	Ammonium polyphosphate	emulsifier
E550	Sodium Silicates (i) Sodium silicate (ii) Sodium metasilicate	anti-caking agent
E551	Silicon dioxide (Silica)	anti-caking agent
E552	Calcium silicate	anti-caking agent
E553a	(i) Magnesium silicate (ii) Magnesium trisilicate	anti-caking agent
E553b	Talc	anti-caking agent
E560	Potassium silicate	anti-caking agent