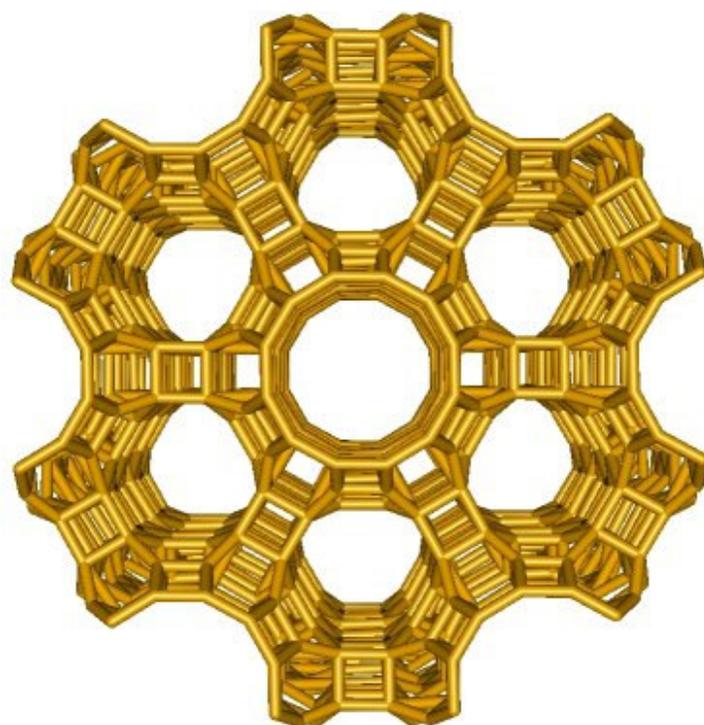


Inorganic Materials Chemistry

Core Module 7



Inorganic Materials Chemistry

6 lectures Module 7 2005

Synopsis

Lecture 1: Introduction: Methods of synthesis and analysis

Lecture 2: Some structural properties of solids

Lecture 3: Magnetism I: Interactions between solids and magnetic fields

Lecture 4: Magnetism II: Cooperative magnetism

Lecture 5: Dielectric Properties: Interactions between solids and electric fields

Lecture 6: Superconductivity

Bibliography:

S. Elliot	<i>'The physics and chemistry of solids'</i>
H. M. Rosenberg	<i>'The solid state'</i>
A. R. West	<i>'Solid state chemistry and its applications'</i>
A. F. Wells	<i>'Structural inorganic chemistry'</i>
L. Smart and E. Moore	<i>'Solid state chemistry. An introduction'</i>
A. K. Cheetham and P. Day	<i>'Solid state chemistry. Techniques'</i>
M. T. Weller	<i>'Inorganic materials chemistry'</i>

Associated Courses

AKD	Transition metals	1 st year
RNP	Solid state structure	1 st year
VC	Structure and bonding	1 st year
RED	Metal-ligand metal-metal bonding	2 nd year
KW	Surface chemistry	2 nd year
PHW	Diffraction	3 rd year
KW	Solid state chemistry	3 rd year

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

- i) describe methods of synthesis of solid state compounds using examples.
- ii) understand the difference between synthesis and modification of materials.
- iii) understand the limitations of techniques for the analysis of materials.
- iv) explain structure types and polymorphism.
- v) explain the main reasons for and types of defects in ionic solids.
- vi) calculate the proportion of defects in a solid.
- vii) explain what is meant by a non-stoichiometric solid and a solid solution.
- viii) understand and explain the behaviour of a paramagnet, antiferromagnet, ferromagnet and ferrimagnet as a function of temperature.
- ix) apply the Curie-Weiss equation and calculate the magnetic moment from the magnetic susceptibility.
- x) explain the effect of domain structure of ferro- and ferrimagnets.
- xi) explain the superexchange mechanism for rock salt metal oxides.
- xii) describe the spinel structure and estimate the net magnetic moment of ferrimagnets.
- xiii) describe the perovskite structure and its relation to ferroelectricity using the tolerance factor.
- xiv) describe the phenomenon of piezoelectricity and pyroelectricity.
- xv) describe the electric and magnetic properties of superconductors.
- xvi) explain the structural characteristics of cuprates, fullerides and borides.
- xvii) qualitatively describe BCS theory of superconductivity.

See Structure Visualisation Package on 'Year 3' page of departmental website for interactive structures.

Lecture 1

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)
Construction (concrete, steels)
Transport (catalytic converters, fuel cells, strong lightweight materials)
Chemicals (catalysts, sensors)
Medicine (artificial joints, bones, and muscle)
Gems (jewellery, cutting tools, lasers)

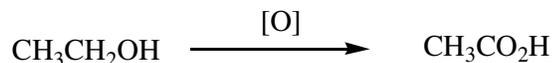
Synthesis of solid state compounds

Molecular synthesis

Characteristics:

1. Solvents
2. Low synthetic temperatures (typically -80 to 250°C)
3. Kinetic control

e.g. Oxidation of alcohols to carboxylic acids



Thermodynamic control would lead to CO_2 and H_2O



Solid state synthesis

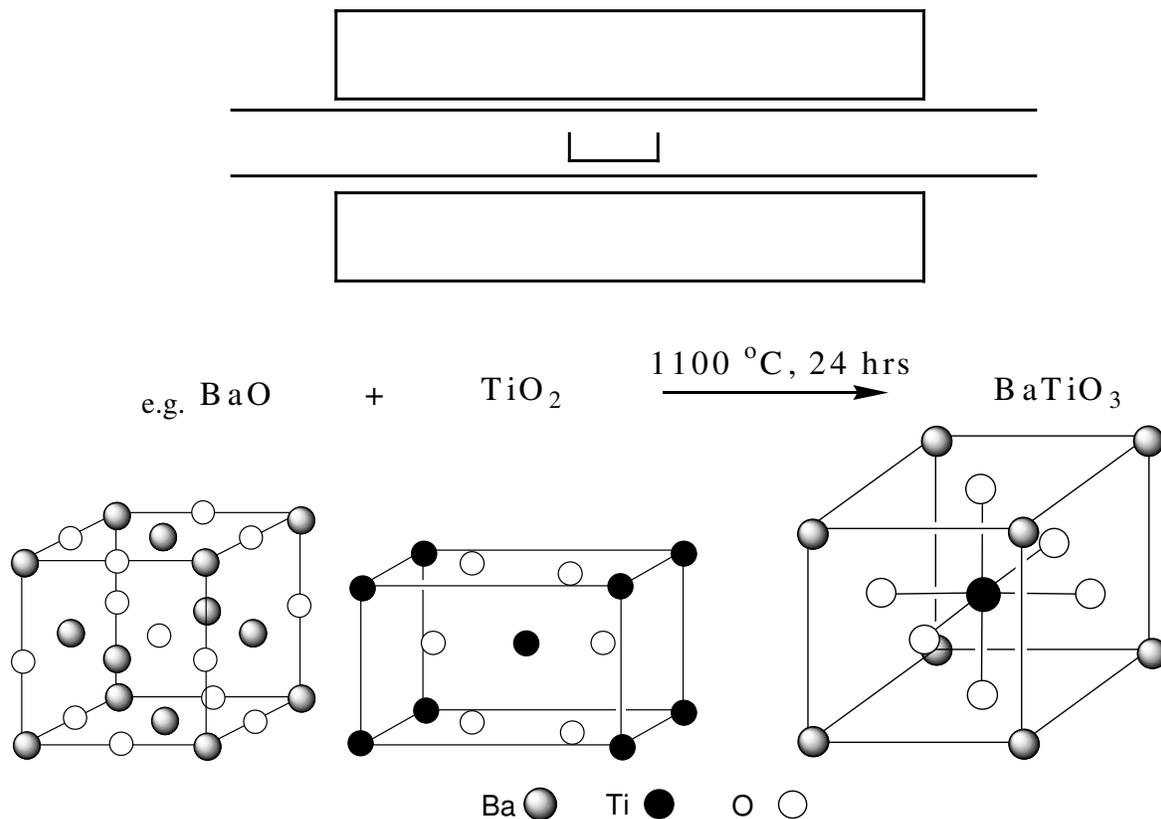
Characteristics:

1. Commonly no solvent
2. High synthetic temperatures (typically $> 300^{\circ}\text{C}$. Can be as high as 3000°C)
3. Thermodynamic control

Synthetic methods

Solid to solid synthesis (e.g. ceramic metal oxides)

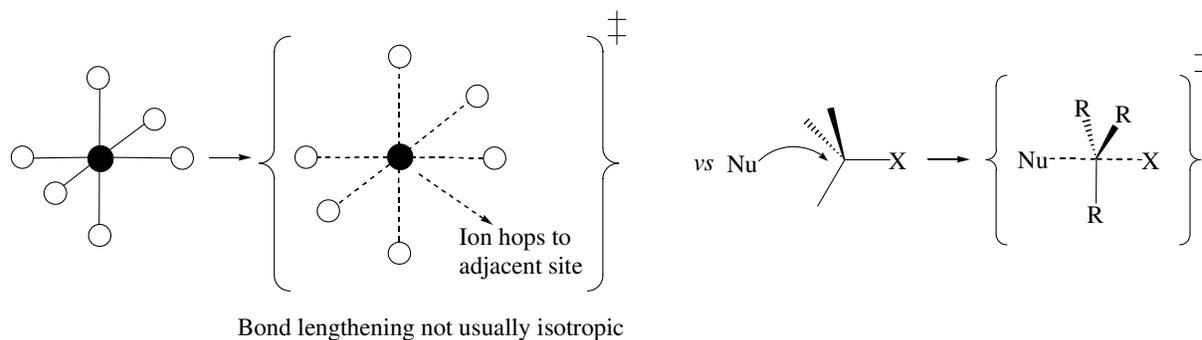
Heating solid precursors. Furnace, Microwaves (dielectric heating and plasmas)



Why are such high temperatures usually required?

Ion diffusion:

Ions have to diffuse through a solid. Many bonds need to be broken and formed giving high activation energy (*c.f.* molecular chemistry where usually only one bond is broken or formed).

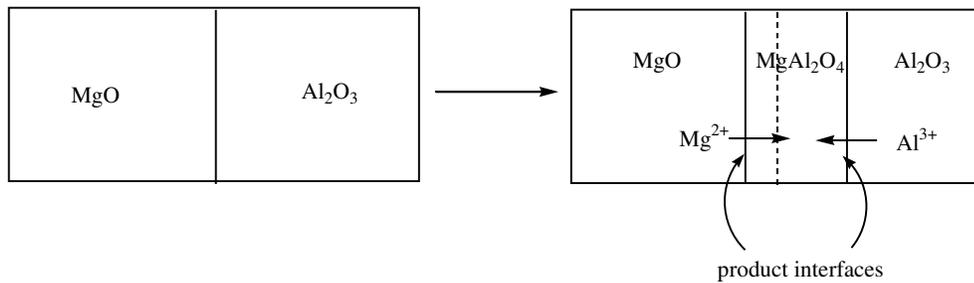


Nucleation and surface area: Ion diffusion requires starting material particles to be in contact. Smaller particles give greater reaction rates.

If the structure of the product is different from the starting materials nucleation will be slow lowering the reaction rate.



Structure:- rock salt corundum spinel



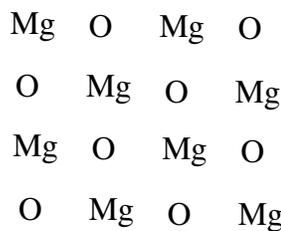
Growth fronts of product interfaces may move at different rates



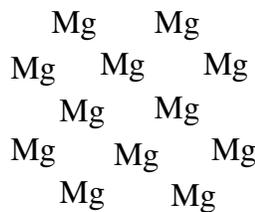
Reaction b) gives 3 times as much product as reaction a)

A particle may also have different surfaces that can react at very different rates.

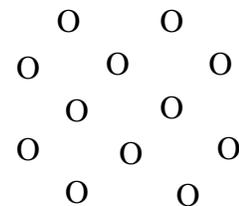
e.g. MgO



{100} face



{111} face



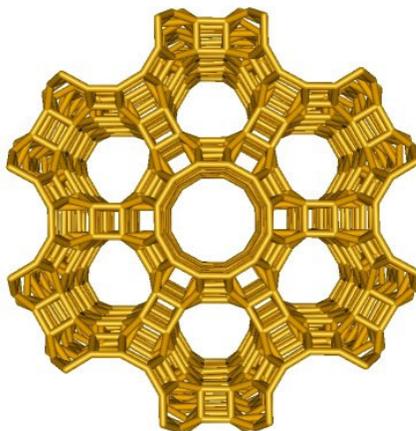
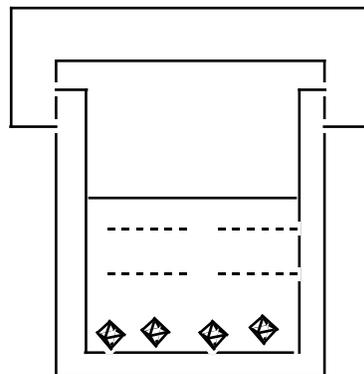
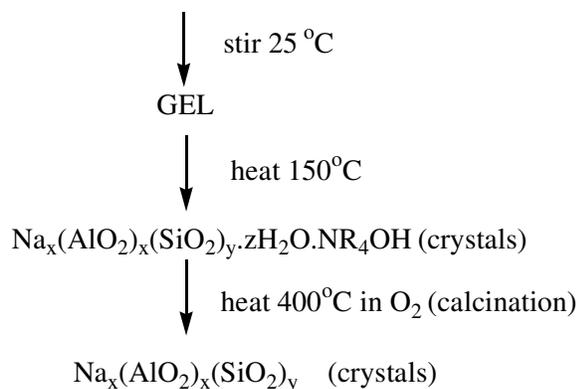
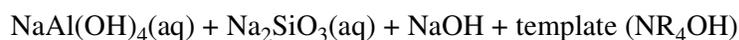
{111} face

There are no general rules that indicate which surface will be the most reactive.

Liquid to solid synthesis

Melts: Very little difference to reaction/crystallisation of molecular compounds. Very high temperature is usually required. Single crystals are commonly grown from melts and knowledge of the relevant phase diagram is beneficial.

Solvothermal methods: e.g. Hydrothermal synthesis of zeolites (aluminosilicates)



The zeolites framework is made up of SiO₂ tetrahedra with the occasional substitution of Al for Si. To compensate the charge difference (Si(+4), Al(+3)) sodium cations are accommodated on the inner surface of the framework.

Gas to solid synthesis

Decomposition of volatile precursors

This technique is used extensively for the preparation of thin films.

e.g. metal organic chemical vapour deposition (MOCVD) of GaAs (III/V semiconductor)



The gaseous precursors are decomposed onto a substrate. Decomposition can occur by heating or photolytically.

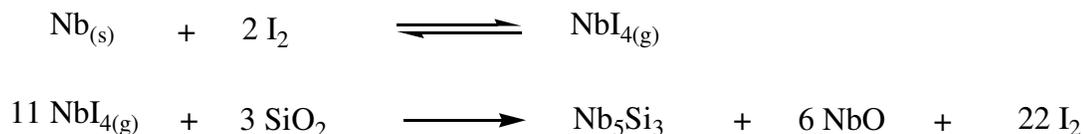
Vapour transport methods

Good for single crystal growth. It can also be used for synthesis.

e.g. Niobium silicide Nb_5Si_3

Nb and SiO_2 do not react if heated under vacuum at normally accessible temperatures (1100°C)

but in the presence of I_2



Modification of solids (ion exchange and intercalation/deintercalation)

Note: Both ion exchange and intercalation/deintercalation occur with conservation of charge.

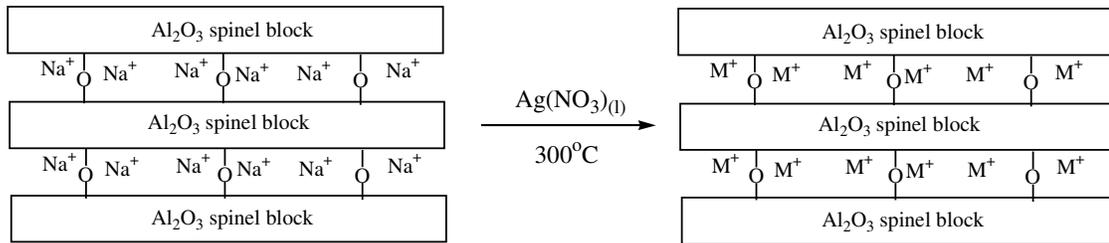
Ion exchange is where the lattice ions of a structure are exchanged (replaced).

e.g. Zeolite-A.



Water softening agent (now used in washing powders instead of phosphates)

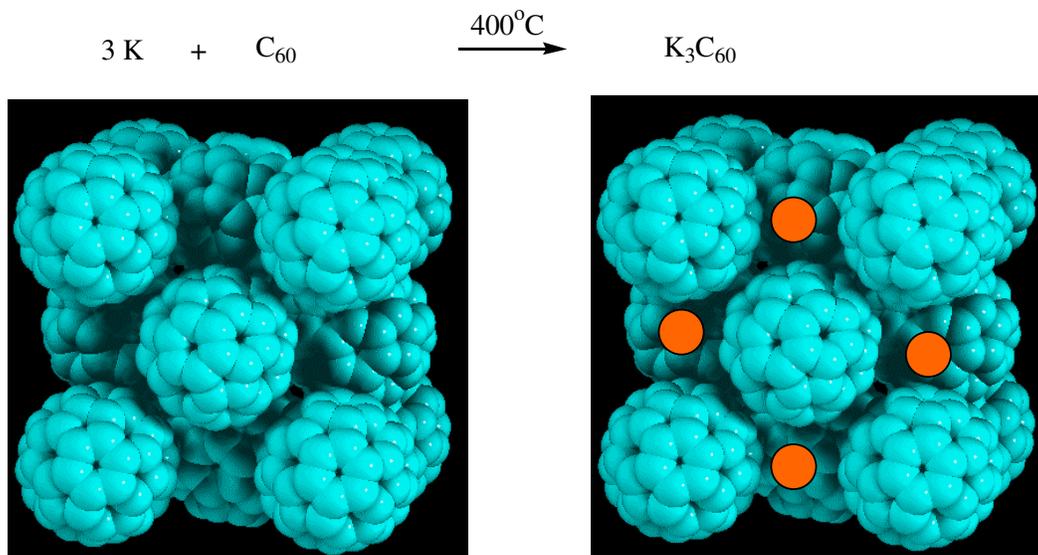
e.g. Fast-ion conductor (batteries) $\text{Na}_2\text{O} \cdot 0.8\text{Al}_2\text{O}_3$



Immerse $\text{Na}_2\text{O} \cdot 0.8\text{Al}_2\text{O}_3$ in molten $\text{Ag}(\text{NO}_3)$. Can exchange M^{2+} ions for 2 Na^+ ions but due to electrostatic interactions exchange is much slower.

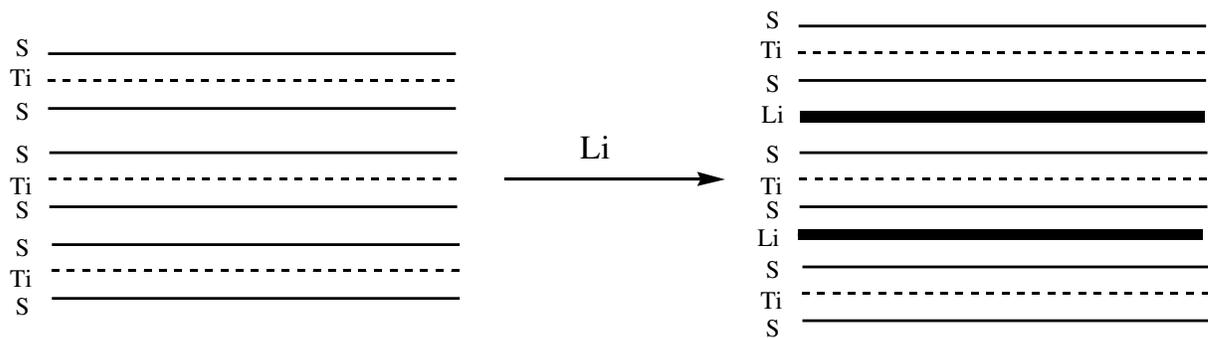
Intercalation is where species are added to a host structure.

e.g. K_3C_{60} (superconductor $< 20\text{ K}$)



The potassium atoms are accommodated in the interstitial sites between C_{60} molecules. An electron is transferred from the potassium atoms to the C_{60} molecules.

e.g. Li_xTiS_2 ($0 < x < 1$) (batteries)



Lithium cations are accommodated between TiS_2 layers. Expansion perpendicular to the layers occurs. An electron is transferred from the lithium atoms to the TiS_2 layers.

Analysis of a solid

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, hardness,)

Some analytical techniques

Diffraction: Single crystal if lucky but usually powders.

X-ray and Neutron diffraction: crystal structure. Neutrons have a magnetic moment that can interact with magnetic ions giving diffraction allowing the magnetic structure to be determined. Note that the structure obtained is an average structure.

Solid State NMR: Local structure and dynamics. Need NMR active nuclei.

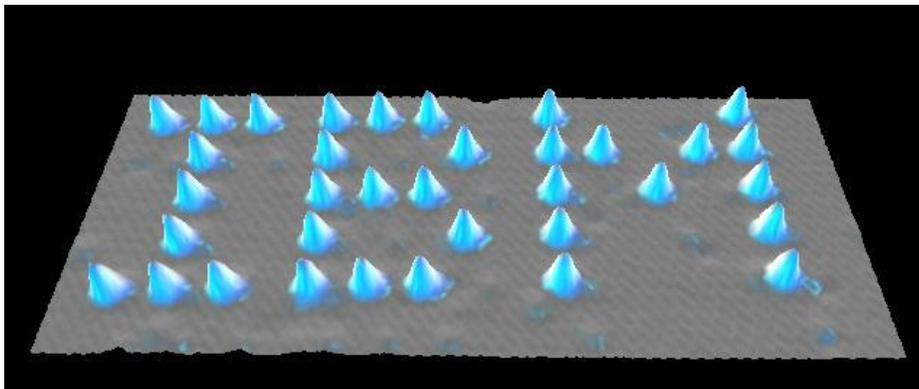
Microscopy:

SEM (scanning electron microscopy): Morphology and particle size distribution. Resolution 0.1-10 μm .

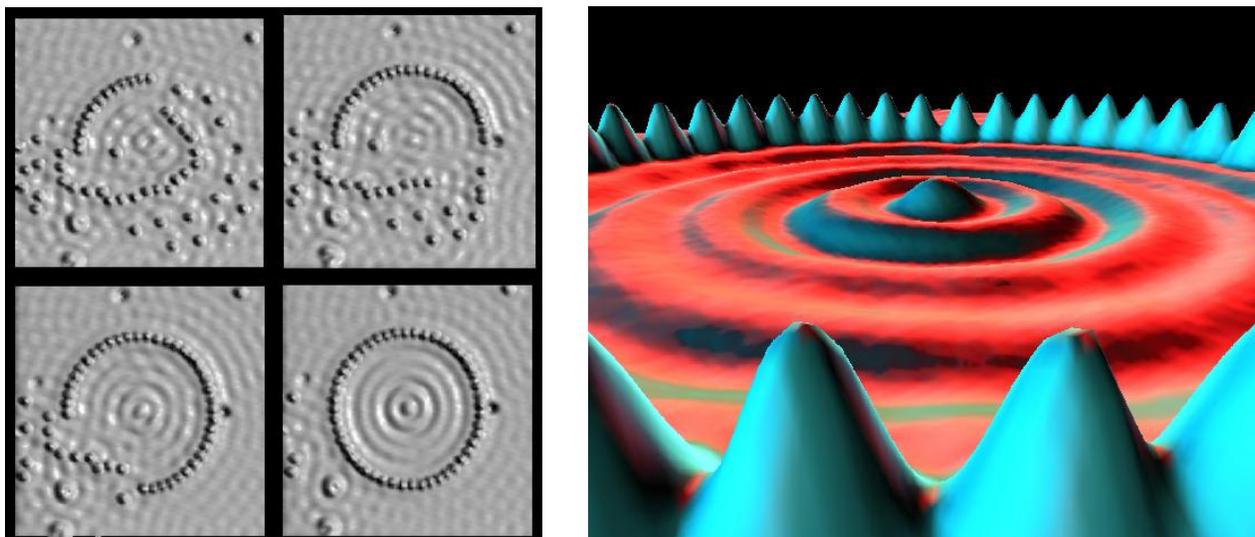
TEM and STEM ((scanning) transmission electron microscopy): Electron diffraction gives information about the crystal structure of individual particles including defects. Resolution 10-100 \AA

EDAXS (Elemental dispersion analyser using X-rays): Elemental analysis of individual particles.

STM (scanning tunnelling microscopy): surface structure. Atom manipulation. \AA resolution.



Xenon on Ni (110) surface



Quantum corral 'particle in a box'

Plus many other spectroscopic techniques

Including:

IR spectroscopy: Local structure

Electron energy loss spectroscopy (EELS): Electronic and surface structure

X-ray fluorescence spectroscopy (XRF): Elemental analysis

Extended X-ray absorption fine structure (EXAFS): Local structure

Summary

	X-ray diffraction	Neutron diffraction	NMR and ESR spectroscopy	SEM	TEM	EDAXS
Elemental analysis						X
Crystal structure	X	X			X	
Local structure	X	X	X		X	
Defects			X		X	
Morphology				X		

Lecture 2

Some structural properties of solids

Crystallinity

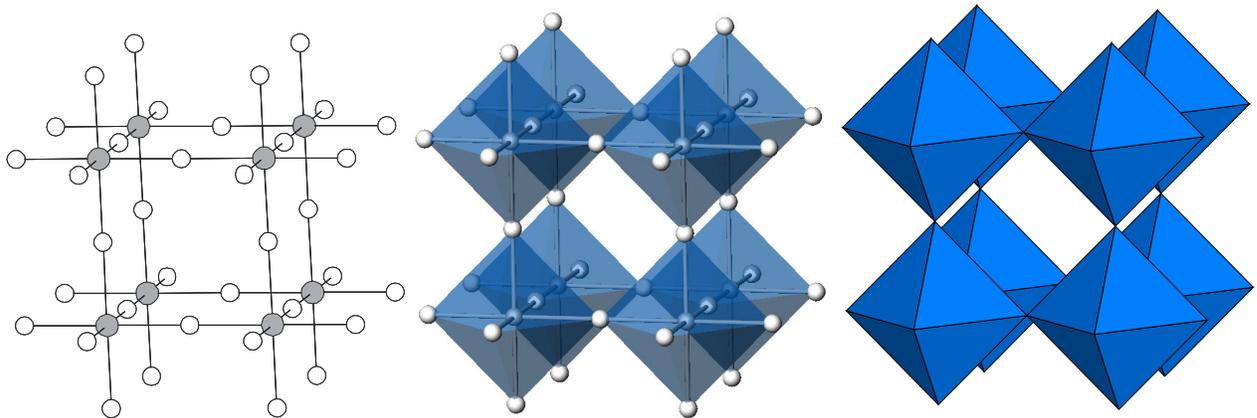
Solids exhibit a continuum of order from perfect crystals to totally amorphous.

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.



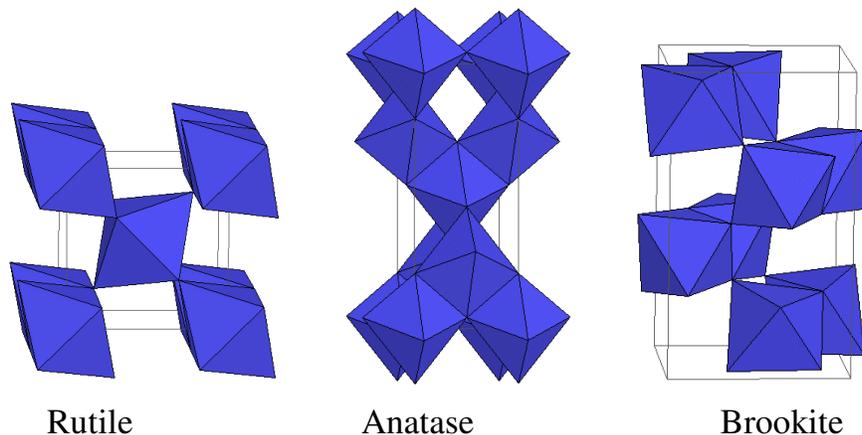
'ball and stick' and polyhedral representations of ReO_3 structure type

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*.

We say 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 . We say NaCl has the rock salt structure type.

Polymorphism



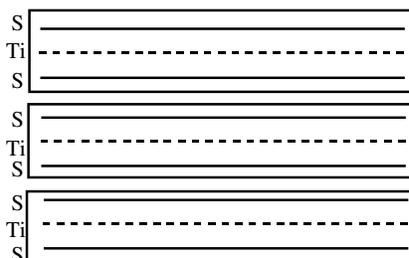
Some elements have allotropes e.g. C (graphite, diamond, fullerenes) and some molecular compounds have isomers e.g. (alkanes).

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 .

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

Dimensionality and porosity

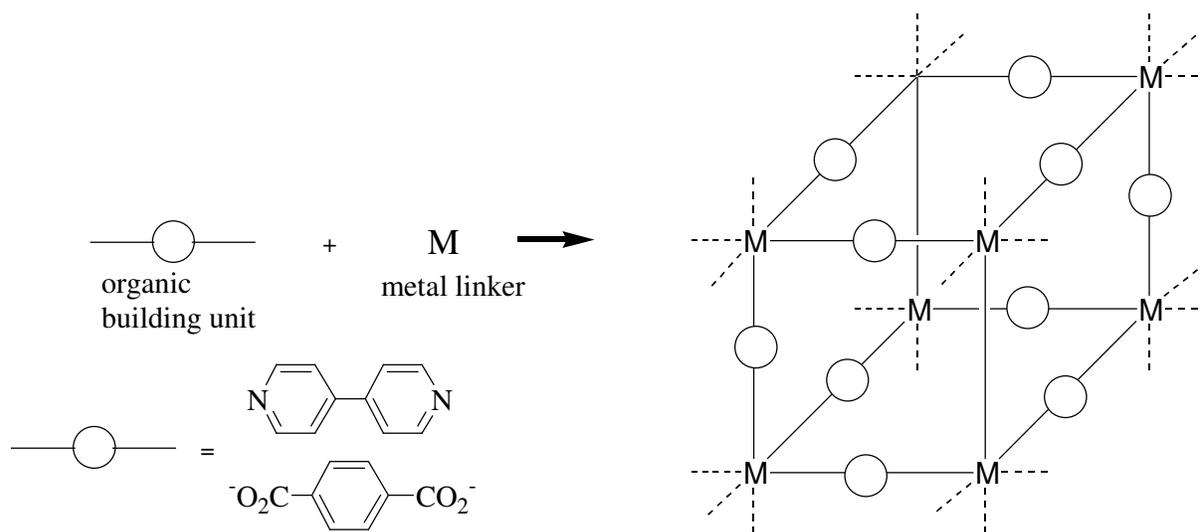
Dimensionality is important in understanding the properties of solids.



TiS_2 has a 2-D layered structure (see p 9). The weak bonding between the layers allows other species to easily enter and be removed from between the layers. TiS_2 can be used for battery applications.

In the summer term course ‘solid state chemistry’ the effects of dimensionality on the electrical properties of materials will be described.

Porosity. Truly porous solids have channels or cavities that are large enough to accommodate atoms or molecules without destruction of the lattice. These include zeolites (see p 7) and newer types of solids including metal-organic frameworks.



Defects and non-stoichiometry in ionic solids

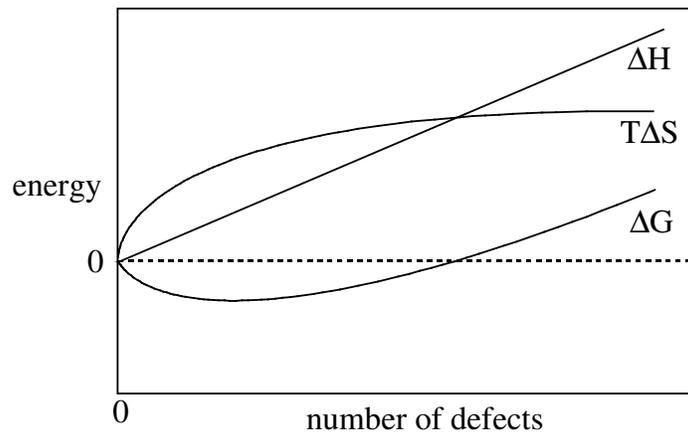
Note: overall charge balance must be maintained.

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.



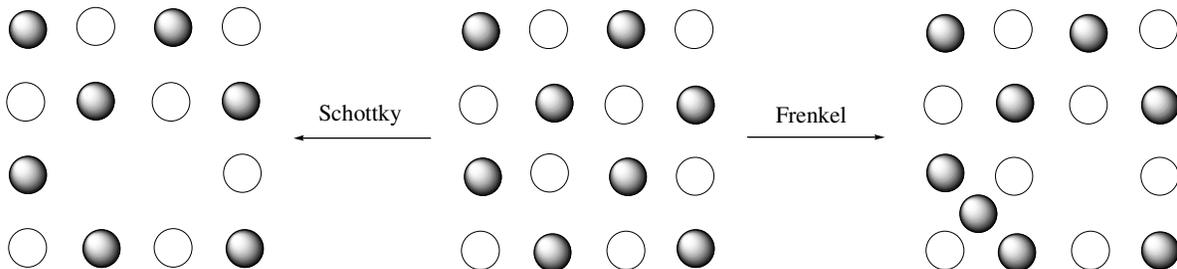
Point defects (*intrinsic*)

Two types:

Schottky defects: **vacancies are present in the lattice.**

Frenkel defects: **vacancy 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.



$$n_S = N \exp(-\Delta H_S/2kT)$$

$$n_F = (N N_i)^{1/2} \exp(-\Delta H_F/2kT)$$

$$n_F \approx N \exp(-\Delta H_F/2kT)$$

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

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	UO ₂ (cation F)	5.45	2.59×10^{-29}
300	CaF ₂ (anion F)	4.49	2.81×10^{-24}
300	AgCl (cation F)	2.56	3.73×10^{-14}
300	AgBr (cation F)	1.92	8.49×10^{-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 Shottky or Frenkel defects dominate.

Point defects (extrinsic)

Introducing different ions into the structure can increase the proportion of defects. This is known as ***doping***.

e.g. In 'solid state chemistry' you will study semi-conductors.

Silicon (group 14) is not a good conductor of electricity. If Si is doped with small amounts (1%) of P (group 15) the conductivity increases significantly. In effect after forming bonds to silicon the remaining electron from P acts as a conduction electron.

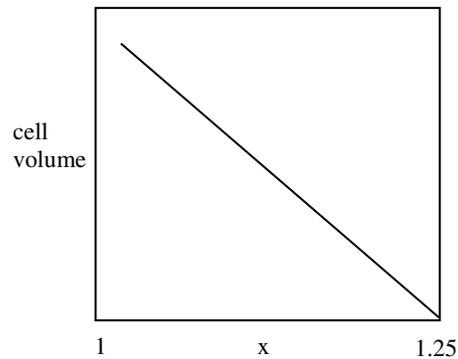
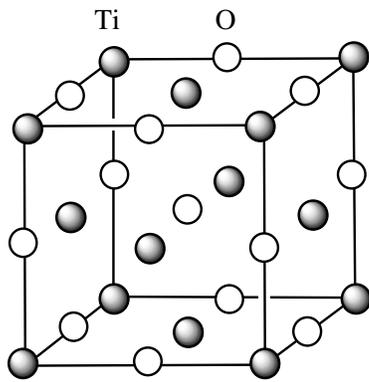
Non-stoichiometry and solid solutions

In non-stoichiometric solids intrinsic and extrinsic defects can occur but to a much larger extent. e.g. Li_xTiS₂. 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. TiO₂ because they have a common structure.

However the lattice parameters (size of the unit cell) of the structure will change gradually.



Consider that $\text{TiO}_{1.25}$ can be rewritten as $\text{Ti}_{0.8}\text{O}$. 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!

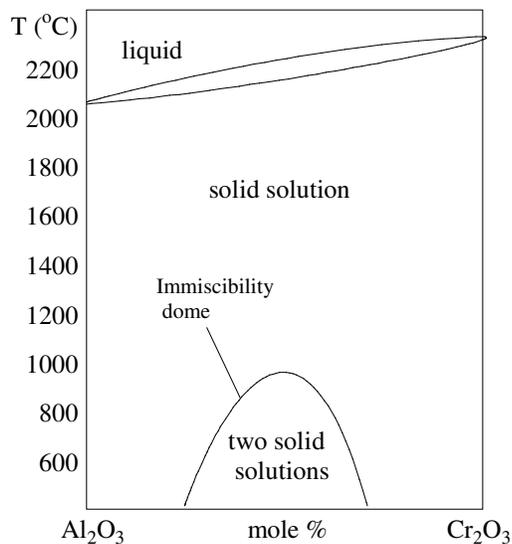
What is the average oxidation state of Ti in $\text{TiO}_{1.25}$?

$\text{Ti}^{2.5+} = 50:50$ 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.

There are two types: *substitutional* where a new atom replaces an existing atom. e.g. by doping.

e.g. Al_2O_3 and Cr_2O_3 can form a substitutional solid solution over the compositional range $(\text{Al}_{2-x}\text{Cr}_x)_2\text{O}_3$ $0 < x < 2$



Interstitial. Atoms are added. e.g. Li_xTiS_2 and C to Fe giving FeC_x $0 < x < 0.09$ (C atoms occupy the interstitial sites of Fe). (stainless steel).

Lecture 3

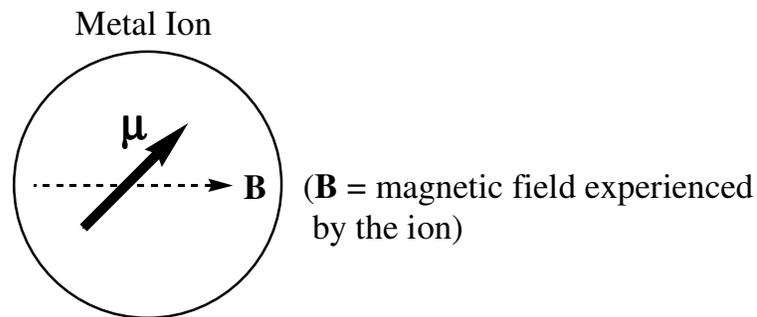
Magnetism: Interactions between solids and magnetic fields

Transition metals and lanthanides can have partially filled valence orbitals that result in unpaired electrons. The angular momentum (J) of unpaired electrons gives rise to magnetic behaviour. Magnetic behaviour is a quantum mechanical phenomenon.

We will only consider solids that have *localised* electrons (spins) (i.e. magnetism of insulators).

We will not consider solids that have *itinerant* electrons (i.e. the magnetism of metals).

Microscopic magnetism

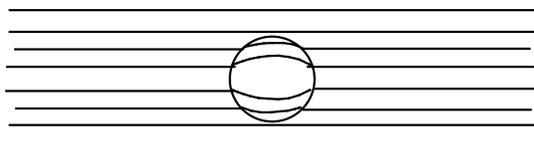


On the microscopic level individual ions with unpaired electrons have a magnetic dipole moment μ . The size of μ depends on the spin and orbital angular moments.

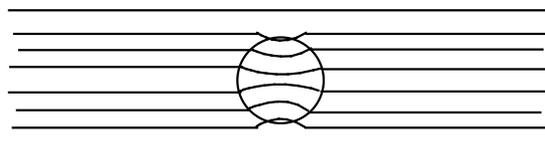
We will look at how in a solid these individual dipoles can interact with each other and behave collectively in a magnetic field.

Types of BULK magnetism

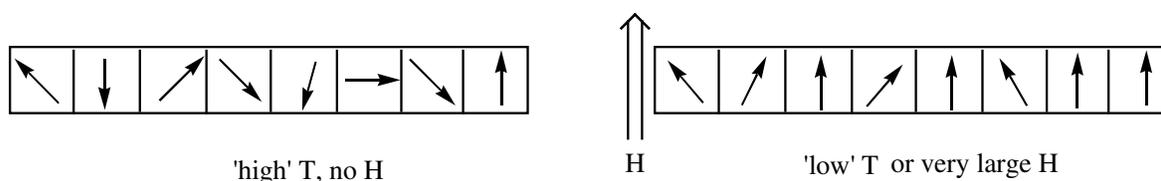
Diamagnetism All solids exhibit diamagnetism. Atoms or molecules with closed shells of electrons are diamagnetic. A diamagnet is repelled by an external magnetic field. It is a result of a perturbation of the orbits of all electrons and is not due to magnetic dipoles. It is a weak phenomenon except in the case of superconductors. Diamagnetism is temperature independent.



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.

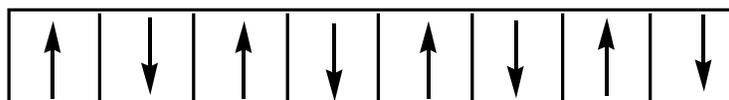


Due to thermal energy the dipoles are orientated randomly but as the temperature decreases there is less thermal energy and the dipoles can begin to align (order) parallel (lowest energy configuration) to an external field.



Paramagnetism is temperature dependent.

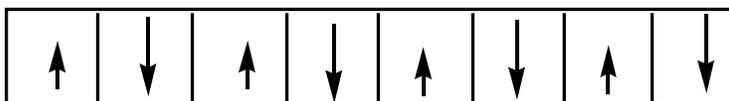
Antiferromagnetism is an example of cooperative magnetism where no applied field is necessary to align dipoles (spins) anti-parallel.



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



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.



Magnitude and behaviour of χ_{mol} for different types of magnetism

Behaviour	typical value of χ_{mol} ($\text{m}^3 \text{mol}^{-1}$)	change of χ_{mol} with increasing temperature	Field dependence (hysteresis) ?
Diamagnetism	-1×10^{-6}	none	no
Paramagnetism	0 to 10^{-2}	decreases	no
Antiferromagnetism	0 to 10^{-2}	increases	maybe
Ferromagnetism	10^{-2} to 10^6	decreases	yes
Ferrimagnetism	10^{-2} to 10^6	variable	yes

Some Theory

Some units and definitions

H = external magnetic field intensity (Am^{-1})

M = magnetisation or magnetic dipole moment per unit volume (Am^{-1})

B = internal magnetic field in the sample ($\text{NA}^{-1}\text{m}^{-1}$, or Tesla (T), Gauss (G) $1\text{T} = 10000\text{G}$)

χ_v = volume magnetic susceptibility (dimensionless)

χ_{mol} = molar magnetic susceptibility ($\text{m}^3 \text{mol}^{-1}$, emu mol^{-1}) sometimes called κ

$$M = \mu_0^{-1} \chi_v B \quad \mu_0 \text{ vacuum permeability} = 4\pi \times 10^{-7} \text{ NA}^{-2}$$

(how the magnetisation (M) is related to the internal magnetic field (B))

$$B = \mu_0 H$$

(how in a vacuum B and H are related)

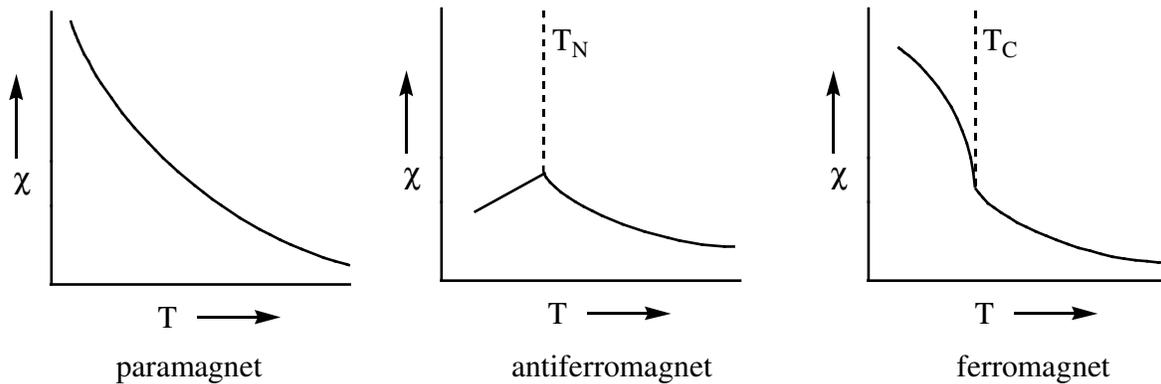
$$B = \mu_0 (H + M)$$

(how B and H are related in a material)

and $\chi_v = \frac{M}{H}$ the magnetisation is usually presented in terms of the magnetic susceptibility χ .

therefore $B = \mu_0 H(1 + \chi_v)$ or $B = \mu_0 \mu_r H$ (where $(1 + \chi_v) = \mu_r$ (the relative permeability))

How does χ vary with temperature for different types of magnetism?



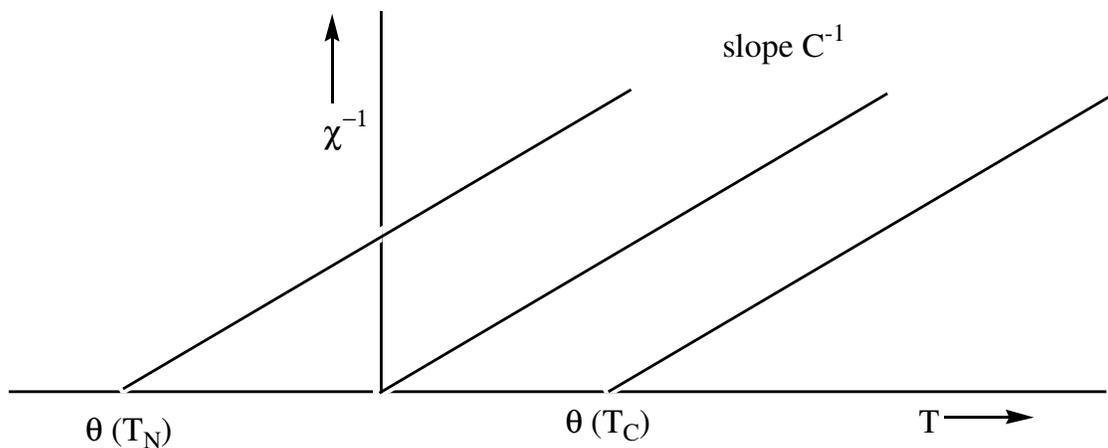
T_N is the Néel temperature (antiferromagnetic-paramagnetic transition temperature)
 T_C is the Curie temperature (ferromagnetic-paramagnetic transition temperature).

Paramagnetism

The Curie law gives the temperature dependence of χ for a paramagnet.

The Curie-Weiss gives the temperature dependence of χ for the paramagnetic region of materials that exhibit a transition between paramagnetic-antiferromagnetic or paramagnetic-ferromagnetic states.

$$\chi = \frac{C}{T} \quad C = \text{Curie Constant} \quad \chi = \frac{C}{T - \theta} \quad \theta = \text{Weiss constant}$$



In an experiment we measure the temperature dependence of M in an applied field. Plotting χ^{-1} vs T gives the effective magnetic moment μ_{eff} . (unit = μ_B (Bohr magneton), $1 \mu_B = 9.274 \times 10^{-24} \text{ JT}^{-1}$)

$$N_A = \text{Avagadro's constant}$$

$$k = \text{Boltzmann's constant}$$

$$\mu_0 = \text{vacuum permeability}$$

$$\chi_{\text{mol}} = \frac{N_A \mu_0}{3kT} \mu_{\text{eff}}^2 \quad \therefore C = \frac{N_A \mu_0}{3k} \mu_{\text{eff}}^2$$

Only applicable to cases where μ_{eff} is temperature independent

μ_{eff} is related to the number of unpaired electrons:

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

Spin only formula

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

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 lanthanides 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.

Lecture 4

Cooperative magnetism

We can consider a paramagnetic compound as the magnetic equivalent of an ideal gas. There is no interaction between the particles (magnetic dipoles) and no order.

If we decrease the temperature of a gas the interaction between molecules increases until order is introduced at the freezing point.

Similarly lowering the temperature of solids increases the interactions between magnetic ions increasing the order.

The ordering of magnetic ions is **cooperative**. (transition over small ΔT)

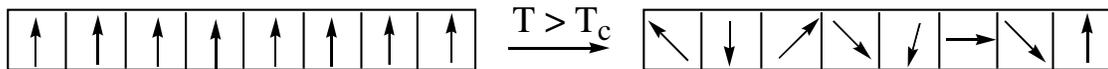
Ferromagnetism

Is usually associated with metals that have an electronic band structure. You will learn more about metals and band structures in solid state chemistry in the summer term.

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

Due to an *exchange interaction* between dipoles a ferromagnet has all the spins aligned in parallel in the absence of an external magnetic field.

The alignment can be broken by heating at temperatures $> T_C$. Fe has a T_C of 1043K.



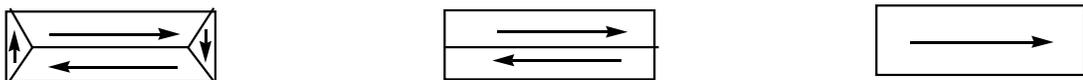
If Fe has a T_C of 1043K why is not all Fe magnetic at room temperature?
and why does placing a magnet next to Fe magnetise it?

Domains

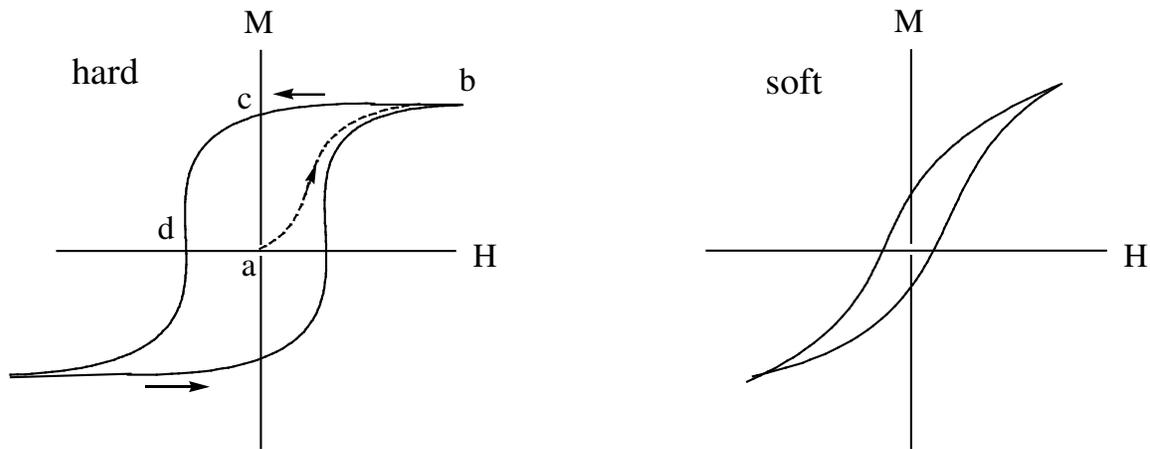
Below T_C ferromagnets are divided into *domains*.

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 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*)



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*.

These M vs H diagrams are known as hysteresis curves

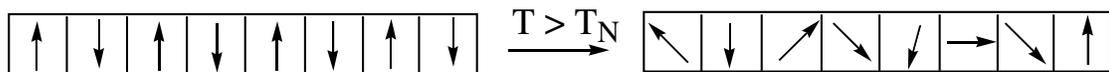
A hard magnet has a large remanent magnetisation and large coercive field: used as permanent magnets and magnetic memory (CrO_2).

A soft magnet has a small remanent magnetisation and a small coercive field: used as transformer cores.

Antiferromagnetism is observed for many metallic and insulating solids.

These include Cr, MnO, FeO, CoO, NiO, FeF_2 .

At low temperatures most paramagnetic compounds become antiferromagnetic ($\mu = 0$). The antiparallel alignment can be broken at temperature $> T_N$.



In contrast to paramagnets and ferromagnets increasing the temperature of an antiferromagnet increases χ until T_N .

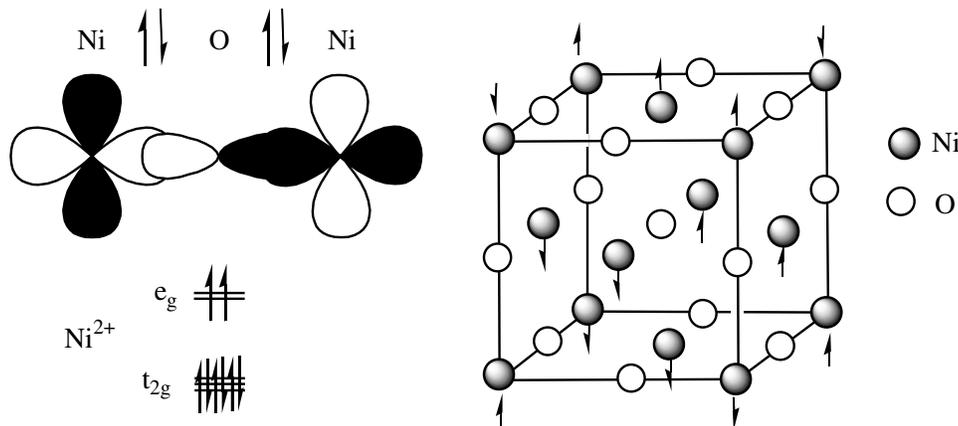
How do the ions couple antiferromagnetically in metal compounds?

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.

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 ($d_{x^2-y^2}$ or d_z^2) orbitals containing an unpaired electron overlap with an O²⁻ 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 known as a sublattice. Below T_N the sublattice structure of NiO can be determined experimentally using neutron diffraction.

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

Ferrimagnetism

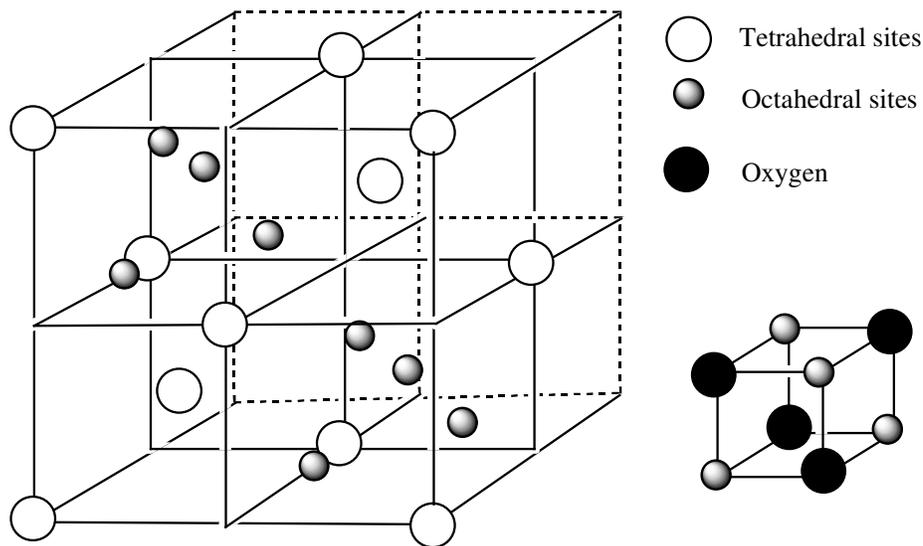
Consider an antiferromagnet that has two sublattices but where the magnetic moment of one sublattice is greater than the other.

This will result in a net spontaneous magnetisation (M) > 0 . As $M > 0$ the solid is no longer an antiferromagnet. These compounds are known as *ferrimagnets*.

Ferrimagnets are very important industrial materials because they have similar properties to ferromagnets. However in contrast to ferromagnets there are many examples of electrically insulating ferrimagnets.

Several examples of ferrimagnets have the spinel and inverse spinel structure.

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 1/2 of the octahedral sites in an ordered manner.

spinel	Inverse spinel
$[A^{2+}]^{tet} [B^{3+}]^{oct}$	$[B^{3+}]^{tet} [A^{2+}, B^{3+}]^{oct}$
$MgAl_2O_4$	$CoFe_2O_4$
$ZnFe_2O_4$	$NiFe_2O_4$
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)

e.g. $NiFe_2O_4$

Oxide lattice provides a weak field for the metal atoms.

$Ni(II)$ d^8 and $Fe(III)$ d^5 are high spin. CFSE for Fe in tetrahedral and octahedral coordination is 0. CFSE for Ni is octahedral > tetrahedral. Therefore Ni goes in octahedral site leading to the inverse spinel structure.

Estimation of the magnetic moment of ferrimagnets

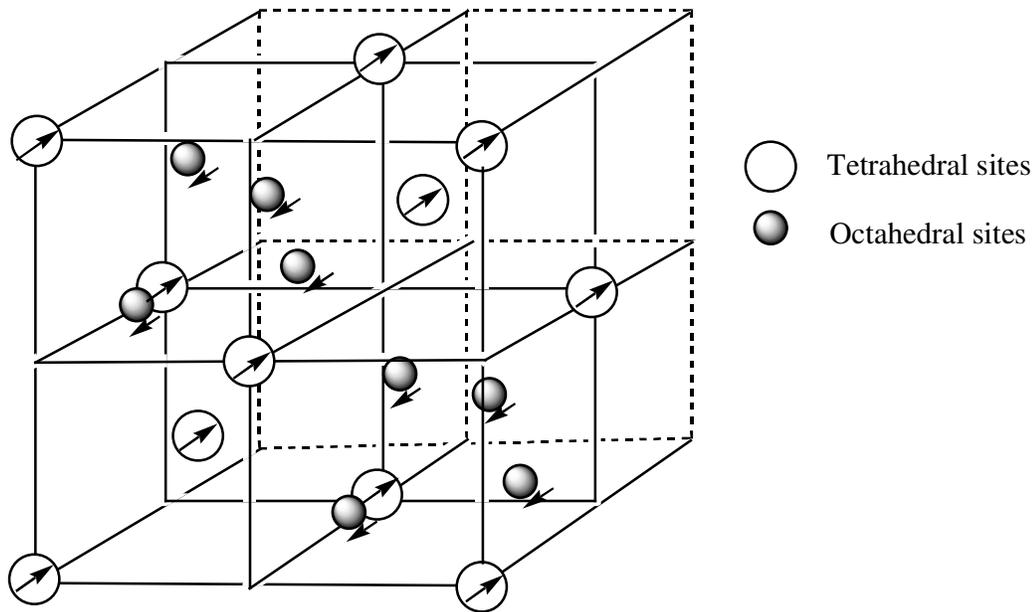
Using $\mu = gS$ as a rough estimate (instead of $\mu_s = g \sqrt{S(S+1)}$) we can calculate the magnetic moment μ for each ion. The saturation (maximum) magnetic moment (μ_{sat}) for a ferrimagnet is then a vector sum of the individual ion moments.

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

e.g. Mn_3O_4 (normal spinel)

ion	$[\text{Mn}^{2+}]^{\text{tet}}, d^5$	$2 \times [\text{Mn}^{3+}]^{\text{oct}}, d^4$	μ_{tot}
No. unpaired electrons	5	2×4	
μ_{ion}	5	2×4	$8 - 5 = 3$

e.g. Fe₃O₄ (inverse spinel)

ion	[Fe ²⁺] ^{oct} , d ⁶	[Fe ³⁺] ^{oct} , d ⁵	[Fe ³⁺] ^{tet} , d ⁵	μ_{tot}
No. unpaired electrons	4	5	5	
μ_{ion}	4	5	5	4 + 5 - 5 = 4

Comparison of estimation and experimental data for M ^{II} Fe ^{III} ₂ O ₄					
M(II)	S	$\mu_{\text{sat calc}}$	$\mu_{\text{sat expt}}$	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

Lecture 5

Dielectric Properties: Interactions between solids and electric fields

One way of classifying solids is their ability to conduct electrons or ions.

	material	σ (ohm ⁻¹ cm ⁻¹)
electronic conduction	metals	$10^1 - 10^5$
	semiconductors	$10^{-5} - 10^2$
	insulators	$< 10^{-12}$
ionic conduction	ionic crystals	$< 10^{-18} - 10^{-4}$
	solid electrolytes	$10^{-3} - 10^1$

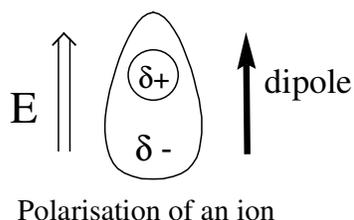
Conduction will be discussed in 'solid state chemistry' in the summer term. We will be concerned with electrical and ionic insulators. *Dielectric materials are insulators.*

Dielectric materials are used as capacitors, heat sensors, oscillators, transducers, optics etc.

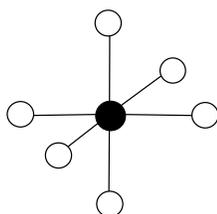
The response of insulators to external electric fields

Note: All materials consist of charged particles and overall have net zero charge.

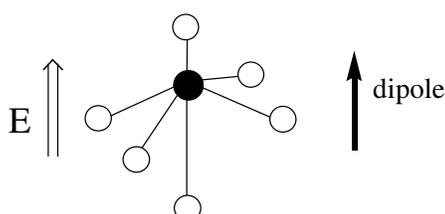
When an external electric field is applied to a solid electrons are displaced and a dipole moment is induced. This is the electronic polarisation.



For ionic solids the ions can also move. This is the ionic polarisation.



Symmetric electric field = zero polarisation
No dipole moment



Application of electric field gives ion displacement
Asymmetric electric field = polarisation and dipole moment

The electronic and ionic polarisations are important for dielectric materials

Note: In the absence of an electric field most solids do not have *bulk* net separation of charge and therefore have no overall dipole moment. Crystals of molecules with permanent dipoles e.g. H₂O in ice, tend to have structures where the dipoles cancel out.

The average dipole moment per unit volume is called the *polarisation*(*P*).

P is related to the applied electric field *E* by the equation:

$$P = \epsilon_0 \chi_e E \quad (\text{c.f. } M = \mu_0^{-1} \chi_v B)$$

where ϵ_0 is the vacuum permittivity ($8.8542 \times 10^{-12} \text{ J}^{-1} \text{ C}^2 \text{ m}^{-1}$) and χ_e is the dielectric susceptibility.

Commonly the dielectric constant (relative permittivity) $\epsilon_r = 1 + \chi_e$ is quoted. (c.f. μ_r) Most ionic solids have ϵ_r between 5 and 10.

ϵ_r is dependent on the temperature and the frequency of the field (if an alternating electric field is applied).

On polarisation a material stores charge. The stored charge can be measured in a parallel plate capacitor and ϵ_r determined.

$Q = C V$

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

$$\epsilon_r = \frac{C_{\text{dielectric}}}{C_{\text{vacuum}}}$$

A good dielectric material should have high *dielectric strength* (not breakdown at high voltages and become conducting) and have low dielectric loss (not lose electrical energy as heat).

Ferroelectrics, piezoelectrics and pyroelectrics

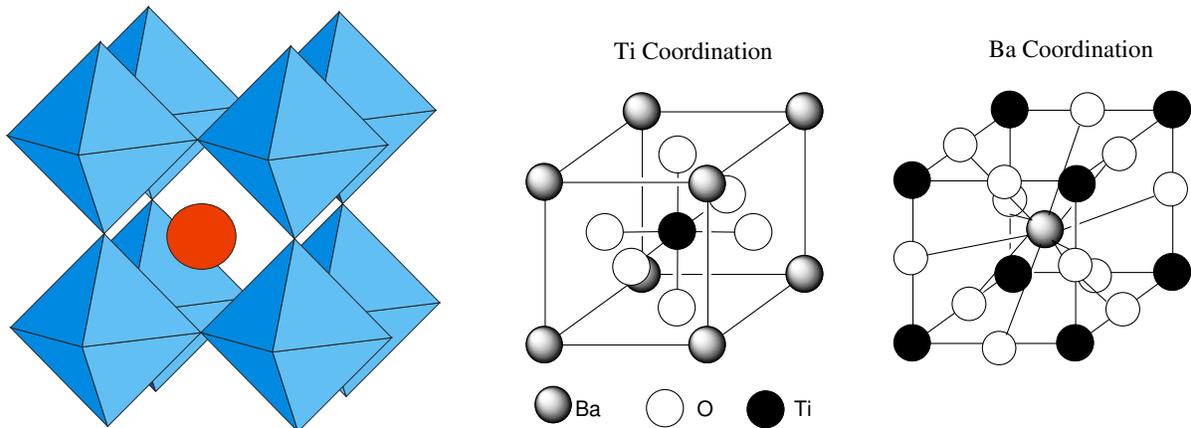
An applied electric field gives rise to polarisation and a dipole moment. For many materials when the electric field is removed the polarisation is lost (paraelectricity).

Most materials have structures where ions are in an asymmetric site (and hence asymmetric local electric field) and therefore have a local dipole moment. However these will cancel in the bulk material unless the structure is non-centrosymmetric. Ferro-, piezo- and pyroelectric materials all have non-centrosymmetric structures.

Ferroelectrics can retain polarisation after the electric field has been removed and have a very high dielectric constant.

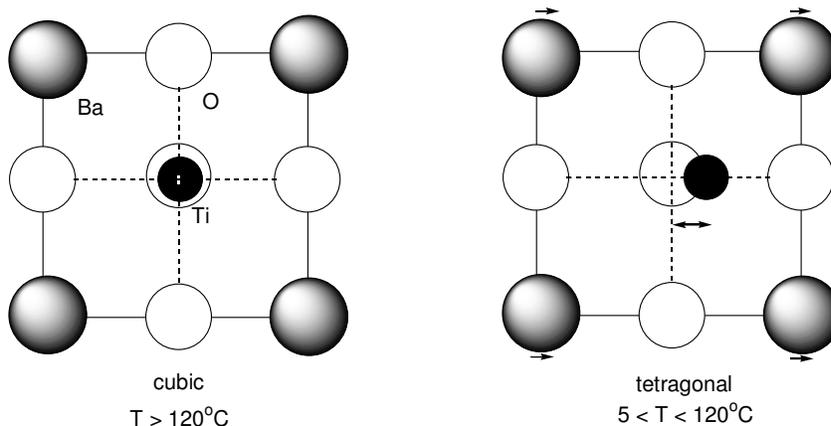
An example of a ferroelectric is BaTiO_3 that has the perovskite ABO_3 structure (related to ReO_3).

$$\epsilon_r \text{BaTiO}_3 = 10^2 - 10^4$$



At temperatures above 120°C the Ti atoms are in a symmetric octahedral TiO_6 site (cubic BaTiO_3 (centrosymmetric)).

Between $5 - 120^\circ\text{C}$ the Ti atoms are displaced along one of the axis of the octahedron (by 0.1 \AA) and polarisation results (tetragonal BaTiO_3 (non-centrosymmetric)).



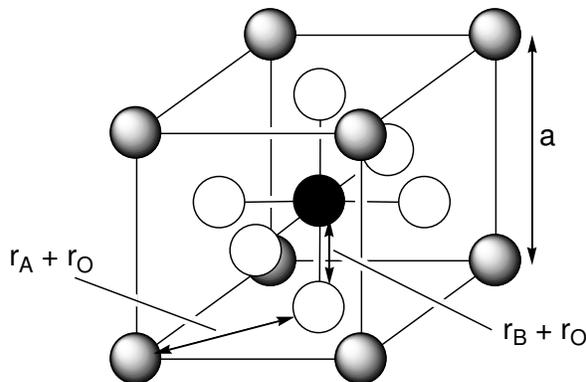
Why does the structure distort?

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
 $a = 2(r_B + r_O)$ 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-} ($r = 126$ pm) $t = 1.002$ (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 $T > 120^\circ C$ the thermal motion of the Ti atom creates enough chemical pressure to retain the ideal cubic perovskite structure.

At $5 < T < 120^\circ C$ the thermal motion no longer compensates for the strain and the structure distorts.

The temperature at which a solid becomes ferroelectric is called the Curie temperature T_C . Above T_C the solid is paraelectric and the dielectric constant follows Curie-Weiss form. c.f. paramagnetic-ferromagnetic transition.

$$\epsilon_r = \frac{C}{T - \theta} \quad \begin{array}{l} \theta = \text{Weiss constant} \\ C = \text{Curie Constant} \end{array}$$

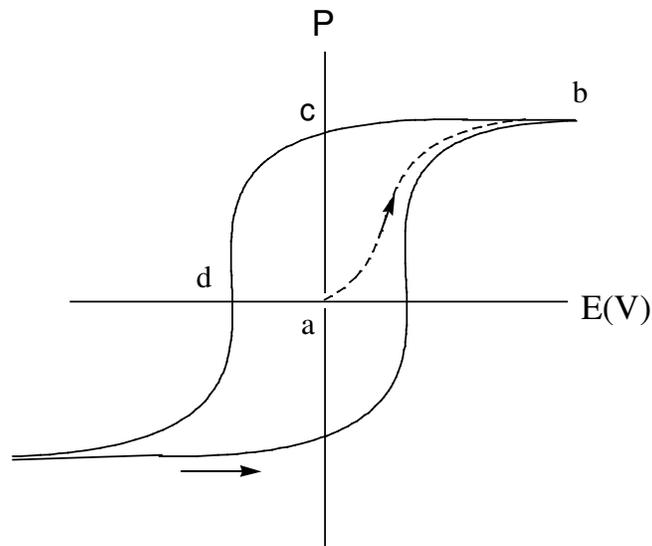
Do the dipoles point in the same direction? (Comparison between ferroelectricity and ferromagnetism).

For a ferromagnet, lowering the temperature below T_C leads to ordering of the spins into domains. Application of an external magnetic field leads to alignment of the domains.

Lowering the temperature of a ferroelectric below T_C leads to a distortion in the structure. However below T_C the dipoles of ferroelectrics do not always form domains because the dipole-dipole interaction is relatively weak.

An applied electric field orders dipoles into domains. Application of a stronger external electric field then aligns the domains.

Due to the domain structure ferroelectrics exhibit hysteresis.



a to b. On application of an electric field individual dipoles are aligned into domains and subsequently the domains are aligned. At b the sample has reached *saturation polarisation*.

b to c. The electric field is returned to 0 but the sample remains polarised this is known as the *remanent polarisation*.

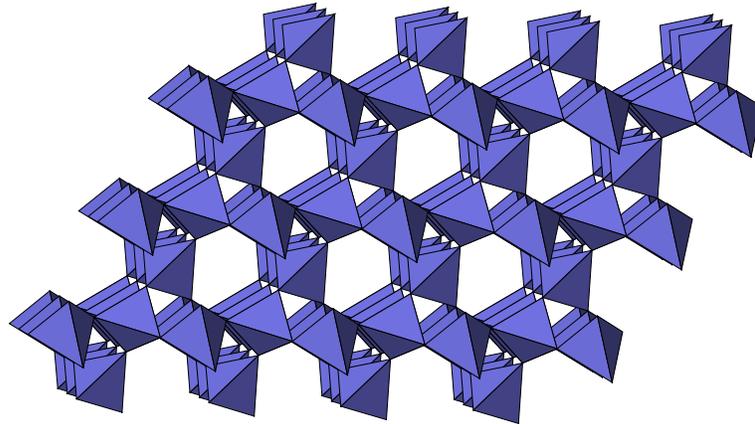
c to d In order to depolarise the sample a field in the opposite direction is required. This is the *coercive field*.

It is also possible to have antiferroelectric and ferroelectric behaviour analogous to that observed in magnetism.

Ferroelectrics are used mainly as capacitors because near the paraelectric-ferroelectric transition large quantities of charge can be stored.

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 piezoelectric. Also tetrahedra do not have a centre of symmetry and often lead to non-centrosymmetric structures. An example is α -quartz.

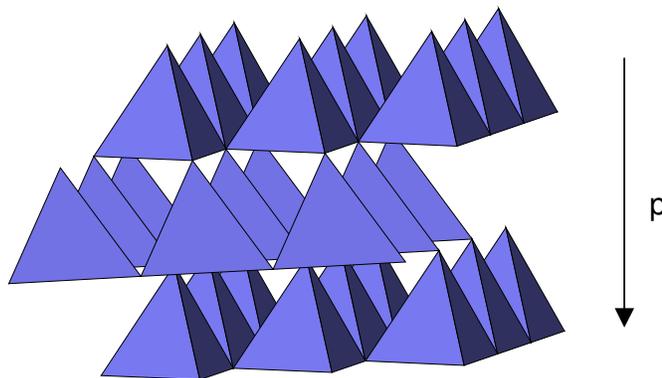


Piezoelectrics are used extensively as transducers for loudspeakers, earphones, inkjet printers, STM, cigarette lighters etc

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.

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).

Relationship between ferroelectrics, pyroelectrics, and piezoelectrics

Polarisation is responsible for the observed behaviour in all cases.

Ferroelectric materials are also pyroelectric and piezoelectric.

Pyroelectric materials are piezoelectric.

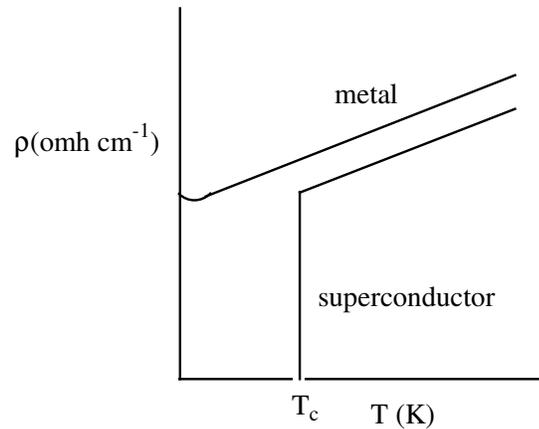
Not all piezoelectric materials are pyroelectric.

Lecture 6

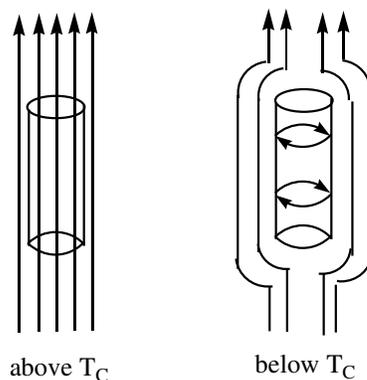
Superconductivity

Superconductors exhibit two remarkable properties.

1. Below a critical temperature T_C zero electrical resistance is observed.



2. Below T_C magnetic flux is expelled $B = 0$ (Meissner effect). Therefore $\chi = -1$ (a superconductor is considered a perfect diamagnet).



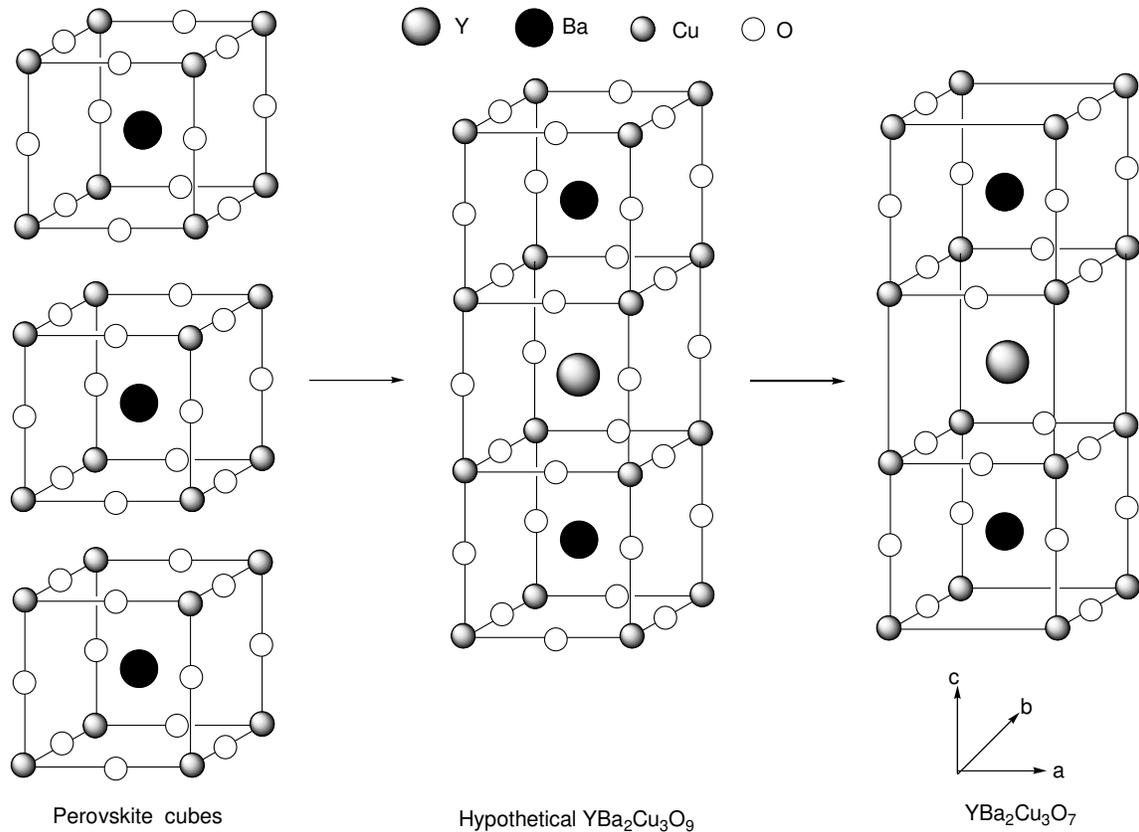
Superconductors are used for the generation of large magnetic fields (such as NMR and MRI) but if the T_C could be increased to $> 300\text{K}$ many technologies (e.g. transport and power generation) would be revolutionised.

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

Cuprates (high T_C superconductors)

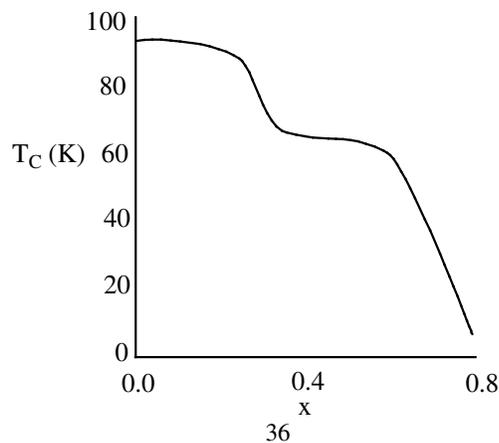
In 1986 the compound $\text{La}_{1.8}\text{Ba}_{0.2}\text{CuO}_4$ was reported to have a T_C of 35K. This compound has the K_2NiF_4 type structure that is related to the perovskites. Later the phases $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ $0 < x < 1$ were investigated and the T_C raised to 93K. The highest T_C to date is about 160K for $\text{HgBa}_2\text{Ca}_2\text{Cu}_3\text{O}_{10}$ under pressure.

Structure of Cuprates

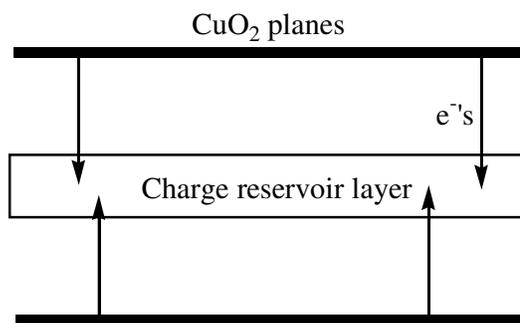
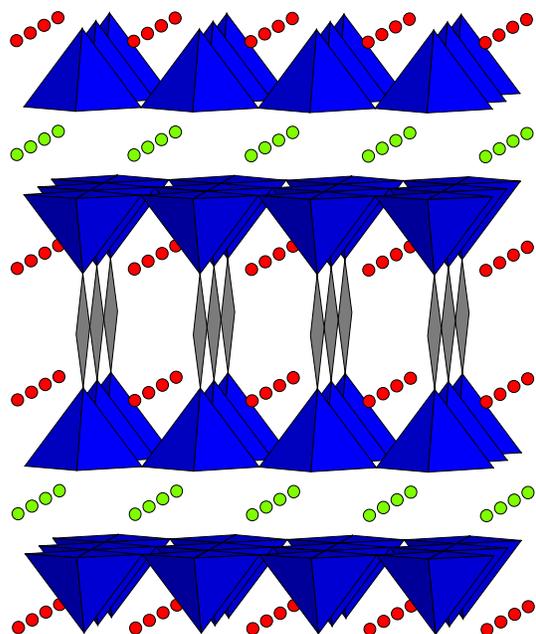


There are two copper sites: A distorted square pyramid of Jahn-teller distorted Cu^{2+} (that form CuO_2 layers) and square planar geometry (that link the layers). Oxygen is removed from the basal planes $(0, \frac{1}{2}, 0)$ for the compositions $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ leading to linear 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 $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ $0 < x < 1$ ranges from 2.33 ($\text{Cu}^{3+}/\text{Cu}^{2+}$) to 1.66 ($\text{Cu}^{2+}/\text{Cu}^+$). T_C is very dependent on the Cu oxidation state and hence the oxygen content. For $\text{Cu}^{2+}/\text{Cu}^+$ $\text{YBa}_2\text{Cu}_3\text{O}_{6.0-6.5}$ antiferromagnetism is observed and superconductivity is suppressed. For $\text{Cu}^{3+}/\text{Cu}^{2+}$ $\text{YBa}_2\text{Cu}_3\text{O}_{6.5-7.0}$ T_C increases with increasing oxygen content.



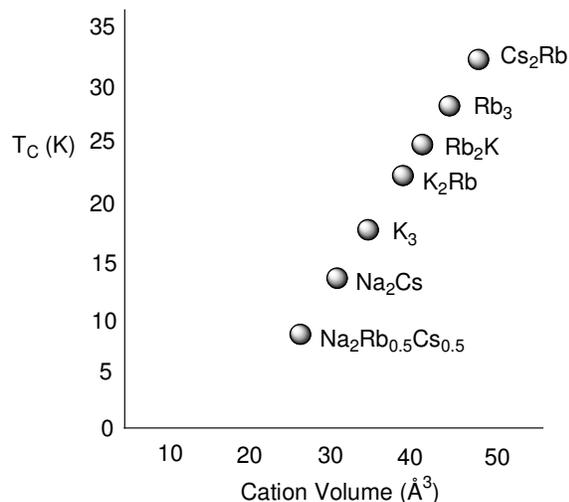
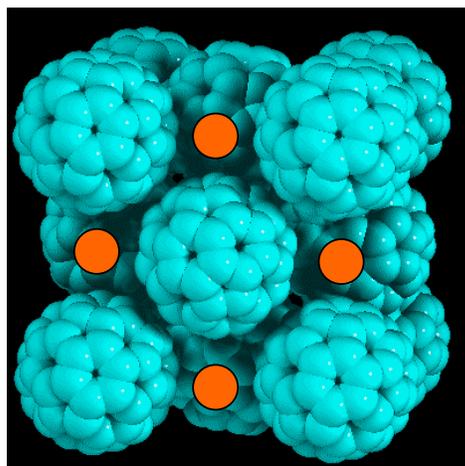
Studies indicate that the important structural features are CuO_2 square planar layers separated by 'charge reservoir layers' that control the average Cu oxidation state in the CuO_2 layers. The average Cu oxidation state should also be $> 2+$. For $\text{YBa}_2\text{Cu}_3\text{O}_7$ the charge reservoir layers are CuO chains.



Fullerides

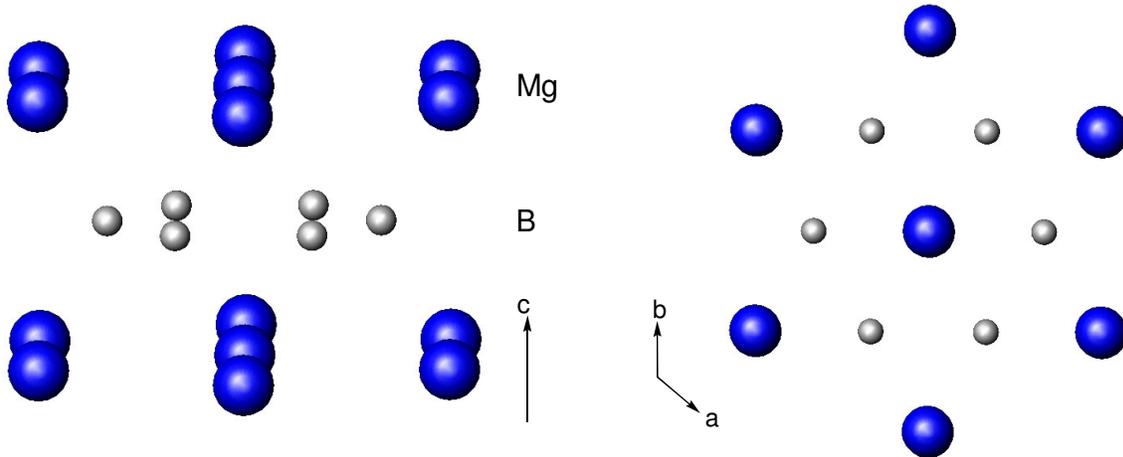
Synthesised by intercalation of electropositive metals into the C_{60} lattice. Electron transfer from the metal to C_{60} gives C_{60}^{n-} anions (fullerides). The orbitals of neighbouring C_{60} molecules overlap forming bands and the electrons are able to move throughout the solid i.e metallic. T_C 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).



Borides

In 2002 a new class of superconductor was discovered. MgB_2 ($T_C = 39\text{K}$) is an intermetallic compound i.e. B atoms are in the interstices of metallic Mg. The search is now on to investigate other intermetallic compounds for superconductivity and modify MgB_2 . The structure is very simple and is based on hexagonal layers of Mg and B.



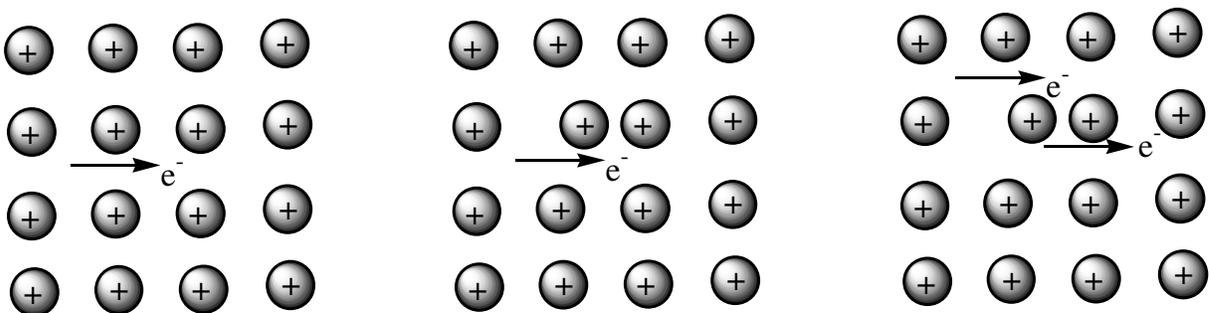
Theory of superconductivity

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 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 Cooper 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.