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: Li batteries and dielectric materials
3. Magnetic Materials: Cooperative magnetism
4. Superconductivity
5. Nanomaterials: synthesis, characterisation and structure
6. Nanomaterials: catalysis and optical properties

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 1\textsuperscript{st} year
MAB Solid state structure 1\textsuperscript{st} year
JML Structure and bonding 1\textsuperscript{st} year
RED Metal-ligand metal-metal bonding 2\textsuperscript{nd} year
TD Surface chemistry 2\textsuperscript{nd} year
RNP Photochemistry 3\textsuperscript{rd} year
MB Diffraction 3\textsuperscript{rd} year
MAB Electronic Structure of Materials 3\textsuperscript{rd} 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) describe the electric and magnetic properties of superconductors.
xiii) explain the structural characteristics of cuprates, fullerides and borides.
xiv) qualitatively describe BCS theory of superconductivity.
xv) understand the structural differences between bulk materials and nanomaterials.
xvi) describe methods of synthesis of solid state compounds using examples.
xvii) understand the difference between synthesis and modification of materials.
xviii) understand the limitations of techniques for the analysis of materials.
xix) describe the methods used to characterise nanomaterials.
xx) understand the relationship between the size of nanoparticles and their physical properties.

See Structure Visualisation Package on ‘Year 3’ page of departmental website for interactive structures.
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)
Energy (Solar panels, 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.

![Diagram 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.

2. Polymorphism

![Diagram of rutile, anatase, and brookite structures]
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 \textit{polymorphism} and individual structures are called \textit{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 \textit{phase}.

3. Dimensionality and porosity

\textit{Dimensionality} is important in understanding the properties of solids. e.g. C$_{60}$, nanotubes, graphite and diamond.

- C$_{60}$ (0-D). \textit{Soluble molecule}.
- Graphite (2-D). \textit{Soft semimetal}.
- Diamond (3-D). \textit{Hard insulator}.
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.

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

Where $n_S$ ($n_F$) = Shottky (Frenkel) defects per unit volume, $\Delta H_S$ ($(\Delta H_F)$) = Shottky (Frenkel) enthalpy of formation, $N$ = number of cation and anion sites per unit volume, $N_i$ = number of interstitial sites per unit volume.
TEM of S vacancies in MoS\(_2\) (scale bar 1 nm) (J. Hong et al, Nature Commun. 2015, 6, 6293)

<table>
<thead>
<tr>
<th>Temperature (K)</th>
<th>Compound (defect)</th>
<th>(\Delta H) (10^{-19}) J</th>
<th>(n/N)</th>
</tr>
</thead>
<tbody>
<tr>
<td>300</td>
<td>MgO (S)</td>
<td>10.57</td>
<td>3.62 x 10(^{-56})</td>
</tr>
<tr>
<td>300</td>
<td>CaO (S)</td>
<td>9.77</td>
<td>5.69 x 10(^{-52})</td>
</tr>
<tr>
<td>300</td>
<td>LiF (S)</td>
<td>3.75</td>
<td>2.14 x 10(^{-20})</td>
</tr>
<tr>
<td>300</td>
<td>LiCl (S)</td>
<td>3.40</td>
<td>1.46 x 10(^{-18})</td>
</tr>
<tr>
<td>300</td>
<td>LiBr (S)</td>
<td>2.88</td>
<td>7.83 x 10(^{-16})</td>
</tr>
<tr>
<td>300</td>
<td>LiI (S)</td>
<td>2.08</td>
<td>1.23 x 10(^{-11})</td>
</tr>
<tr>
<td>300</td>
<td>(\beta)-AgI (cation F)</td>
<td>1.12</td>
<td>1.33 x 10(^{-6})</td>
</tr>
<tr>
<td>500</td>
<td>LiCl</td>
<td>3.40</td>
<td>1.99 x 10(^{-11})</td>
</tr>
<tr>
<td>750</td>
<td>LiCl</td>
<td>3.40</td>
<td>7.35 x 10(^{-8})</td>
</tr>
<tr>
<td>1000</td>
<td>LiCl</td>
<td>3.40</td>
<td>4.46 x 10(^{-6})</td>
</tr>
</tbody>
</table>

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 \(\Delta H\) (\(\Delta H_S\) or \(\Delta H_F\)) will determine if Shottky 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. 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$_2$Cu$_3$O$_{7-x}$ (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.

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$_{1.25}$ ?
$\text{Ti}^{2.5+} = 50:50$ 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. e.g. lasers and steel.

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

e.g. Al$_2$O$_3$ and Cr$_2$O$_3$ can form a substitutional solid solution over the compositional range (Al$_{2-x}$Cr$_x$)$_2$O$_3$ 0 < $x$ < 2. $x$ < 0.05 (ruby)
Interstitial. Atoms are added. e.g. C to Fe giving FeC\textsubscript{x} 0 < x < 0.09 (C atoms occupy the interstitial sites of Fe). (steel).
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 (\(\mu\text{m-mm}\))
batteries and fuel cells

Lithium ion batteries (rechargeable)

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.

\[\text{e.g. } x\text{Li}^0 + \text{graphite (C}_6) \xrightarrow{\text{intercalation}} \text{Li}_x\text{C}_6 \quad 0 < x < 1\]

\[\text{LiCoO}_2 \xrightarrow{\text{deintercalation}} x\text{Li}^+ + e^- + \text{Li}_x\text{CoO}_2 \quad 0 < x < 0.5\]
Energetics

\[ E_{\text{cell}} (V) = E_{\text{anode}} - E_{\text{cathode}} \]

Power (W) = voltage (V) x current (A)
Charge (Ah) = current (A) x time (h) \( 1 \text{ Ah} = 3600 \text{ C} \)

Energy (Wh) = Power (W) x time (h) \( 1 \text{ Wh} = 3600 \text{ J} \)
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

A series of multiple cells can achieve higher energy
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

\[
\begin{align*}
\text{LiC}_6 & \rightarrow e^- + \text{Li}^+ + \text{graphite (C}_6) \\
e^- + \text{Li}^+ + \text{CoO}_2 & \rightarrow \text{LiCoO}_2 \\
e^- + \text{Li}^+ + \text{CoO}_2 & \rightarrow \text{LiCoO}_2 \quad \text{E}^\circ \sim +1 \text{ V} \\
e^- + \text{Li}^+ + \text{graphite (C}_6) & \rightarrow \text{LiC}_6 \quad \text{E}^\circ = -3 \text{ V}
\end{align*}
\]

\[ E_{\text{cell}} = 1 \cdot (-3) = 4 \text{V} \]
\[ \Delta G = -nFE \quad (F = \text{Faraday constant (96500 C mol}^{-1}) \) = -386000 J = -107.2 \text{ Wh mol}^{-1} \]
\[ \text{LiC}_6 = 79 \text{ g mol}^{-1}, \text{CoO}_2 = 91 \text{ g mol}^{-1} \]

Theoretical specific Energy = -107.2/0.079 = 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

Maximise energy density and specific energy
Kinetics of charge and discharge are 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 atomic manipulation)


How is it possible to manipulate individual atoms with pm precision?
Piezoelectric 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.

**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, $\varepsilon_r$.

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 ($\varepsilon_r$) determined.
An example of a ferroelectric is BaTiO$_3$ that has the perovskite ABO$_3$ structure (related to ReO$_3$).

\[ \varepsilon_r \text{ BaTiO}_3 = 10^2 - 10^4 \]

At temperatures above 120°C the Ti atoms are in a symmetric octahedral TiO$_6$ site (cubic BaTiO$_3$ (centrosymmetric)). Between 5 - 120°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)).

**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

\[ a = 2 \left( r_B + r_O \right) \text{ and } a = \sqrt{2} \left( r_A + r_O \right) \]

Therefore to obtain ideal contact between A, B and O

\[ 2 \left( r_B + r_O \right) = \sqrt{2} \left( r_A + r_O \right) \]

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

\[ t \left( r_B + r_O \right) = \sqrt{2} \left( r_A + r_O \right) \]

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 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.
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 $\alpha$-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.

![Pyroelectric structure diagram](image)

The ZnO₄ 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.
**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.

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

Metal Ion

(B = magnetic field experienced by the ion)

On the microscopic level individual ions with unpaired electrons have a magnetic dipole moment $\mu$ (sometimes called spin). The size of $\mu$ depends on the spin and orbital angular moments.

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

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

Spin only formula
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)

<table>
<thead>
<tr>
<th>ion</th>
<th>Unpaired electrons</th>
<th>$\mu_S$ (calc)</th>
<th>$\mu_{S+L}$ (calc)</th>
<th>$\mu_{\text{eff}}$ (observed)</th>
</tr>
</thead>
<tbody>
<tr>
<td>V$^{3+}$</td>
<td>1</td>
<td>1.73</td>
<td>3.00</td>
<td>~1.8</td>
</tr>
<tr>
<td>V$^{4+}$</td>
<td>2</td>
<td>2.83</td>
<td>4.47</td>
<td>~2.8</td>
</tr>
<tr>
<td>Cr$^{3+}$</td>
<td>3</td>
<td>3.87</td>
<td>5.20</td>
<td>~3.8</td>
</tr>
<tr>
<td>Mn$^{2+}$</td>
<td>5 (high spin)</td>
<td>5.92</td>
<td>5.92</td>
<td>~5.9</td>
</tr>
<tr>
<td>Fe$^{2+}$</td>
<td>4 (high spin)</td>
<td>4.90</td>
<td>5.48</td>
<td>5.1 – 5.5</td>
</tr>
<tr>
<td>Co$^{2+}$</td>
<td>3 (high spin)</td>
<td>3.87</td>
<td>5.20</td>
<td>4.1 – 5.2</td>
</tr>
<tr>
<td>Ni$^{2+}$</td>
<td>2</td>
<td>2.83</td>
<td>4.47</td>
<td>2.8 – 4.0</td>
</tr>
<tr>
<td>Cu$^{2+}$</td>
<td>1</td>
<td>1.73</td>
<td>3.00</td>
<td>1.7 – 2.2</td>
</tr>
</tbody>
</table>

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.
**Collective (bulk) magnetism**

The magnetic susceptibility $\chi$ is a measure of how magnetic a material is. $\chi$ 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.

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.

![Ferromagnetism Diagram](image)

$T_C$ 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.

![Ferrimagnetism Diagram](image)

**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 Antiferromagnetism
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 \(O^2-\) \(p\) 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.

Above \(T_N\) thermal energy is greater than the superexchange interaction and the spins no longer align giving paramagnetic behaviour.
**Superexchange leading to Ferrimagnetism**

Consider an antiferromagnet that has two 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 $\text{AB}_2\text{X}_4$ e.g. MgAl$_2$O$_4$.

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.

<table>
<thead>
<tr>
<th>Spinel</th>
<th>Inverse Spinel</th>
</tr>
</thead>
<tbody>
<tr>
<td>$[\text{A}^{2+}]<em>{\text{tet} \text{[B}^{3+}]</em>{\text{oct}}}$</td>
<td>$[\text{B}^{3+}]<em>{\text{tet} \text{[A}^{2+}, \text{B}^{3+}]</em>{\text{oct}}}$</td>
</tr>
<tr>
<td>MgAl$_2$O$_4$</td>
<td>CoFe$_2$O$_4$ NiFe$_2$O$_4$</td>
</tr>
<tr>
<td>BaFe$_2$O$_4$ (credit card strips, speakers)</td>
<td>Fe$_3$O$_4$ (magnetite) (loadstone)</td>
</tr>
</tbody>
</table>

Not all spinels have clear preference of metal ions for particular coordination sites. Many examples contain mixed metal sites e.g. MnFe$_2$O$_4$ 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$_2$O$_4$

   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 $\mu$ for each ion. The saturation (maximum) magnetic moment ($\mu_{sat}$) 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)

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e.g. NiFe$_2$O$_4$ (inverse spinel)

<table>
<thead>
<tr>
<th>ion</th>
<th>$[\text{Ni}^{2+}]^{\text{oct}, d^8}$</th>
<th>$[\text{Fe}^{3+}]^{\text{oct}, d^5}$</th>
<th>$[\text{Fe}^{3+}]^{\text{tet}, d^5}$</th>
<th>$\mu_{tet}$</th>
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<td>No. unpaired electrons</td>
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<td>5</td>
<td>5</td>
<td></td>
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<tr>
<td>$\mu_{ion}$</td>
<td>2</td>
<td>5</td>
<td>5</td>
<td>2 + 5 − 5 = 2</td>
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Comparison of estimation and experimental data for $\text{M}^\text{II}\text{Fe}^{\text{III}}\text{O}_4$

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<th>S</th>
<th>$\mu_{\text{sat calc}}$</th>
<th>$\mu_{\text{sat expt}}$</th>
<th>$T_N$</th>
<th>Discrepancy</th>
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<td>Mn</td>
<td>5/2</td>
<td>5</td>
<td>4.55</td>
<td>573</td>
<td>90% normal</td>
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<td>Fe</td>
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<td>4</td>
<td>4.1</td>
<td>858</td>
<td>s.o. coupling</td>
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<tr>
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<td>3.94</td>
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<tr>
<td>Ni</td>
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<td>2.3</td>
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<tr>
<td>Cu</td>
<td>1/2</td>
<td>1</td>
<td>1.3</td>
<td>726</td>
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<tr>
<td>Mg</td>
<td>0</td>
<td>0</td>
<td>1.1</td>
<td>713</td>
<td>90% inverse</td>
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**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 $\text{BaFe}_2\text{O}_4$ 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 hysteresis 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$_2$O$_4$).
A soft magnet has a small remanent magnetisation and a small coercive field: used as transformer cores (Si doped Fe).
Superconductivity

Superconductors exhibit two remarkable properties:
Zero electrical resistance and the Meissner effect (an external magnetic field is ejected).
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 $> 300$K many technologies (e.g. transport and power generation) would be revolutionised.

Superconductivity was discovered by Onnes in 1911 for Hg ($T_C = 4.2$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 $K_2\text{NiF}_4$ 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. (but there are higher claims)


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$_2$Cu$_3$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 YBa$_2$Cu$_3$O$_{7-x}$ 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$_2$Cu$_3$O$_{6.0-6.5}$ antiferromagnetism is observed and superconductivity is suppressed. For Cu$^{3+}$/Cu$^{2+}$ YBa$_2$Cu$_3$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 YBa$_2$Cu$_3$O$_7$, the charge reservoir layers are CuO chains.

**Borides**

In 2002 a new class of superconductor was discovered. MgB$_2$ ($T_c = 39K$) is an intermetallic compound i.e. B atoms are in the intersticies 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.

**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$_x$FeAs

**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$_3$C$_{60}$ (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)
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 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.

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)
Nanoparticles

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

\[ V_{\text{Ag}} = \frac{4}{3} \pi r^3 = 0.0213 \text{ nm}^3 \]

\[ V_{\text{np}} = 4.18 \text{ nm}^3 \]

\[ A_{\text{Ag}} = \pi r^2 = 0.093 \text{ nm}^2 \]

\[ A_{\text{np}} = 4\pi r^2 = 12.56 \text{ nm}^2 \]

74% packing efficiency ca. 145 Ag atoms
94% packing efficiency ca. 127 Ag atoms

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.

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

\[
\text{HAuCl}_4 + \text{NaBH}_4 + \text{N(C}_8\text{H}_{16})_4\text{Br} \xrightarrow{\text{toluene, water}} \text{Au}_{\text{np}} + \text{byproducts}
\]

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.

\[
\text{CdO} + \text{Se} + \text{P(C}_3\text{H}_{17})_3 \xrightarrow{} \text{CdSe}_{\text{np}} + \text{byproducts}
\]

\[
\text{Ti(OiPr)}_4 + 2\text{H}_2\text{O} + \text{C}_{18}\text{H}_{33}\text{CO}_2\text{H (oleic acid)} \xrightarrow{} \text{TiO}_2_{\text{np}} + 4\text{iPrOH}
\]

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

\[
\text{Pt(acac)}_2 + \text{Fe(CO)}_5 + \text{C}_{18}\text{H}_{35}\text{NH}_2 \xrightarrow{300 \degree\text{C}} \text{PtFe} + \text{byproducts}
\]

\[
\text{C}_{14}\text{H}_{29}\text{CH(OH)}\text{CH}_2(\text{OH}) \quad \text{1,2-hexadecanediol}
\]
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 sensing) and processing to make materials containing isolated nanoparticles e.g. for catalysis.
Characterisation of Nanoparticles

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.

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 \(\tau\) = particle size, \(\kappa\) = shape factor, \(\lambda\) = x-ray wavelength, \(\beta\) = full width half maximum (fwhm) in radians (1 radian = 180/\(\pi\) degrees), \(\theta\) = 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° 2\(\theta\), has a fwhm of 0.88° (0.0154 radians). Assume a shape factor of 0.9, \(\tau = 7\) nm.

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


Butterfly wings at increasing magnification

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

Transmission electron microscopy (TEM) of Ag nanoparticles


Quantum corral ‘particle in a box’
(AFM) Atomic Force Microscopy: Measures deflection of a tip as it is scanned across the surface of a material. Sub nm resolution now possible.

 Plus many other spectroscopic techniques
 Including:

 EDAXS (Elemental dispersion analyser using X-rays): Part of SEM and TEM instruments allowing elemental analysis of individual particles.
 Solid state NMR spectroscopy: Local structure and dynamics (need active nuclei)
 Electron spin resonance (EPR): Local structure and defects
 Electron energy loss spectroscopy (EELS): Electronic and surface structure
 X-ray fluorescence spectroscopy (XRF): Elemental analysis
 X-ray photoelectron spectroscopy (XPS): surface composition and oxidation states

 Summary

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<th>X-ray diffraction</th>
<th>Neutron diffraction</th>
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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 (E<sub>g</sub>) will increase with decreasing size.

![Graph showing luminescence vs wavelength for CdTe nanoparticles](image)

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.

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 nanostructured materials

Nanotubes

e.g. TiO$_2$ nanotubes formed electrochemically by etching Ti metal foil with HF.

Used for non-wetting and antibacterial surfaces e.g. metal surgical implants

Photocatalysis

OH$^-$ and O$_2^-$ are strong oxidizing agents and will degrade organic compounds to CO$_2$ and H$_2$O. TiO$_2$ (titania) is used to clean surfaces, reduce air pollution and clean drinking water. Can add to materials including plastics, glasses and concrete.
Nanosheets

e.g. graphene from graphite (a 2D material 1 carbon atom thick)

Lots of potential applications in the electronics industry, smart packaging and possibly solar energy conversion (transparent metal).

Hierarchical structures

Integrated circuits with <100 nm features use lithography (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.
An application of Nanotechnology-Solar Energy Conversion

The energy problem

Current global energy requirement about 15 TW

If the underdeveloped world wants a western lifestyle at least 50 TW required by 2050.

Energy from the sun at the Earth’s surface about 100000 TW.
Photons to Fuels
Nature does this with photosynthesis in plants, algae and bacteria.

\[
6 \text{H}_2\text{O} + 6 \text{CO}_2 \xrightarrow{\text{hv}} \text{C}_6\text{H}_{12}\text{O}_6 + 6 \text{O}_2
\]

Key processes are 1) light collection; 2) separation of charge (electrons for reduction chemistry and holes for oxidation chemistry); 3) Redox catalysis to form ‘fuels’ e.g. NADPH and carbohydrates in plants.

But plants etc are living (regeneration of the light collectors and catalysts), and are $< 3\%$ efficient. Growth is not quick enough.

Artificial Systems
We need to collect light, separate charge and catalyse reactions using Earth abundant elements with long lifetime. Inorganic semiconductors can absorb light across a bandgap and separate charge and many are resistant to oxidation.

Target reactions for solar fuels synthesis include water spitting (sea water ideally) and CO$_2$ reduction. e.g.

\[
2 \text{H}_2\text{O} \xrightarrow{\text{hv}} 2 \text{H}_2 + \text{O}_2 \quad \Delta G^0 = 237 \text{ kJmol}^{-1} \equiv 1.23 \text{ eV} \equiv 976 \text{ nm}
\]

\[
2 \text{H}_2\text{O} + \text{CO}_2 \xrightarrow{\text{hv}} \text{CH}_3\text{OH} + \text{O}_2 \quad \Delta G^0 = 229 \text{ kJmol}^{-1} \equiv 1.19 \text{ eV} \equiv 944 \text{ nm}
\]

Complicated kinetics and extra over potential required to increase rates.
**Wish list:**

Maximise light collection: absorb across the red and blue using a small band gap semiconductor or two semiconductors with different bandgaps.

Maximise charge separation: cause separation in space of electrons and holes to reduce recombination.

Maximise catalysis: new materials for reduction and oxidation, in separate regions of space.

Increase light collection and catalysis by increasing surface area = nanostructured surfaces.

A single material is unlikely to satisfy all these criteria. Need to interface several materials.

High surface area for light collection. Two band gaps can cover more of the solar spectrum. Products are separated in space.

Prototype device (Nocera et al, Science 2011, 334, 645–648) uses three buried Si cells in series to obtain 1.8 eV. Two nanostructured catalysts used for the redox reactions. Efficiency ca. 6%.