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Magnetic Properties of Materials

Lecture 10

Dielectric Properties of Materials

Lecture 11

Magnetic Properties of Materials

Lecture 12

New Lecturer: A/Prof. Toby Hudson

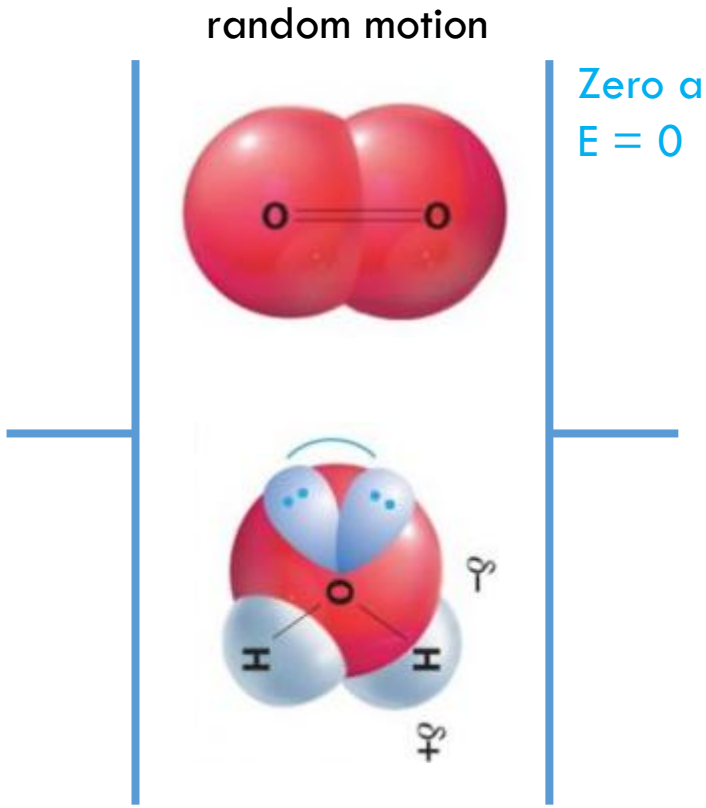
Statistical Mechanics

First On-Line Test

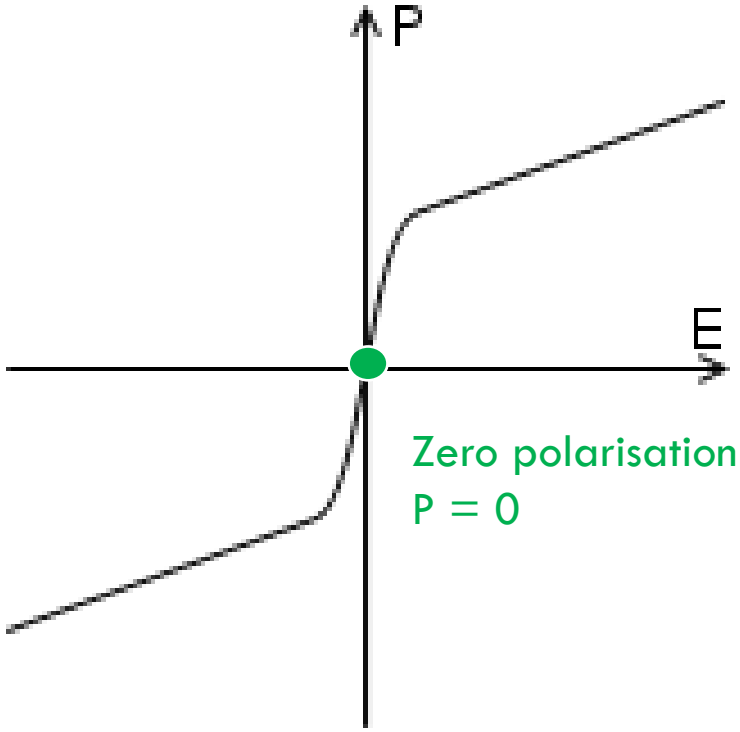
- **Worth:** 5% of overall grade
- **How to complete:** Online via "Assignments" in Canvas
- **Due:** The test is open for 1 week and closes 11:59 pm Sunday at the end of Week 5
- **Duration:** You have one hour to complete the test. You can have one attempt only (i.e., not like weekly quizzes)
- **Description:** The test contains 15 multiple choice questions.
- **Content:** Material from lectures 2 to 11, including pre-lecture videos 1-3, all worksheets, and tutorials 1 and 2
- **Specific things that will be tested:** ability to identify molecules with the same point group symmetry (note that this can often be done visually without needing to work out all of the symmetry operations and assignment of point group symbols); definitions of the various types of symmetry operations (including those that incorporate translation); Miller indices; application of the Bragg Equation; information that can be extracted from diffraction patterns; structural descriptions of various ionic lattices; Born-Mayer and lattice enthalpy trends; understandings of the nature of electron delocalisation and therefore mechanism for electron conduction in various materials we've encountered (1D/2D/3D); understanding of key parameters in the measurement of dielectric and magnetic materials.

Revision: Polarisation (P) in an Electric Field (E)

Paraelectric Behaviour



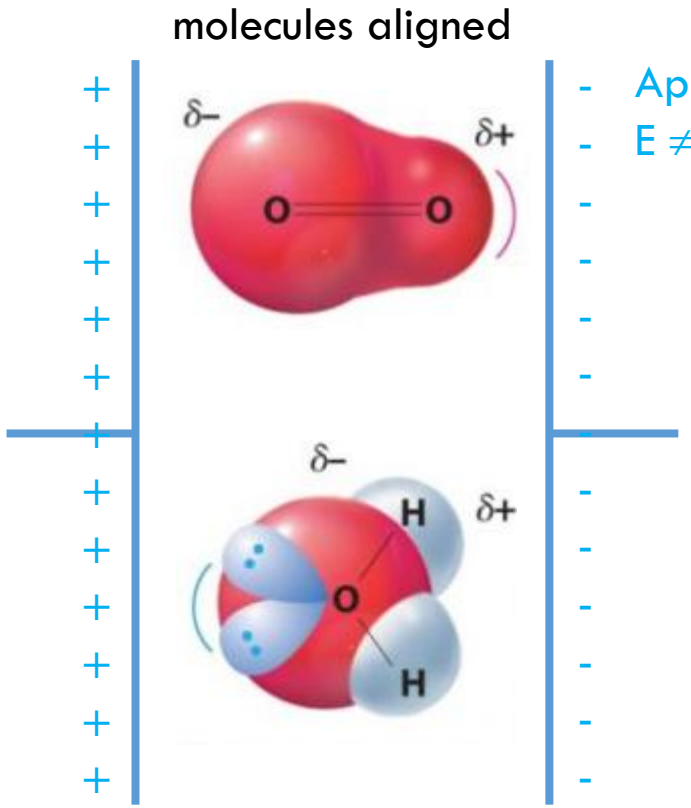
Polarisation



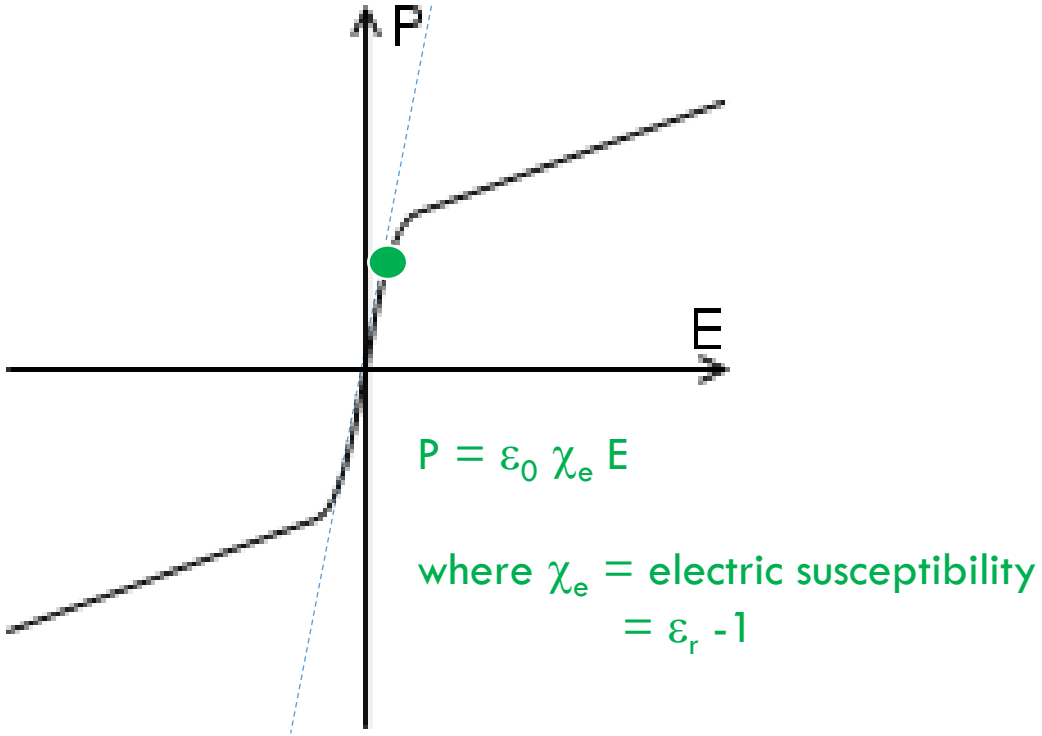
Paraelectric loop

Revision: Polarisation (P) in an Electric Field (E)

Paraelectric Behaviour



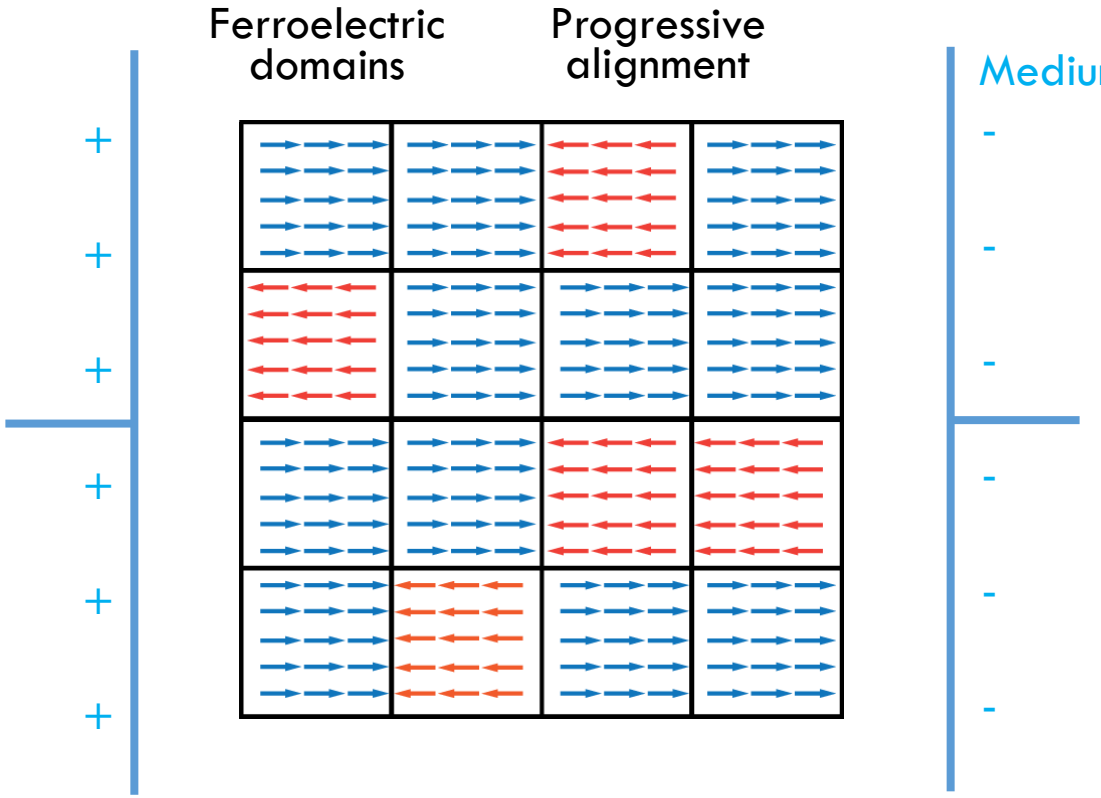
Polarisation



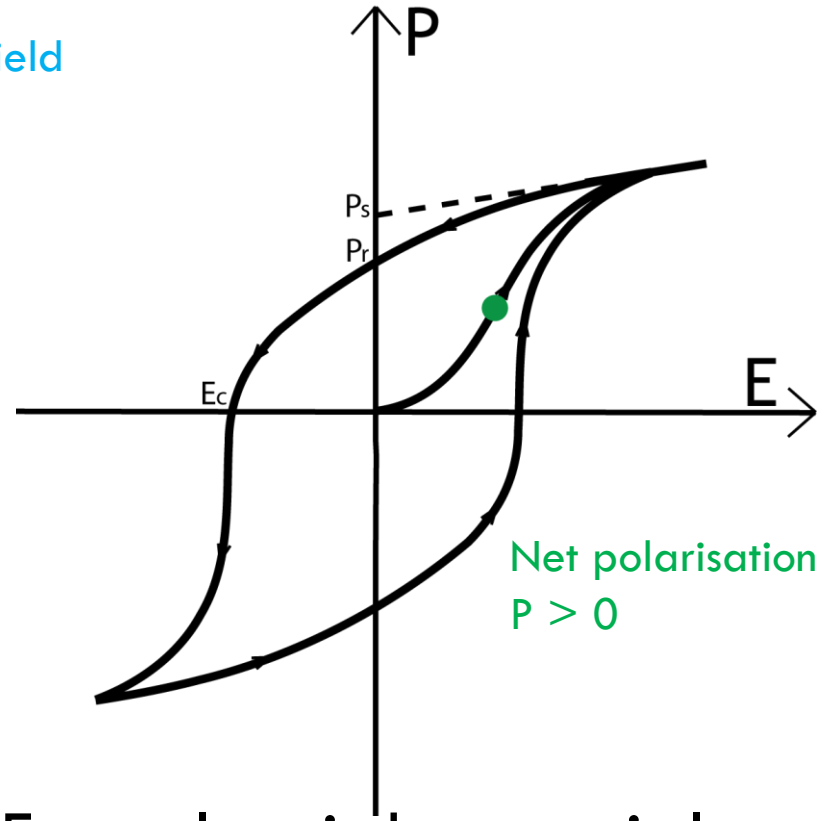
Paraelectric loop

Revision: Polarisation (P) in an Electric Field (E)

Ferroelectric Behaviour



Polarisation



Ferroelectric hysteresis loop

Outline

- The origin of magnetism in materials
  - The magnetic moment of an atom/ion
  - Crystal-field effects on magnetism in crystals
- Measuring and classifying magnetism in materials
  - Diamagnetism *vs.* paramagnetism
  - Ferromagnetism, antiferromagnetism, ferrimagnetism
  - Curie's Law, magnetisation and magnetic susceptibility
- The origins of ordered magnetism in materials
  - Direct exchange
  - Superexchange

Magnetic Moment of an Atom/Ion

- The electrons and nuclei of an atom/ion can have net **spin**, and therefore a **magnetic moment**.
- The magnetic moment is inversely proportional to the mass of the particle.
  - nuclear magnetic moments are very small compared to the magnetic moments of unpaired electrons (by a factor of ~1800)
    - E.g., Bohr magneton, $\mu_B = 9.27 \times 10^{-24}$ Am^2; nuclear magneton $\mu_N = 5.05 \times 10^{-27}$ Am^2)

Particle name (symbol)	Magnetic dipole moment (10^{-27} J·T^{-1})	Spin quantum number (dimensionless)
electron (e^-)	−9 284.764	$\frac{1}{2}$
proton (H^+)	14.106 067	$\frac{1}{2}$
neutron (n)	−9.662 36	$\frac{1}{2}$
muon (μ^-)	−44.904 478	$\frac{1}{2}$
deuteron ($^2H^+$)	4.330 7346	1
triton ($^3H^+$)	15.046 094	$\frac{1}{2}$
helion ($^3He^{++}$)	−10.746 174	$\frac{1}{2}$
alpha particle ($^4He^{++}$)	0	0

en.wikipedia.org/wiki/Magnetic_moment

Mass	Element	Magnetic dipole moment[7][8] (nuclear magneton units)	Nuclear spin number[7]
Formula		μ_Z/μ_N (measured)[9]	I
1	H	2.79284734(3)	1/2
2	H	0.857438228(9)	1
7	Li	3.256427(2)	3/2
13	C	0.7024118(14)	1/2
14	N	0.40376100(6)	1
19	F	2.628868(8)	1/2
23	Na	2.217522(2)	3/2
31	P	1.13160(3)	1/2
39	K	0.39147(3)	3/2

en.wikipedia.org/wiki/Nuclear_magnetic_moment

Ion	Number of unpaired electrons	Spin-only moment /μ_B	observed moment /μ_B
Ti^{3+}	1	1.73	1.73
V^{4+}	1		1.68–1.78
Cu^{2+}	1		1.70–2.20
V^{3+}	2	2.83	2.75–2.85
Ni^{2+}	2		2.8–3.5
V^{2+}	3	3.87	3.80–3.90
Cr^{3+}	3		3.70–3.90
Co^{2+}	3		4.3–5.0
Mn^{4+}	3		3.80–4.0
Cr^{2+}	4	4.90	4.75–4.90
Fe^{2+}	4		5.1–5.7
Mn^{2+}	5	5.92	5.65–6.10
Fe^{3+}	5		5.7–6.0

en.wikipedia.org/wiki/Magnetochemistry

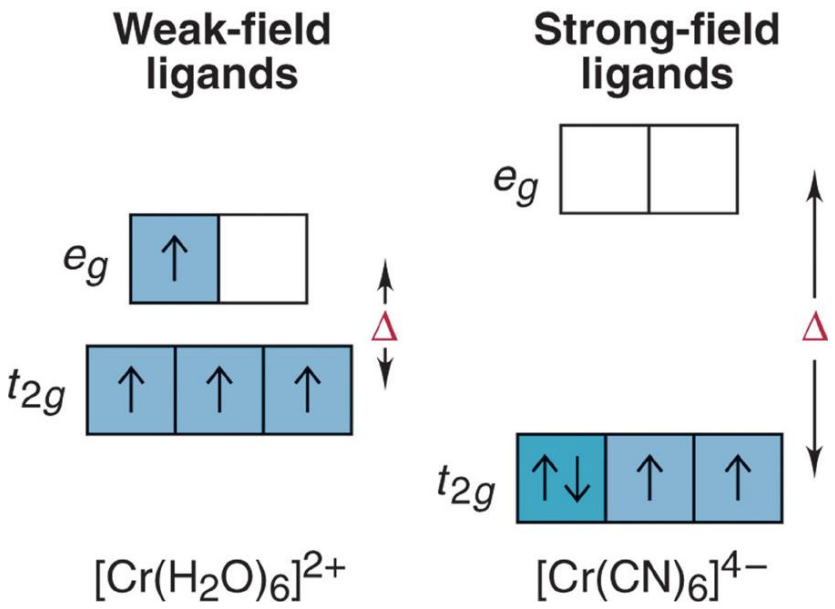
Magnetic Moment of an Atom/Ion

Electrons have magnetic moments associated with their spin quantum number, $s = \pm ½$.

The <u>total</u> spin angular momentum quantum number for an atom/ion, S, is the sum of the spin quantum numbers ($s = \pm ½$) for all the outer shell electrons.

high-spin Cr^{2+}

$S = 4(+½) = 2$



low-spin Cr^{2+}

$S = 3(+½) + (–½) = 1$

Figures from Silberberg, "The Molecular Nature of Matter and Change" 3rd Edition (2003), McGraw-Hill

Measuring Magnetism

Magnetic materials consist of many magnetic atoms.

The magnetic moment per unit volume is the **magnetization, $\mathbf{M}$,** of the material.

When placed in a magnetic field, $\mathbf{H}$,

$$\mathbf{M} = \chi\mathbf{H}$$

where χ is the **magnetic susceptibility** of the material.

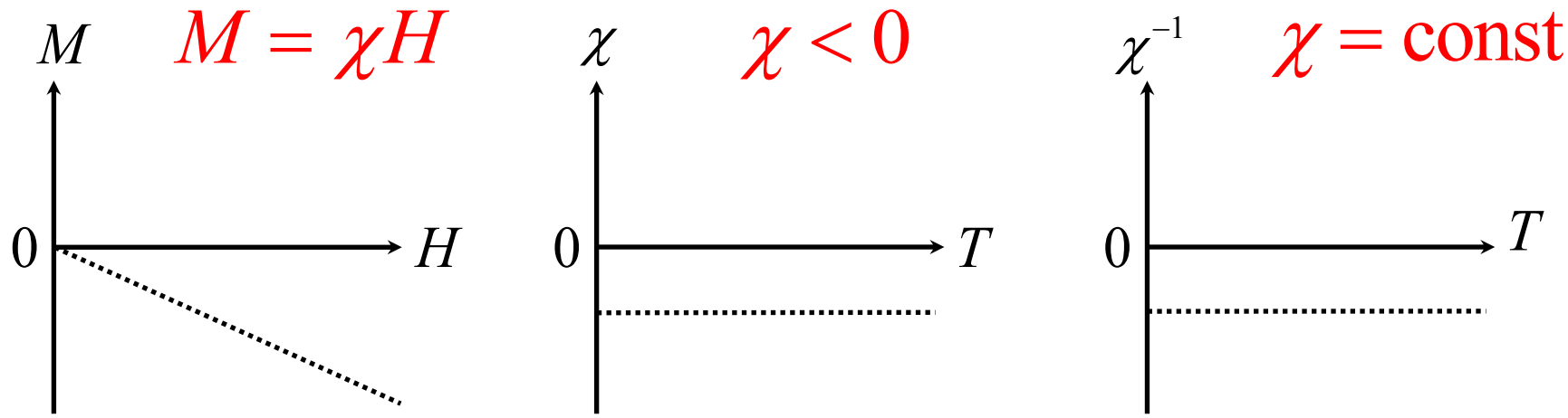
Magnetic materials are broadly characterised by measuring their:

- Magnetisation as a function of applied magnetic field
- Susceptibility as a function of temperature

Diamagnetism

All materials show a weak negative **diamagnetic** susceptibility due to the polarisation of electron pairs by an applied magnetic field.

- There is no magnetisation at zero applied field.
- Susceptibility is negative (diamagnetism is a repulsive force).
- The magnetic susceptibility is temperature-independent.



Applications of Diamagnetism

Superconductors have large negative diamagnetic susceptibility, χ, meaning they repel a magnetic field.



	Material	χ_m [$\times 10^{-5}$ (SI units)]
⟹	Superconductor	-10^5
	Pyrolytic carbon	−40.9
	Bismuth	−16.6
	Neon	−6.74
	Mercury	−2.9
	Silver	−2.6
	Carbon (diamond)	−2.1
	Lead	−1.8
	Carbon (graphite)	−1.6
	Copper	−1.0
	Water	−0.91

Applications of Diamagnetism

Most electrons in living things are paired, and hence diamagnetic.



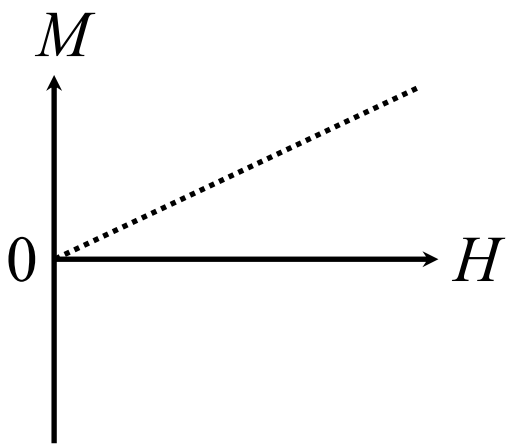
https://www.nature.com/articles/35037782
https://en.wikipedia.org/wiki/Andre_Geim

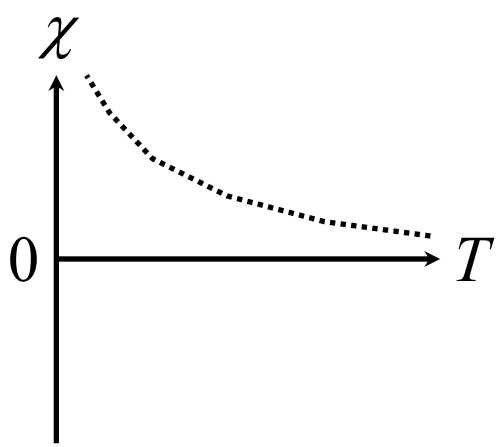
Paramagnetism

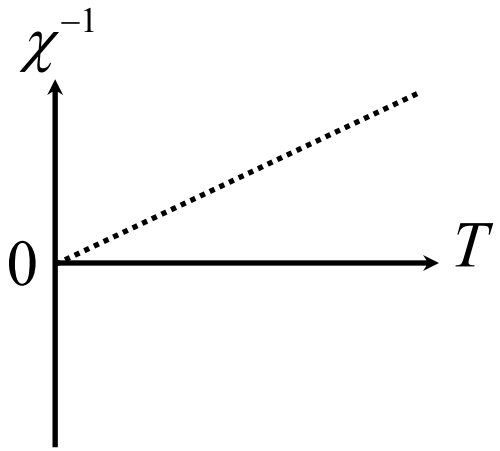
Paramagnetic materials have unpaired electrons that can be aligned by a magnetic field to give a positive susceptibility.

- There is no magnetisation at zero applied field.
- Susceptibility is positive (paramagnetism is an attractive force).
- The magnetic susceptibility obeys *Curie's Law*:

$$\chi = \frac{C_{\text{Curie}}}{T}$$

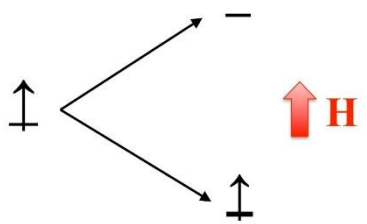






Increasing T can provide thermal energy to overcome energy gap between states.

not aligned state



aligned state

Long-range Magnetic Order

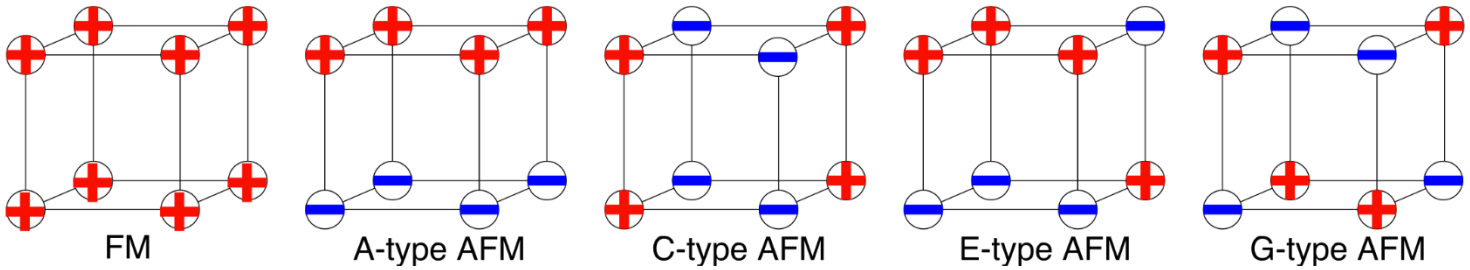
Magnetic atoms arranged in periodic lattices (crystals) have the potential for **long-range magnetic order.**

Most applications of solid-state magnetic materials exploit long-range-ordered, rather than paramagnetic or diamagnetic, states.

↑ ↑ ↑ ↑ ↑ ↑ ↑ ↑ ↑ **Ferromagnetic (FM)**

↑ ↓ ↑ ↓ ↑ ↓ ↑ ↓ ↑ **Antiferromagnetic (AFM)**

There are a huge variety of possible types of magnetic order in 3D materials. E.g., even for the simplest case of a cubic unit cell with parallel spins of equal magnitude we can have:



Magnetic Exchange

Most long-range order is a consequence of **magnetic exchange**.

Magnetic exchange interactions are essentially electrostatic interactions among the outer-shell electrons of a magnetic atom and those of its neighbours.

The energy of the system (i.e., a crystal) can be lowered by moving like charges (i.e., electrons) further apart from one another (i.e., **electron delocalisation**).

Magnetic order arises because electronic delocalisation is subject to selection rules concerning their possible spin orientations.

Two types of magnetic exchange are:

- **Superexchange**
- **Double exchange**

Superexchange

Superexchange is an indirect exchange interaction between non-neighbouring magnetic atoms, mediated by non-magnetic atoms in between them.

- Consider magnetic atoms bridged by oxygen. The partially-occupied e_g orbitals of the magnetic atoms overlap with a fully occupied p-orbital of oxygen.
- The Pauli exclusion principle dictates that electrons in the same orbital have opposite spin (paired spins).

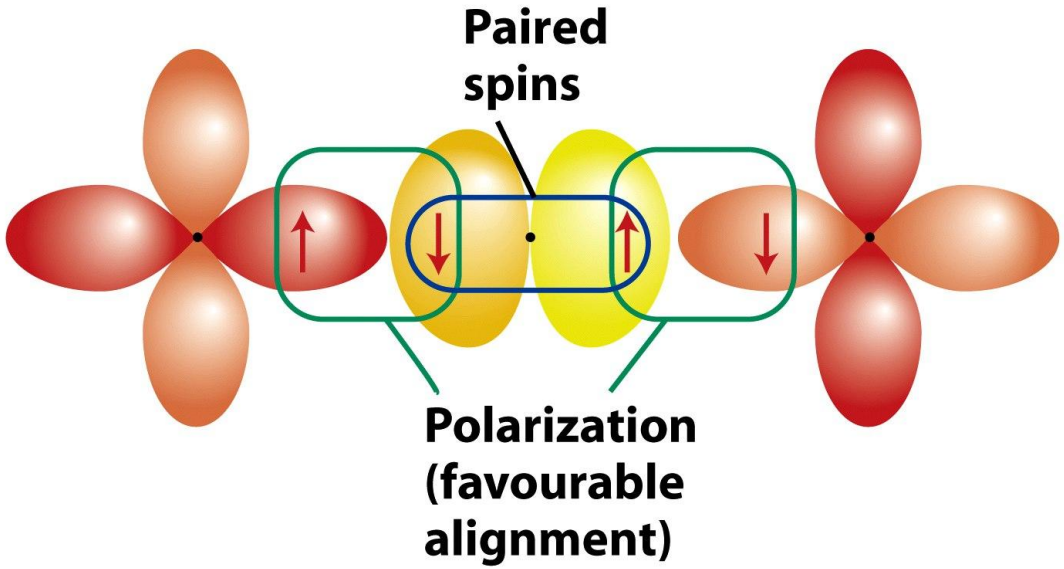


Figure from Shriver and Atkins, "Inorganic Chemistry" 4th Edition (2006), Oxford

Superexchange

Superexchange is an indirect exchange interaction between non-neighbouring magnetic atoms, mediated by non-magnetic atoms in between them.

- The lowest-energy state will be the one in which all these electrons have the greatest opportunity to delocalise by mixing with excited state configurations.
- Opposite alignment of the spins in the overlapping orbitals lowers the energy and favours **antiferromagnetic** ordering.

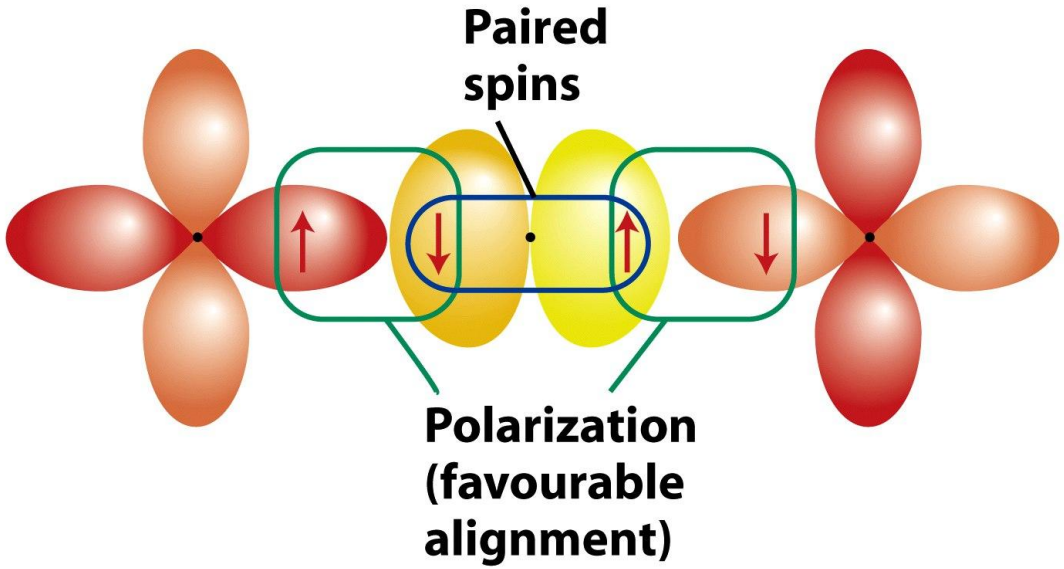
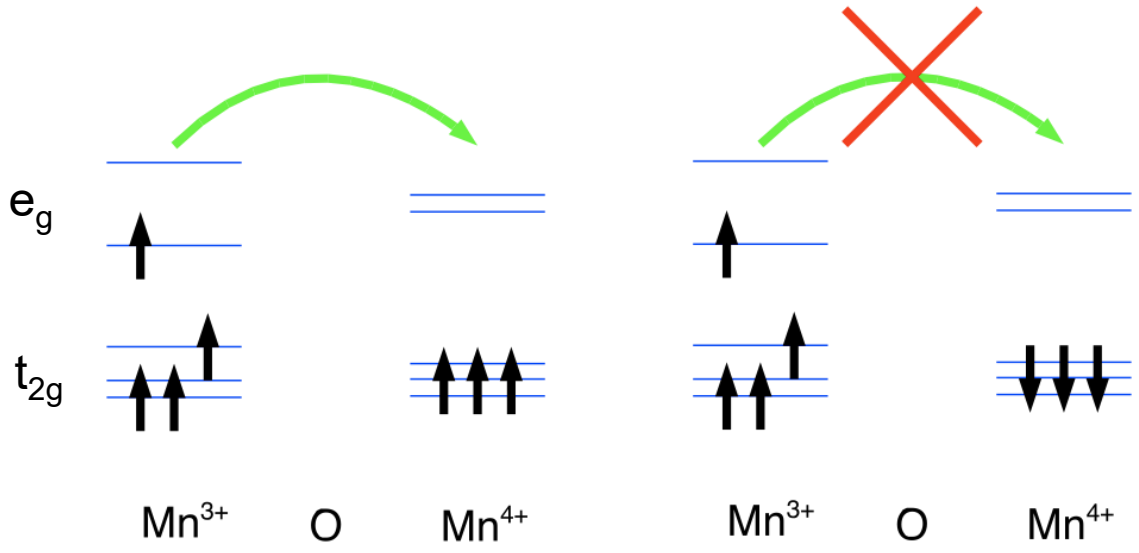


Figure from Shriver and Atkins, "Inorganic Chemistry" 4th Edition (2006), Oxford

Double Exchange

Double exchange is the exchange of an unpaired electron between magnetic ions in different oxidation states.

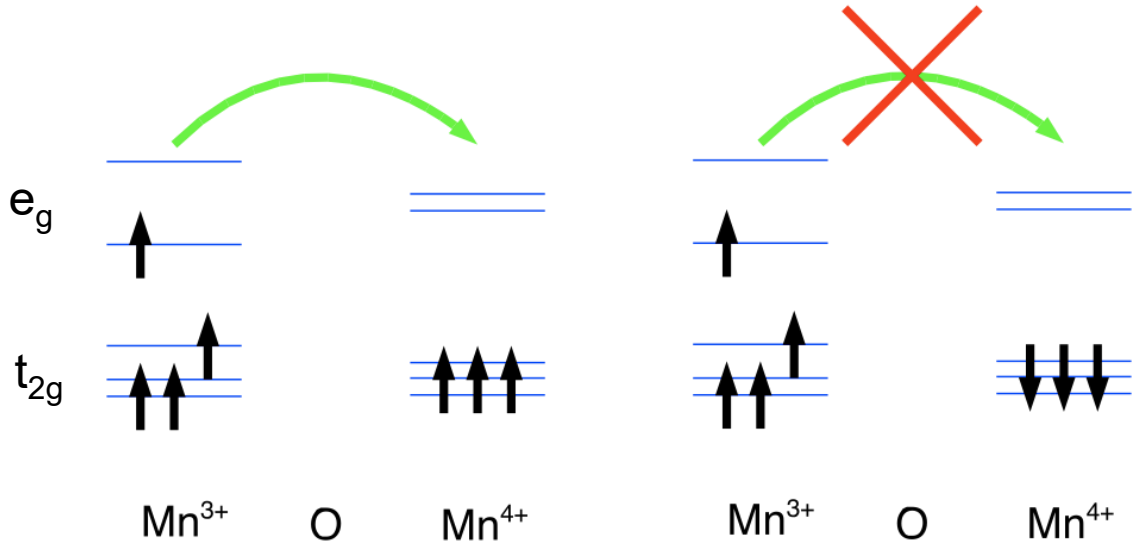
- In the ground state, all the electrons on each ion are aligned according to Hund's rule.
- Moving an unpaired electron from one ion to an empty orbital of a neighbouring ion is favourable if the electrons do not have to change spin direction.



Double Exchange

Double exchange is the exchange of an unpaired electron between magnetic ions in different oxidation states.

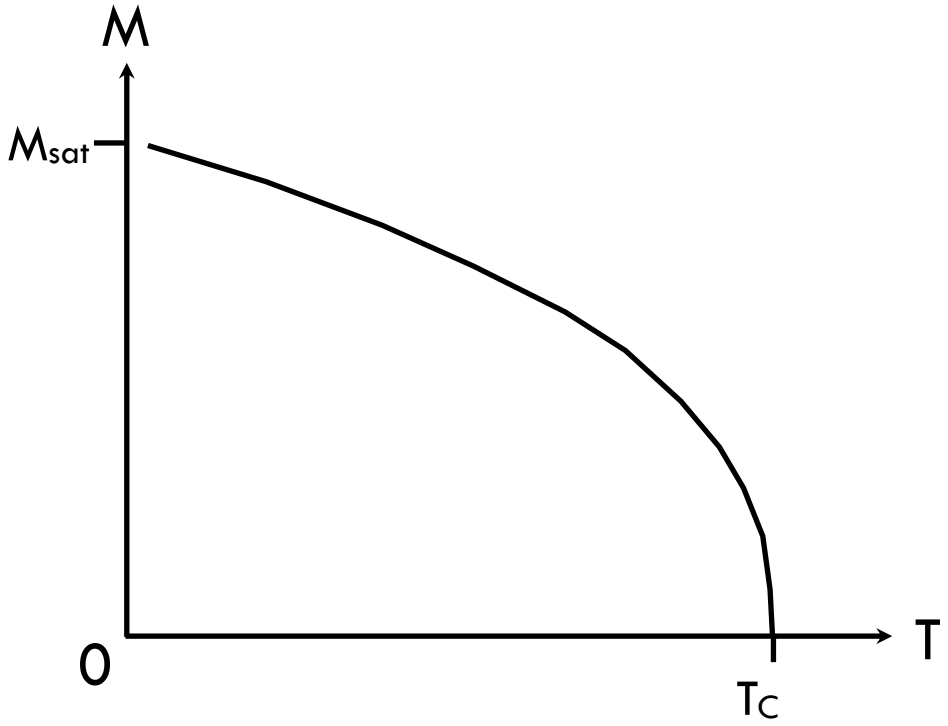
- The lowest-energy state will be the one in which all these electrons have the greatest opportunity to delocalise.
- Alignment of spins in the donor ion and acceptor ion lowers the energy and favours **ferromagnetic** ordering.
- In extended systems (i.e., mixed-valence ionic crystals), this leads to conducting behaviour.



Ferromagnetism

Spontaneous ('zero-field') magnetization ↑ ↑ ↑ ↑ ↑ ↑ ↑ ↑ ↑

- Ferromagnetic (FM) materials have a net spontaneous magnetisation, M_{sat}, below the Curie temperature, T_C. The net magnetic moment appears on cooling in a second-order phase transition.



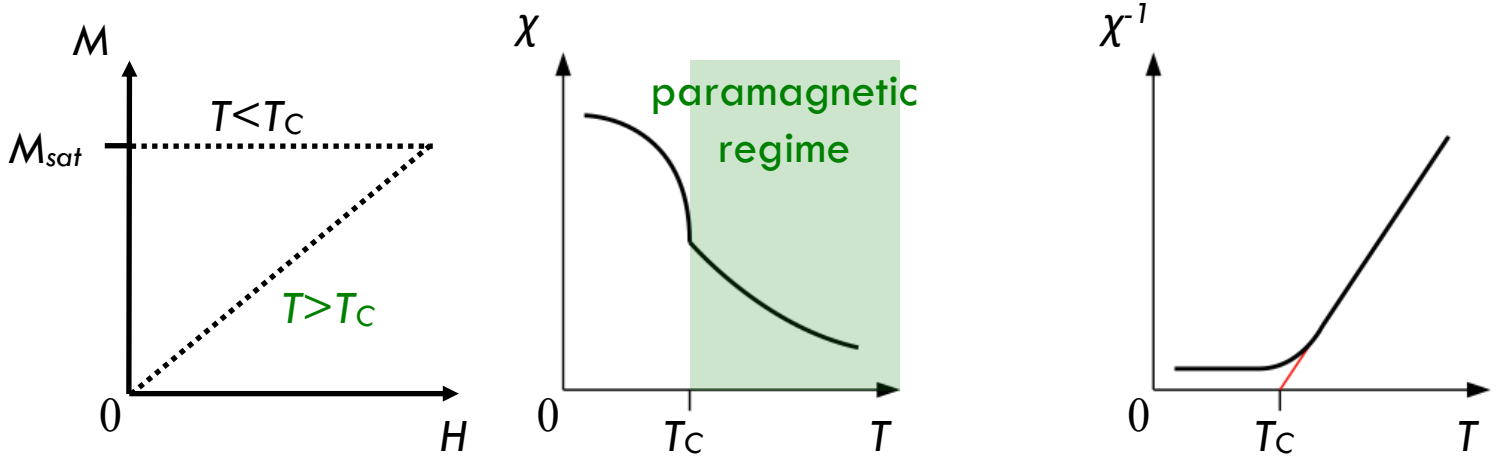
Ferromagnetism

Magnetic susceptibility

- At high temperatures ($T > T_C$), the magnetic susceptibility of a ferromagnet obeys a modified version of the Curie law (for paramagnets), the Curie-Weiss law:

$$\chi = \frac{C}{T - \theta}$$

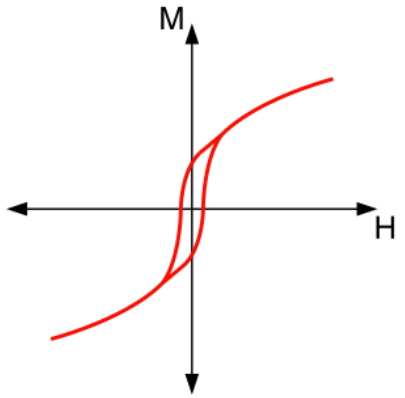
- For ferromagnets, $\theta > 0$ and $\theta = T_C$, the Curie temperature.



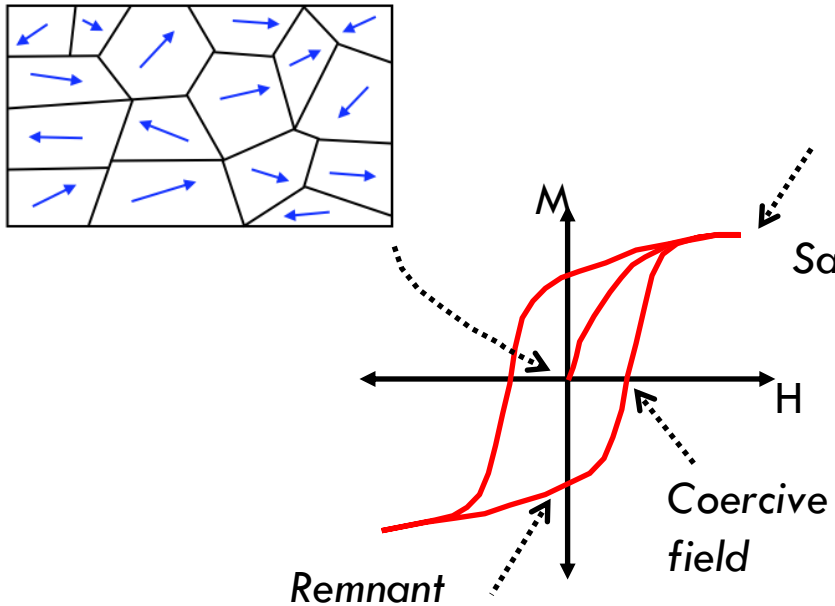
Ferromagnetism

Magnetisation hysteresis curve

- Below T_C, magnetised FM materials can be reoriented by an applied field.
- The shape of the **hysteresis loop** affects the possible applications.
- In practice, the microscopic domain structure means that there will often be no net magnetisation until an external field has been applied at least once.



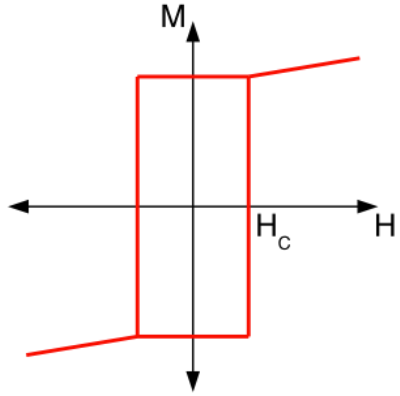
Easily reoriented: good for transformer cores



Saturation magnetisation

Coercive field

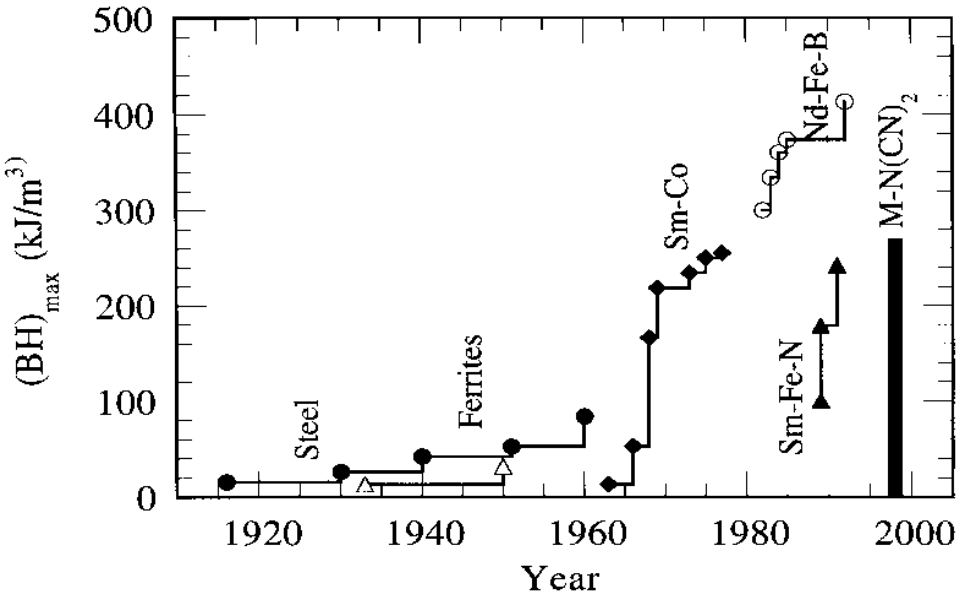
Remnant magnetisation



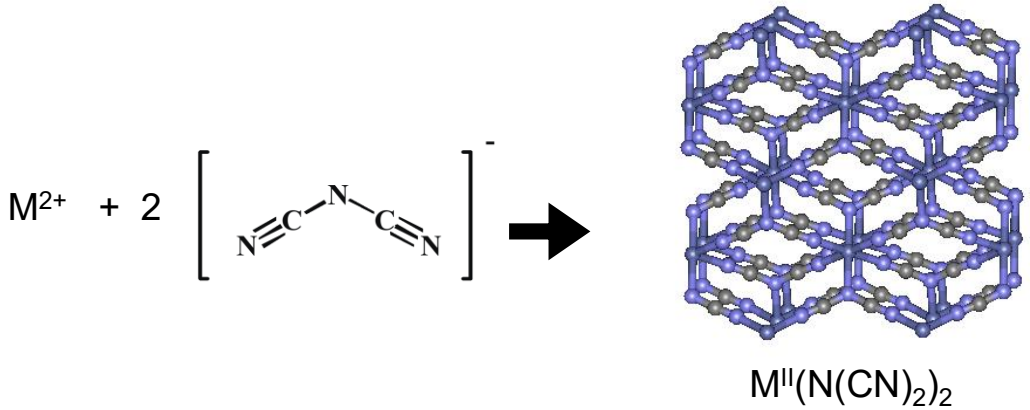
Hard to reorient: good for data storage

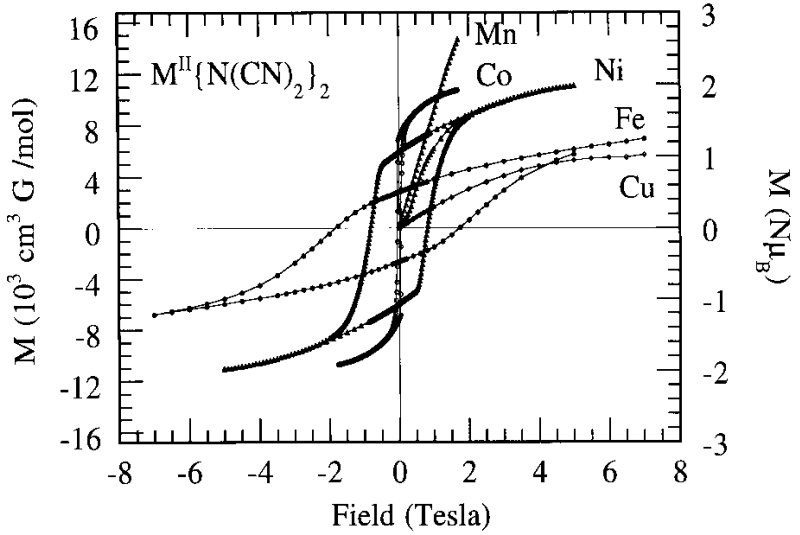
History of High Strength Ferromagnets

Figure-of-Merit for strength



Recent work on Molecular Magnets





Antiferromagnetism

No net magnetisation ↑ ↓ ↑ ↓ ↑ ↓ ↑ ↓ ↑

- In antiferromagnetic (AF) materials, the atomic magnetic moments align in opposite directions at zero applied field, cancelling each other out.

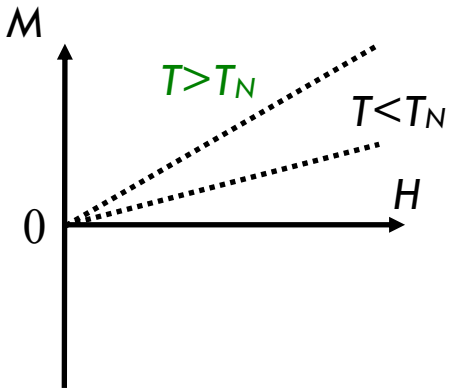
Antiferromagnetism

Magnetic susceptibility

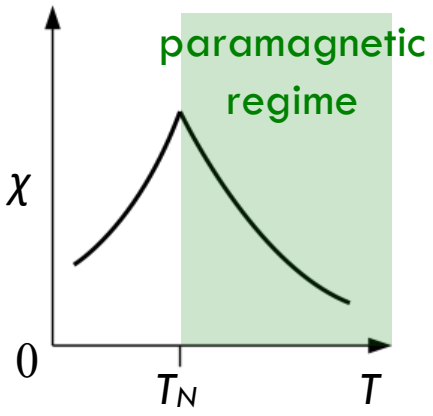
- At high temperature, the magnetic susceptibility of an antiferromagnet obeys the Curie-Weiss law:

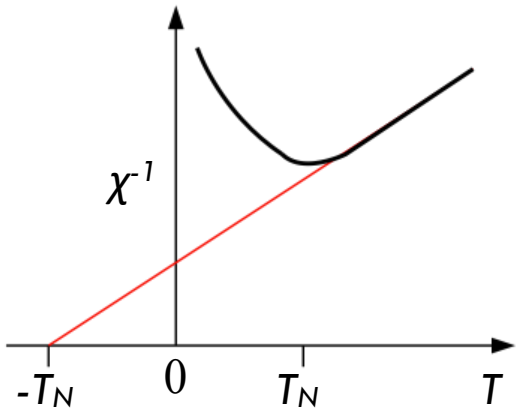
$$\chi = \frac{C}{T - \theta}$$

- For antiferromagnets, $\theta < 0$ and $\theta = -T_N$, where T_N is the Néel temperature.



Magnetism increases more rapidly above T_N due to thermal energy "helping" to align the spins.

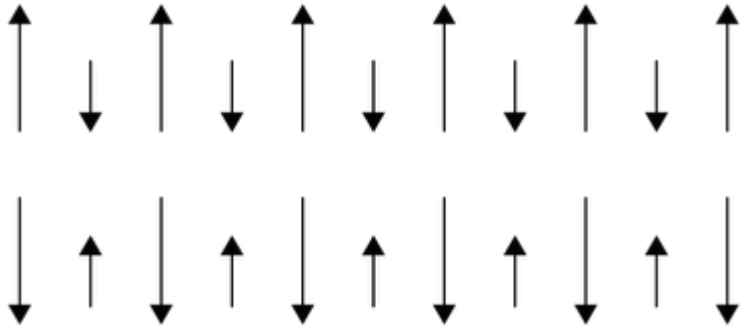




Worksheet question

Ferrimagnetism

Ferrimagnetic materials have opposing moments, similar to antiferromagntic materials; however, the antiparallel moments do not cancel each other out.



Spontaneous ('zero-field') magnetisation

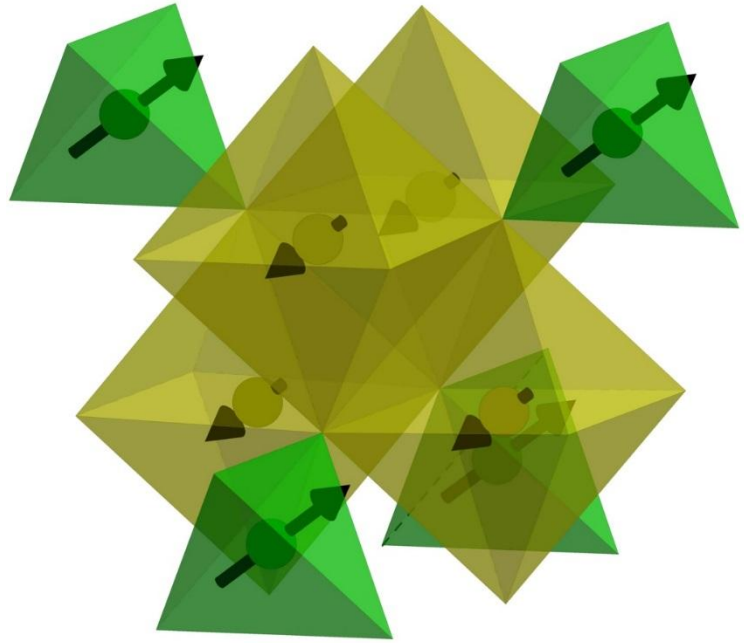
Ferrimagnetism

Example: Magnetite Fe_3O_4 – "lodestone"

- Magnetite is a ferrite. Ferrites have **inverse spinel** structures (see next slide), in which $Fe^{3+}O_4$ tetrahedra are located among sheets of edge-sharing $(M^{2+},Fe^{3+})O_6$ octahedra (M = Fe, Ni, Cu, Mg...).

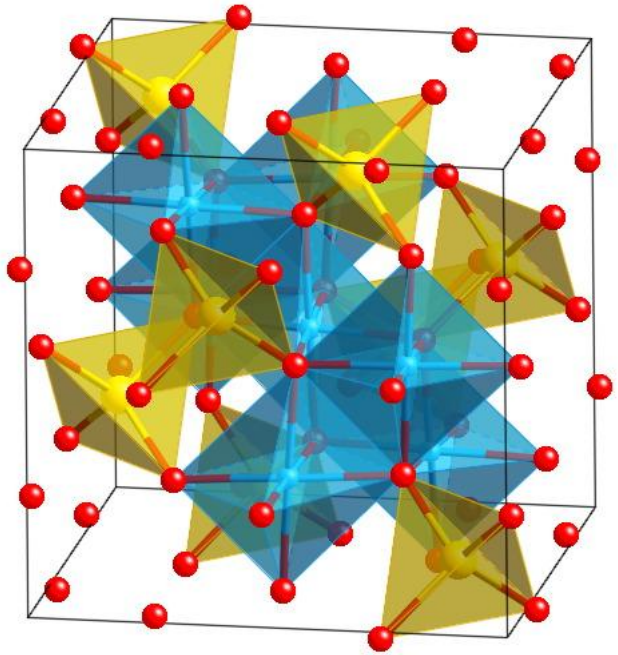
- Fe_3O_4 shows high conductivity due to the process $Fe^{2+} \rightleftharpoons Fe^{3+} + e^-$.

- Ferrites are ferrimagnetic. The tetrahedral and octahedral sites have opposite but unequal magnetic moments, which leaves a net moment in the direction of the stronger one. (Note also that there are twice as many octahedra as tetrahedra.)



https://materialsproject.org/materials/mp-19306/

Octahedral and tetrahedral holes



Spinel: $\left(A^{2+}\right)_{tet}\left(B^{3+}\right)_{2oct}O_4$

Inverse spinel: $\left(B^{3+}\right)_{tet}\left(A^{2+}B^{3+}\right)_{2oct}O_4$

Anion	Filling of Interstitial Sites		Structure	Examples
Packing	T_d	O_h		
ccp (fcc)	-	all	rock-salt	NaCl, MgO, LaN
	-	1/2	cadmium chloride	$CdCl_2$, $NiCl_2$
	half	-	zinc blende (sphalerite)	ZnS, CuCl, BN
	all	-	anti-fluorite	Na_2O, Li_2S
	1/8	1/2	spinel	$MgAl_2O_4$

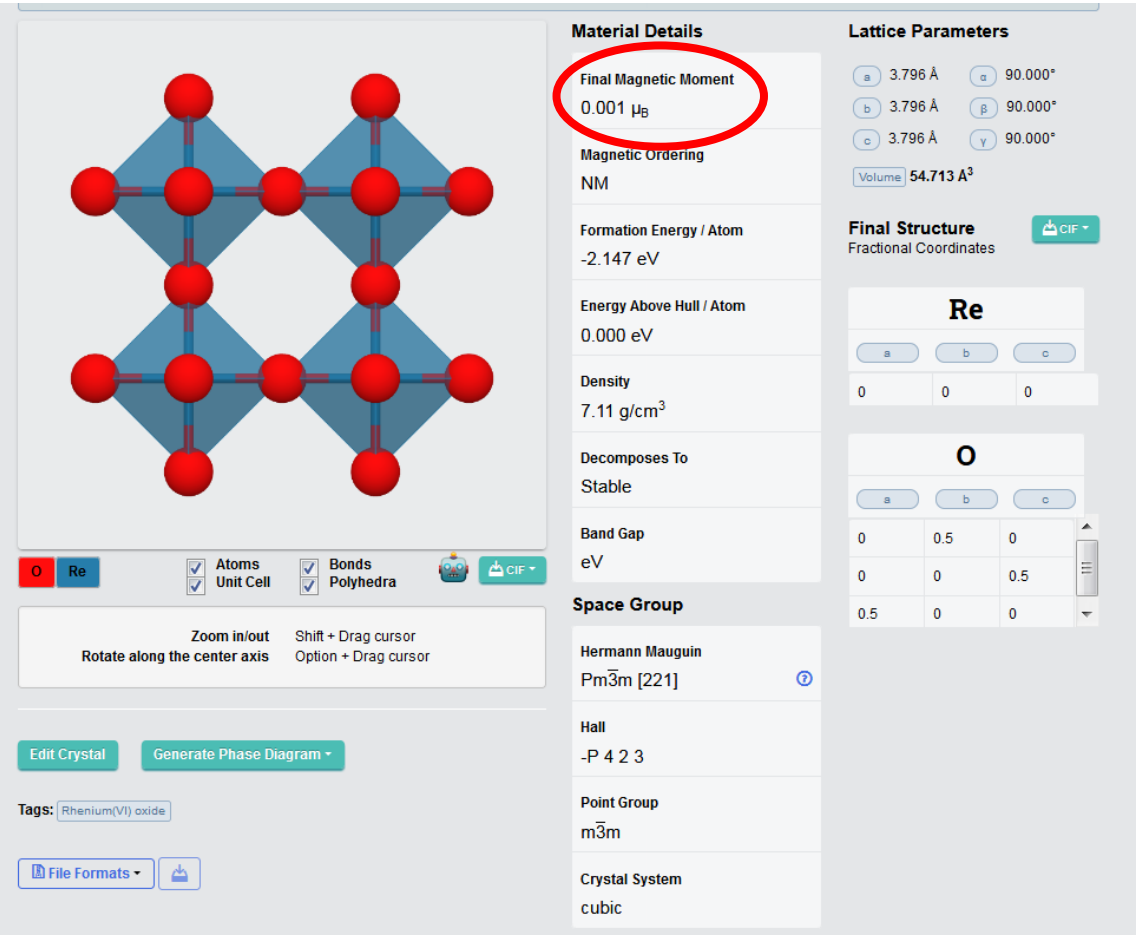
Magnetic behaviour of delocalised electrons

Delocalised electrons don't align magnetically in the same way that localised electrons do.

They commonly display Temperature Independent Paramagnetism (TIP; also 'Pauli Paramagnetism'), i.e., a constant positive magnetic susceptibility that doesn't vary with changing temperature.

This paramagnetism arises from a small imbalance of spin-up electrons near the Fermi energy in the presence of a magnetic field.

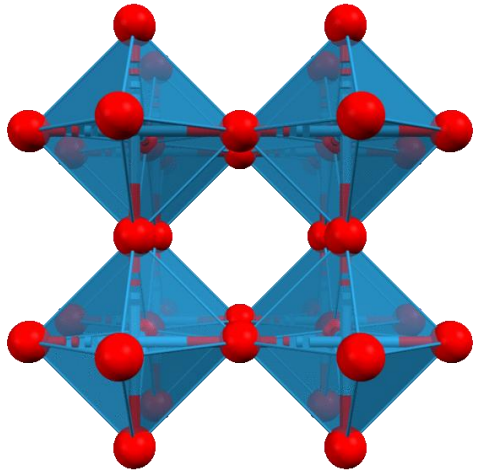
ReO_3 $5d^1$ is a conductor (see next slide)



https://materialsproject.org/materials/mp-190/
https://doi.org/10.1016/0022-4596(72)90038-2

Trends in Electronic Conductivity

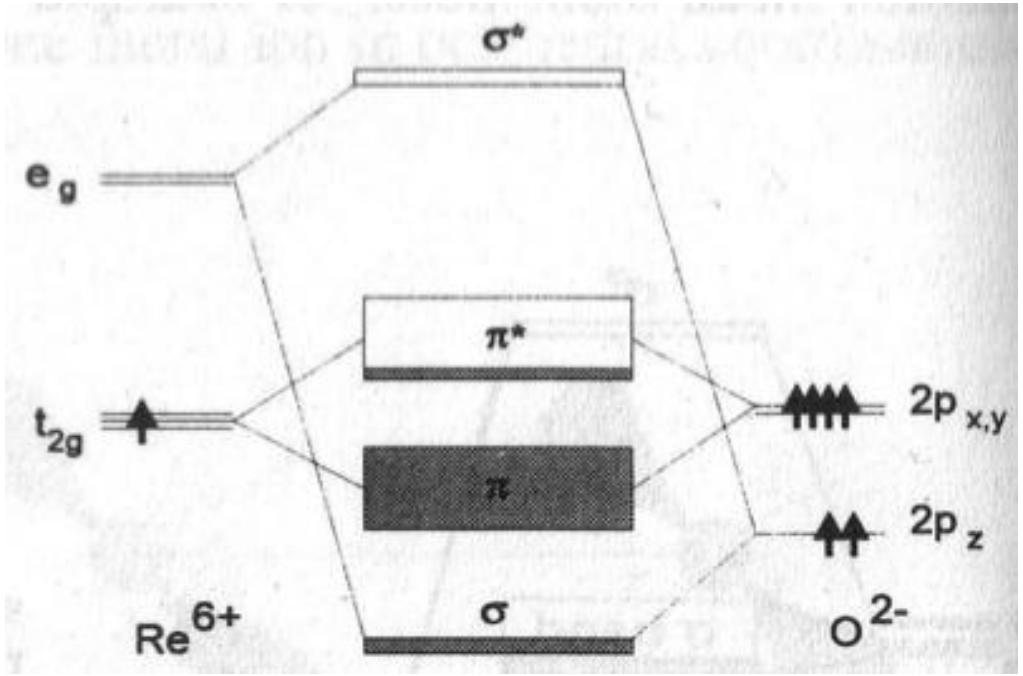
Rhenium Oxide



ReO_3

$5d^1$

metallic



Band structure of ReO_3

Figures from Weller "Inorganic Materials Chemistry"

Learning Outcomes

After this lecture you should be able to

- Explain the different exchange interactions that can lead to bulk magnetism.
- Explain their behaviour in applied magnetic fields.
- Identify a material as diamagnetic, paramagnetic, ferromagnetic, or antiferromagnetic on the basis of magnetometry measurements.
- Complete the lecture worksheet, be able to answer all questions in this week's on-line quiz (covering electronic, dielectric & magnetic properties), and start preparing for the on-line test to be held in week 5 (covering content from lectures 2 to 11).

Further reading: Shriver & Atkins, "Inorganic Chemistry", Oxford, 5th Ed. (2010): Chapter 8.15, 14, 20.1c; Weller, "Inorganic Materials Chemistry", Oxford (1994): pp 55-57.