Aalto University
School of Chemical
Engineering

Functional Inorganic Materials
Lecture 12:
Magnetic and multiferroic oxides

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Lecture Exercise 12 is a MyCourses Quiz

Contents

Two sources of magnetism:

1. Motion of electrically charged particles
2. Spin magnetic moments

Here we focus mainly on (2)

- Brief summary of **magnetism**
  - Magnetical ordering of material
  - Effect of on magnetic properties
  - Applications
- **Magnetic** oxides
  - Binary *d*-metal oxides
  - Ferrites
  - Garnets
- **Multiferroic** materials

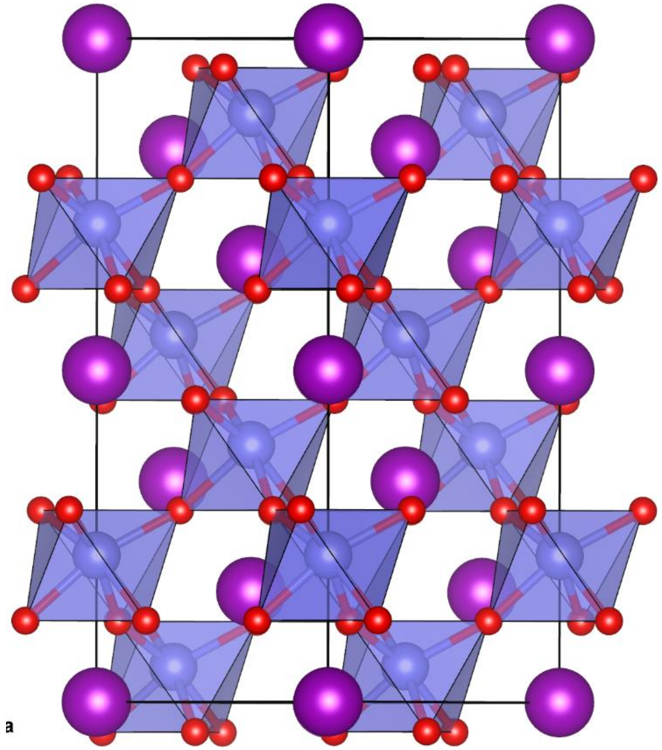
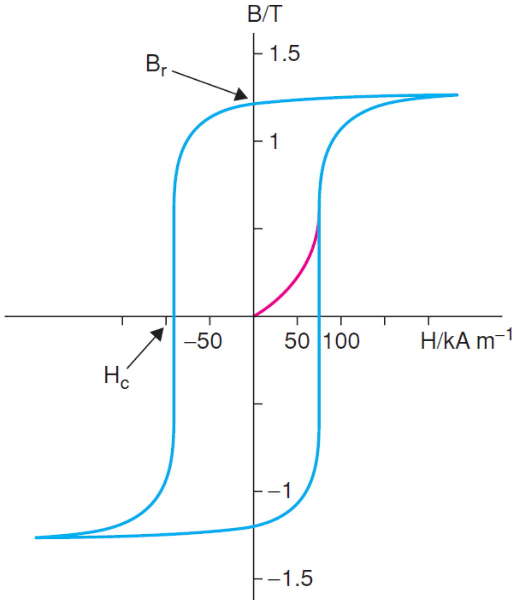


Figure: AJK

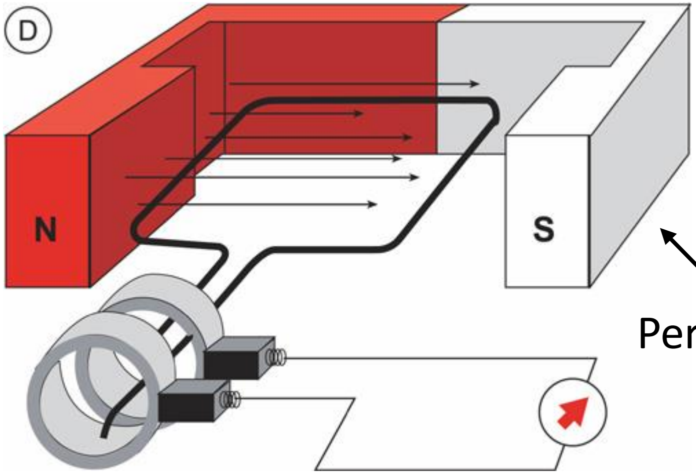


Everyday magnetism

Lodestone (magnetite Fe_3O_4)

Electromagnetic induction

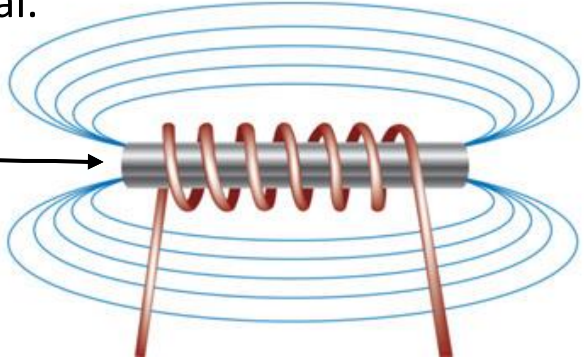
In most applications, an electromagnet is used instead of a permanent magnet. Still, the core is ferromagnetic material.



http://www.edu.helsinki.fi

Permanent (ferro)magnet

Core



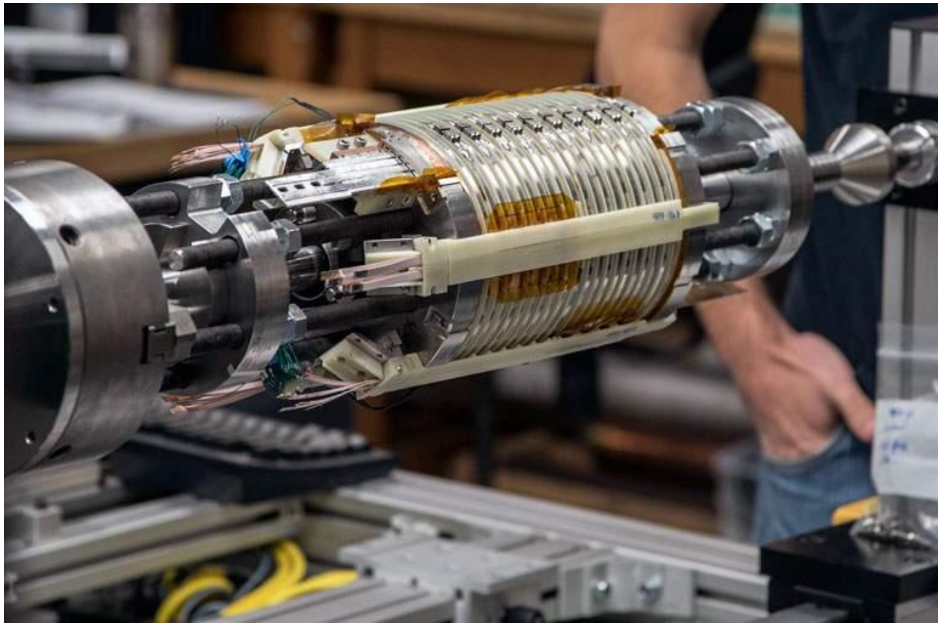
Generator, P = ~2.8 kW

Electric motor ~50 kW

Generator, P = ~800 MW

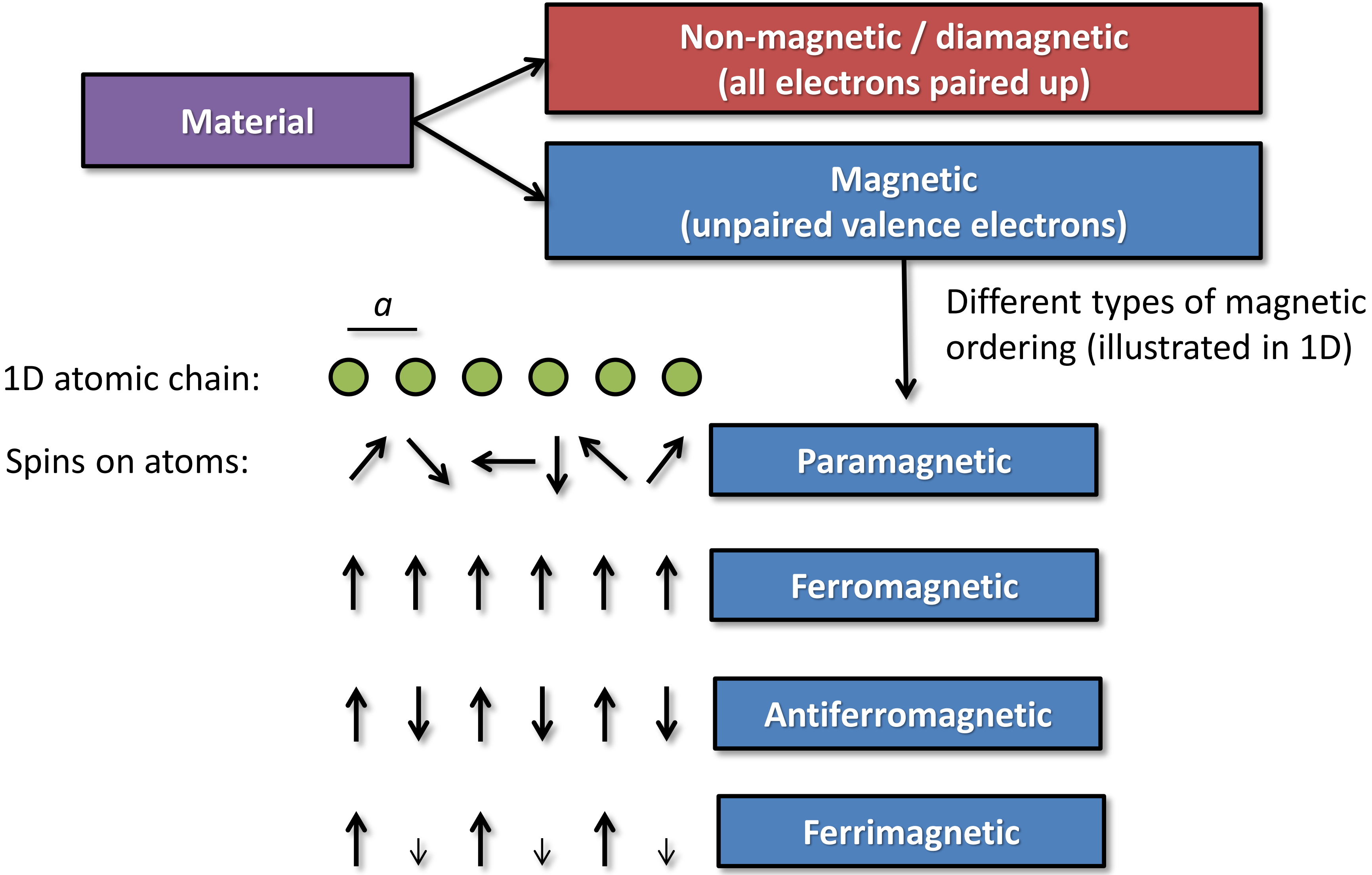
Superconducting magnets

- Electromagnet made from coils of superconducting wire.
- When current has been injected and power supply turned off, the magnetic field remains as long as $T < T_C$ (transition temperature)
- Very important for science, medicine, and technology
  - Magnetic resonance imaging (MRI)
  - NMR and mass spectrometers
  - Particle accelerators
  - Fusion reactors (eventually)



One coil of 32 Tesla superconducting magnet (National High Magnetic Field Laboratory, link). Coils: **YBCO** (2 coils), Niobium-Tin (3 coils), and Niobium-Titanium (2 coils)
(Earth's magnetic field at surface: 25 to 65 μT)

Spin-based magnetism



Material

Non-magnetic / diamagnetic (all electrons paired up)

Magnetic (unpaired valence electrons)

Different types of magnetic ordering (illustrated in 1D)

1D atomic chain:

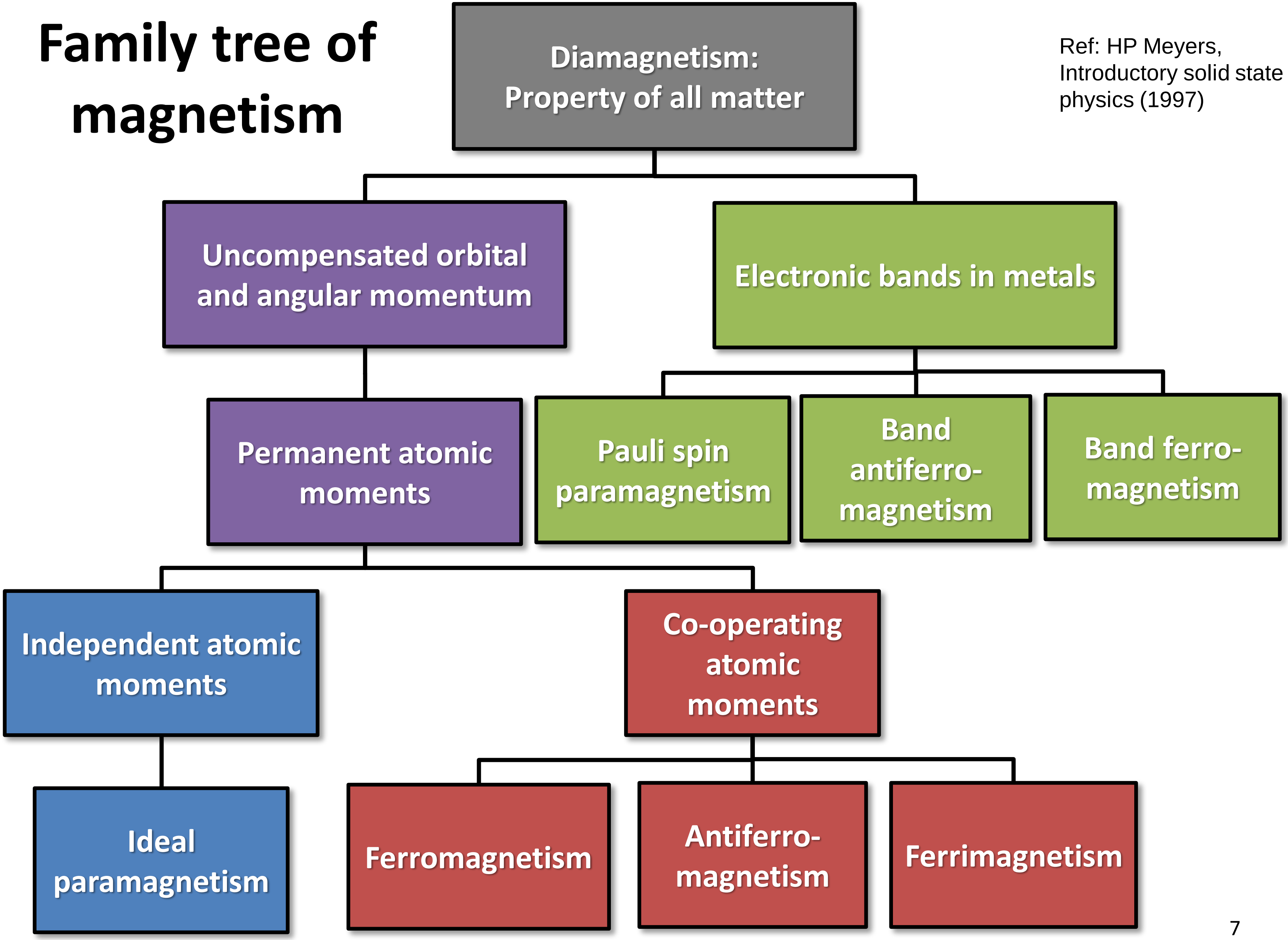
Spins on atoms:

Ref: West p. 445-446

Figure: AJK

Family tree of magnetism

Ref: HP Meyers, Introductory solid state physics (1997)



- Diamagnetism: Property of all matter
  - Uncompensated orbital and angular momentum
    - Permanent atomic moments
      - Independent atomic moments
        - Ideal paramagnetism
      - Co-operating atomic moments
        - Ferromagnetism
        - Antiferro-magnetism
        - Ferrimagnetism
  - Electronic bands in metals
    - Pauli spin paramagnetism
    - Band antiferro-magnetism
    - Band ferro-magnetism

Magnetic susceptibility

- When a substance is placed in a magnetic field *H* (units A m^{-1}), the magnetic induction *B* (units T, tesla) is

$$B = \mu H = \mu_0 H + \mu_0 M$$

Where μ is *permeability*, μ_0 is the permeability of free space ($4\pi * 10^{-7}$ H m^{-1}, H = henry) and *M* is the magnetic moment or **magnetization** of the sample

- Magnetization = **magnetic moment per unit volume or mass**
- $\mu_0 H$ is the induction generated by the field alone and $\mu_0 M$ is the additional induction contributed by the sample
- The magnetic susceptibility, χ, is defined as the ratio of magnetization *M* to field *H*:

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

- In other words: **high magnetization** *M* means **high susceptibility** χ
- Susceptibility χ is the most important measurable quantity for the characterization of magnetic properties
  - Provides a measure of the **response of a sample to an applied magnetic field**
  - Somewhat analogous to polarizability (response to an applied electric field)

Ref: West p. 446

Classification based on susceptibility χ

- The different kinds of magnetic behavior may be distinguished by the values of χ
  - In *diamagnetic* materials, χ is very small and slightly negative
  - In *paramagnetic* materials, χ is small and positive
  - In *ferromagnetic* materials, $\chi > 1$ and such materials are strongly attracted to a magnetic field.
  - In *antiferromagnetic* materials, χ is positive and comparable to paramagnetic substances (or somewhat smaller).

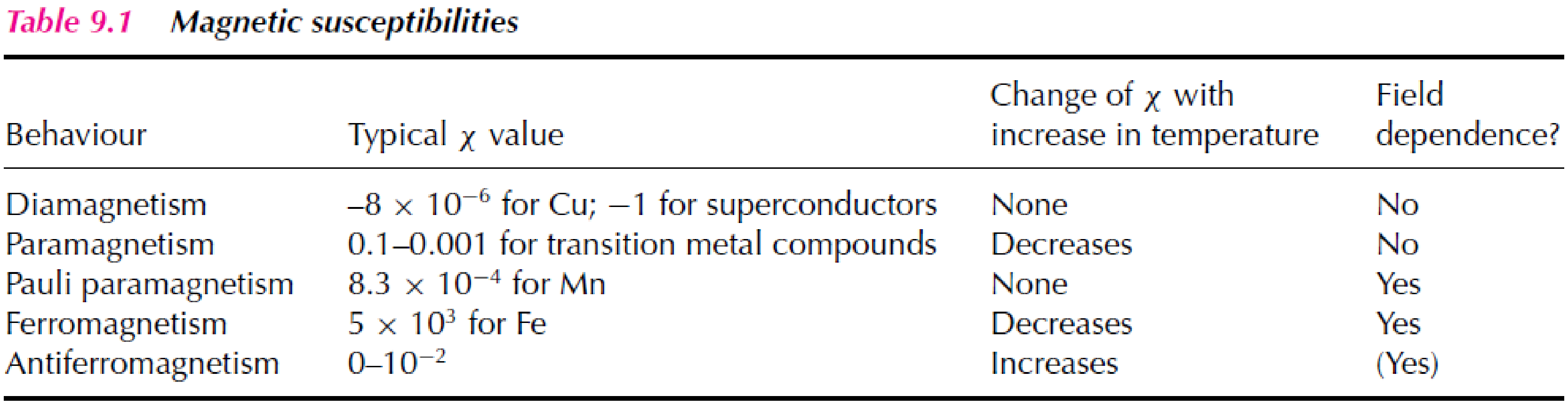


Table 9.1 ***Magnetic susceptibilities***

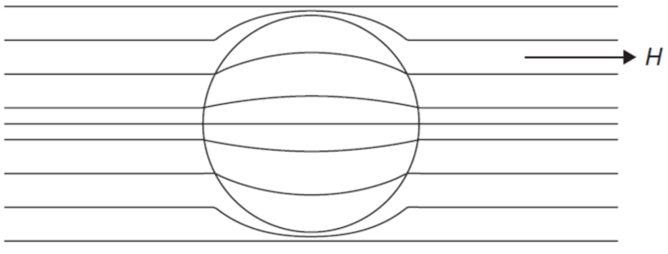
Behaviour	Typical χ value	Change of χ with increase in temperature	Field dependence?
Diamagnetism	-8×10^{-6} for Cu; -1 for superconductors	None	No
Paramagnetism	0.1–0.001 for transition metal compounds	Decreases	No
Pauli paramagnetism	8.3×10^{-4} for Mn	None	Yes
Ferromagnetism	5×10^{3} for Fe	Decreases	Yes
Antiferromagnetism	$0–10^{-2}$	Increases	(Yes)

Ref: West p. 447

Dia- and paramagnetism

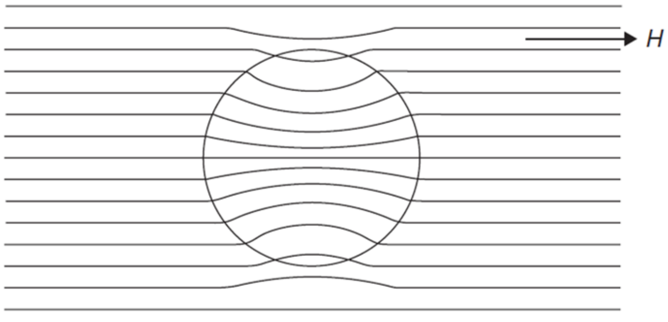
- Diamagnetism is a property of all materials
- When diamagnetism dominates, there is a slight repulsion by a magnetic field
  - Diamagnetism is associated with orbital motion of electrons in atoms.
  - This orbital motion generates a small electric field
  - In the presence of an external field, the orbital motion is modified slightly to give a magnetic moment that opposes the applied field leading to a slight repulsion effect which is explained by Lenz’s law of electromagnetism.
  - Superconductors represent a special, extreme type of diamagnetism since they repel magnetic fields completely, leading in magnetic levitation
- Paramagnetic materials are attracted by a magnetic field

Diamagnetic



(a)

Paramagnetic



(b)

Temperature dependence of magnetism

- Ordered magnetic structures lose their ordered structures above a certain temperature
  - ***Curie temperature***, T_c for ferromagnets and ferrimagnets
  - ***Néel temperature***, T_N for antiferromagnets
- The spins become disordered and the materials become paramagnetic

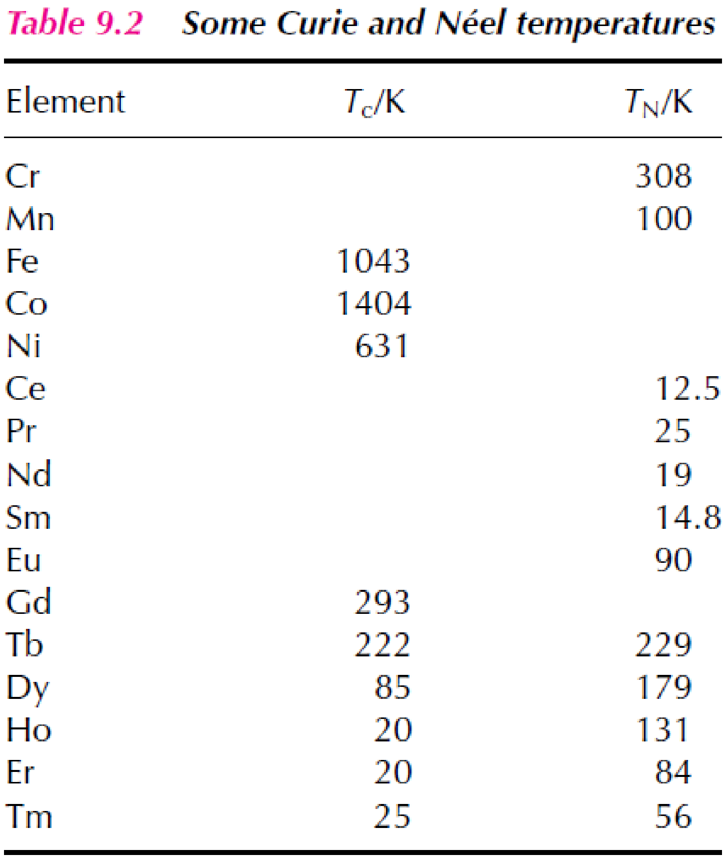


Table 9.2 Some Curie and Néel temperatures

Element	T_c/K	T_N/K
Cr		308
Mn		100
Fe	1043	
Co	1404	
Ni	631	
Ce		12.5
Pr		25
Nd		19
Sm		14.8
Eu		90
Gd	293	
Tb	222	229
Dy	85	179
Ho	20	131
Er	20	84
Tm	25	56

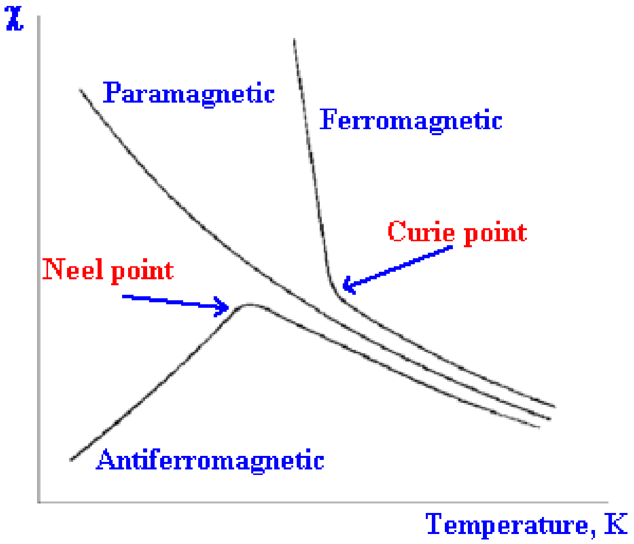
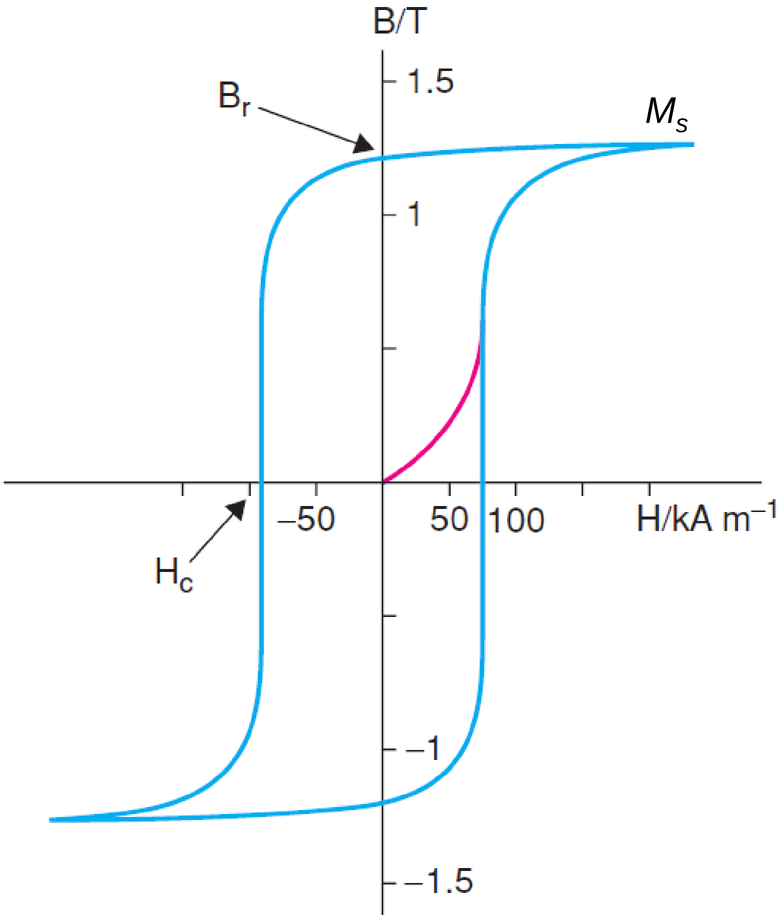


Figure: Robert John Lancashire

Ferromagnetism

Ref: West p. 453

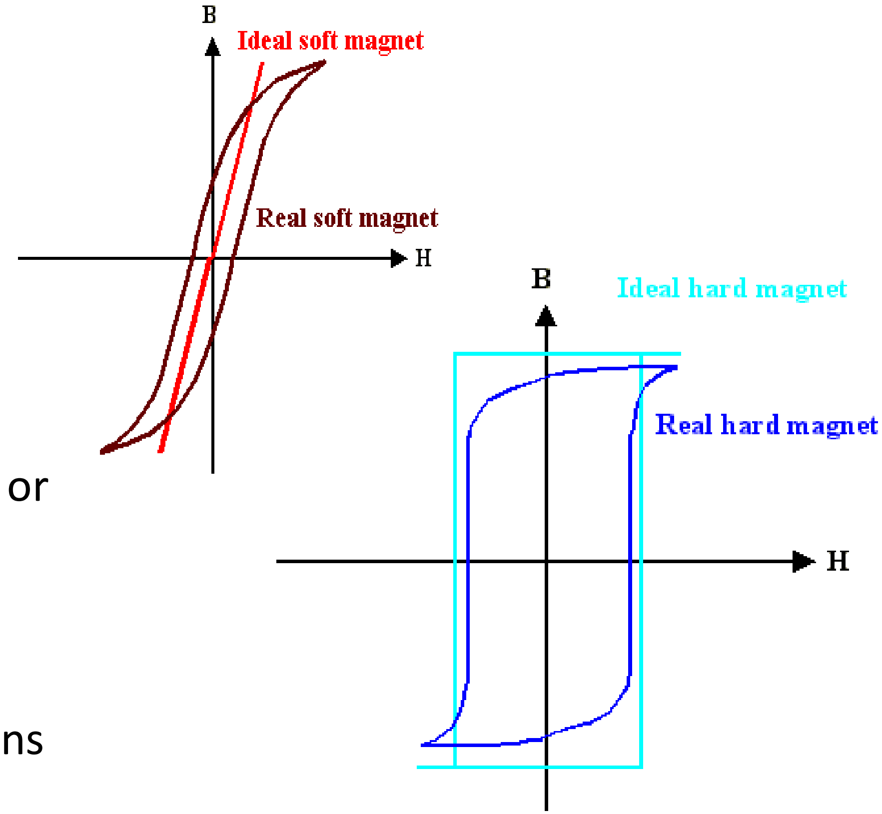
- The response of ferromagnetic materials to an applied magnetic field, H, is similar to that of ferroelectrics in an applied electric field.
- A ***hysteresis loop*** occurs in the plot of magnetisation, M, or induction, B, against H
- During magnetisation and demagnetisation in an alternating magnetic field, energy is dissipated, usually as **heat**.
- During one complete cycle, this amount of energy, the ***hysteresis loss*** (BH product) is proportional to the area inside the hysteresis loop.
- The ***remanence***, B_r or M_r, is the residual magnetization at zero applied field
- The ***saturation magnetisation***, M_s, is the maximum magnetisation achievable with an applied field.



Rectangular hysteresis loop showing **coercivity**, H_c and **remanence**, B_r (or M_r)

Soft and hard magnetic materials

- Materials with **low** coercivity, H_c are magnetically **soft**
  - Coercivity is the reverse field required to achieve demagnetization
  - Soft materials also have low permeability and a small-area hysteresis loop
  - Applicable for example in transformers
- Materials with **high** coercivity, H_c (and high B_r or M_r) are magnetically **hard**
  - Hard to demagnetize and can be used as permanent magnets
  - B_r (or M_r) is the magnetization that remains after the field has been switched off



Ref: West p. 454

Table 9.4 ***Some soft and hard magnetic materials***

Material	Coercivity/kA m^{-1}	Saturation magnetisation/kA m^{-1}	Curie temperature/°C
γ-Fe_2O_3	~25	~370	600
Co-coated γ-Fe_2O_3	~50	~370	
CrO_2	~60	~500	128
Fe powder	~120	~1700	

Data for some magnetic materials

Material	Coercivity (kA/m)
Nickel	0.056–23
Ferrite $Zn_xFeNi_{1-x}O_3$	1.2–16
Alnico	30–150
SmCo (*e.g.* $SmCo_5$)	500–2800
NdFeB (*e.g.* $Nd_2Fe_{14}B$)	900–2800

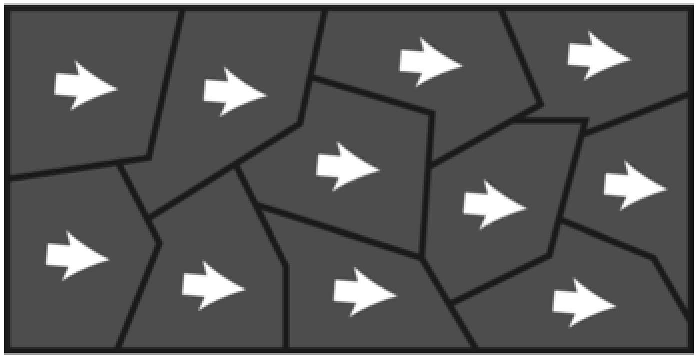
Alnico: ferromagnetic Co, Ni-based material is present as a large number of small crystalline regions embedded in an Al-based matrix.

These small regions are magnetized in the same direction and it is difficult to demagnetize them or change their magnetic orientation.

Data: Wikipedia

Ferromagnetic domains

Domains before magnetization

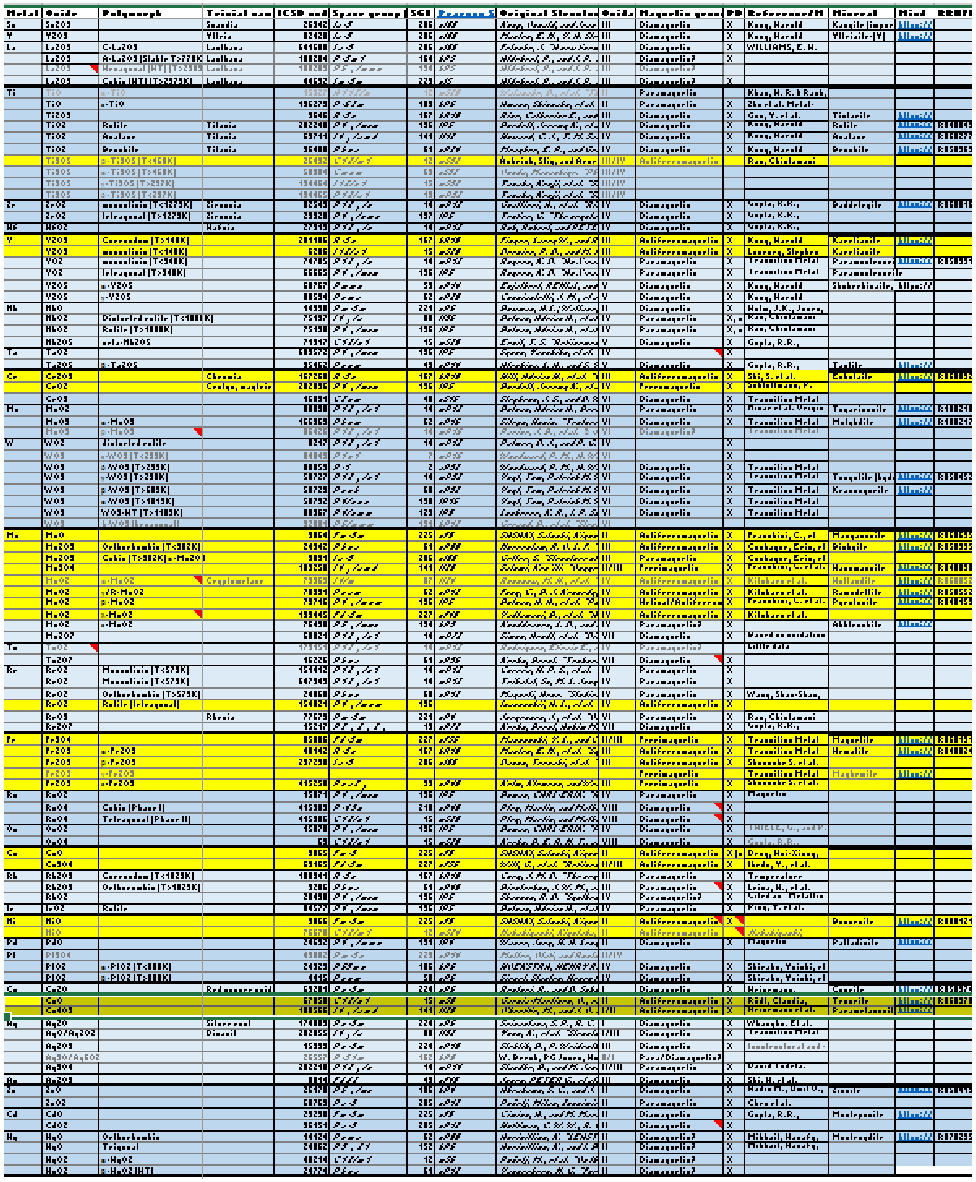


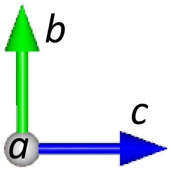
Domains after magnetization

- Ferromagnetic materials have a **domain** structure
  - Ferroelectrics also have a domain structure (polarization)
- Within each domain, the spins align parallel, but unless the material is in the *saturation condition*, different domains have different spin orientations.

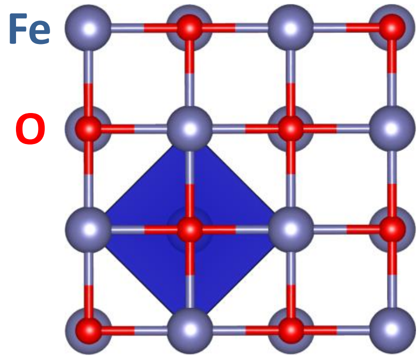
Magnetic binary oxides

- Primarily 3*d* metal oxides (narrow 3*d* band enables localized electrons)
- Figure shows an overview of a list of ~100 binary transition metal oxides (data collected by Inorganic Materials Modelling group at Aalto CHEM)
- About 1/4 of binary transition metal oxides have some magnetic order (yellow rows)
- Examples
  - MnO, FeO, CoO, NiO, CuO
  - CrO_2, Cr_2O_3, MnO_2, Fe_3O_4 (magnetite), γ-Fe_2O_3 (maghemite),
  - Ferrimagnetic iron oxides were important for the development of magnetic storage (tape storage)



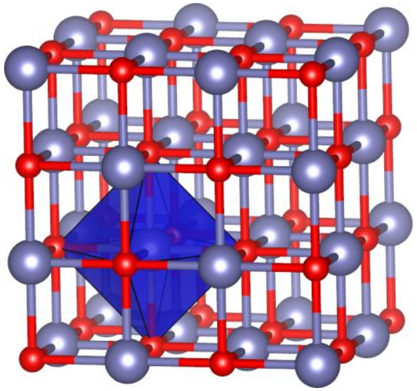


Example of magnetism in Fe$_x$O$_y$

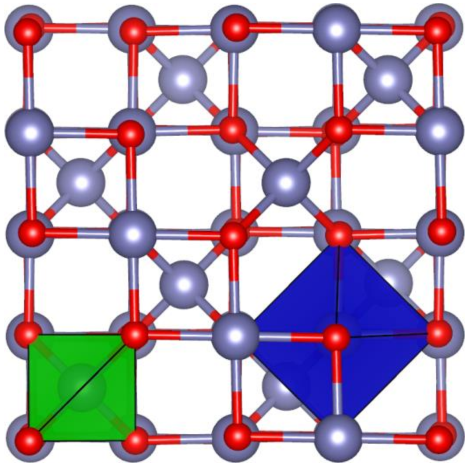


FeO (wüstite)
Iron(II) oxide (*Fm*-3*m*)

Paramagnetic



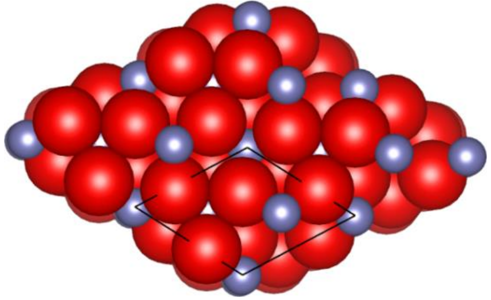
O_2 →



Fe$_3$O$_4$ (magnetite)
Iron(II,III) oxide (*Fd*-3*m*)

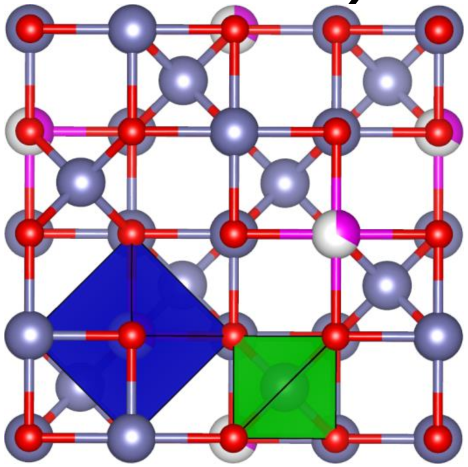
Ferrimagnetic

“Normal” iron(III) oxide α-Fe$_2$O$_3$ (hematite) has corundum structure, weak ferromagnet at room temp.:



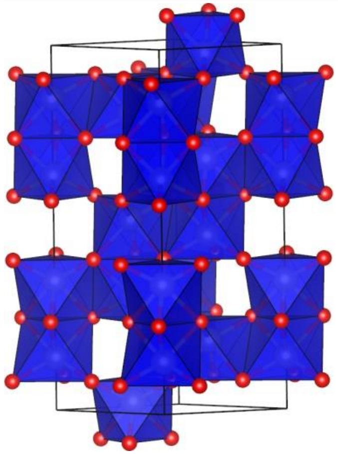
Inverse spinel

O_2 →



γ-Fe$_2$O$_3$ (maghemite)
Iron(III) oxide (*P*4$_1$32)

Ferrimagnetic



Figures: AJK

Inverse spinels

- AB_2O_4, with all A cations at octahedral sites
- Half of the B cations at octahedral sites
- Other half of the B cations at tetrahedral sites
- For example: $MgIn_2O_4$ (*Fd*-3*m*)
  - *fcc* anion lattice
  - Mg in octahedral interstitials (1/4 occupied)
  - In in octahedral interstitials (1/4 occupied)
  - In in tetrahedral interstitials (1/8 occupied)

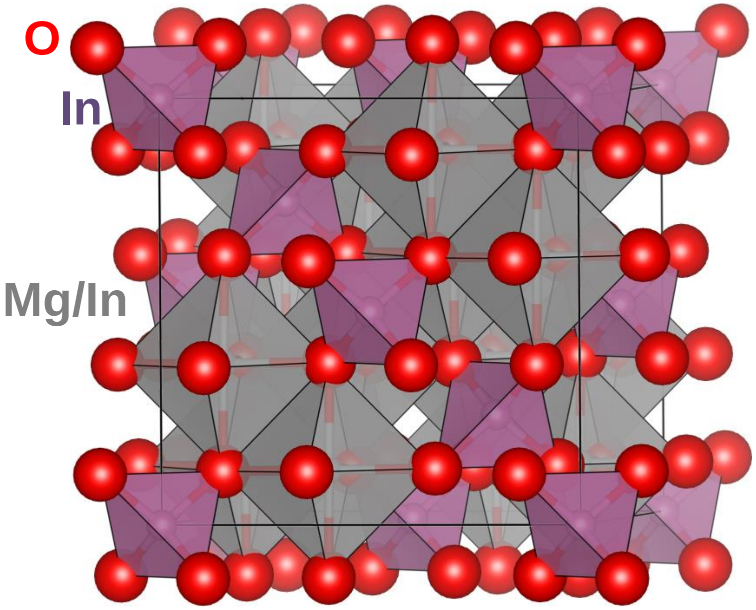
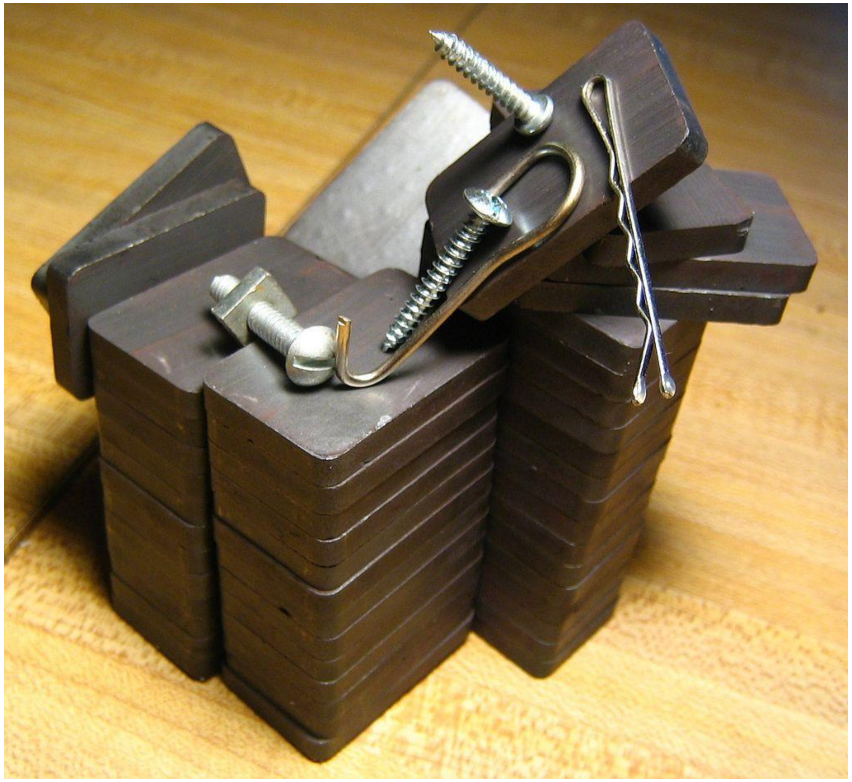


Figure: AJK

- Not all inverse spinels adopt such ideal distribution, often there is disorder beyond the ideal ordering
- With one metal: Fe_3O_4 with A = Fe(II) and B = Fe(III)
  - Fe(II) in octahedral interstitials (1/4 occupied)
  - Fe(III) in octahedral interstitials (1/4 occupied)
  - Fe(III) in tetrahedral interstitials (1/8 occupied)

Ferrites

- Many commercially important oxides are magnetic **spinels**, known as *ferrites*, with formula MFe_2O_4
  - M is a divalent ion such as Fe^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, Mg^{2+}
- Electrically nonconductive and ferrimagnetic
- Can be soft or hard
- Soft:
  - Manganese-zinc ferrite ($Mn_aZn_{1-a}Fe_2O_4$)
  - Nickel-zinc ferrite ($Ni_aZn_{1-a}Fe_2O_4$)
- Hard:
  - $CoFe_2O_4$
- Barium ferrite is one of the most important "ferrites", but the structure is different (see later)



Wikipedia

Ferrite magnets

Yttrium iron garnet (YIG)

- Garnets are a large family of complex oxides, some of which are important ferrimagnetic materials
- One of the most important is yttrium iron garnet (YIG), $Y_3Fe_5O_{12}$
- YIG and other rare earth garnets are ferrimagnetic with T_C in the range 548–578 K (μ = 5 BM, Bohr Magneton)
- Microwave, acoustic, optical, and magneto-optical applications, e.g. microwave YIG filters

Orbital moment plays some role (at least at T = 0 K)

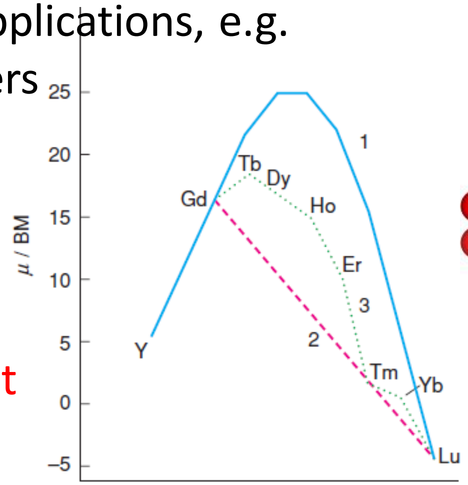
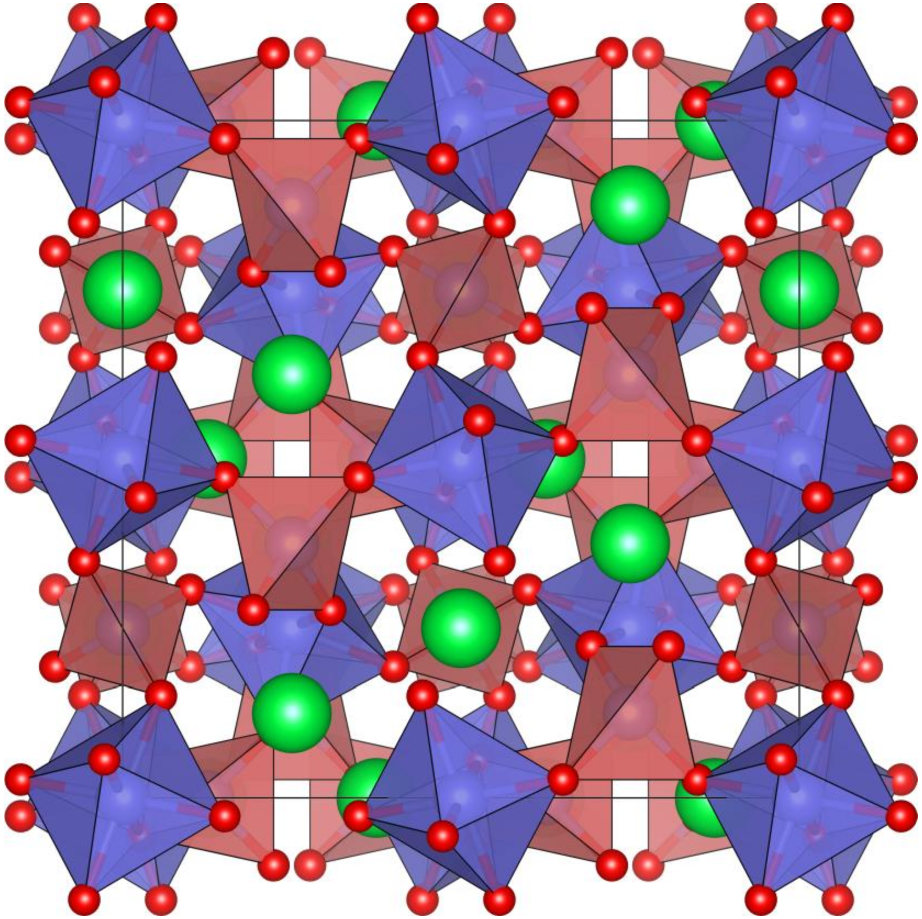


Figure 9.12 *Variation of magnetic moment at 0 K of garnets. Curve 1, calculated, spin + orbital formula; curve 2, calculated, spin only formula; curve 3, experimental. Data from Standley, Oxide Magnetic Materials, © 1972 Clarendon Press.*



Ia-3*d*

Figure: AJK

Barium ferrite

- Mineral $PbFe_{12}O_{19}$ is called *magnetoplumbite*. Its barium analogue, $BaFe_{12}O_{19}$, BaM, is an important component of **permanent magnets**
  - Stable, high corrosion resistance, high coercivity
- Magnetoplumbite has a five-layer repeat unit of *close-packed* layers. Four layers contain *cp* oxide ions. In the fifth layer, one of four oxide ions is replaced with large divalent ion (Pb^{2+}, Ba^{2+})
- The magnetic structure of BaM is complex as Fe^{3+} ions occupy five sets of crystallographic sites
- However, the net effect is that in the formula unit $BaFe^{12}O^{19}$, eight Fe^{3+} ions have spins oriented in one direction and the remaining four are antiparallel, giving a resultant of four Fe^{3+} ions with total μ = 20 BM.

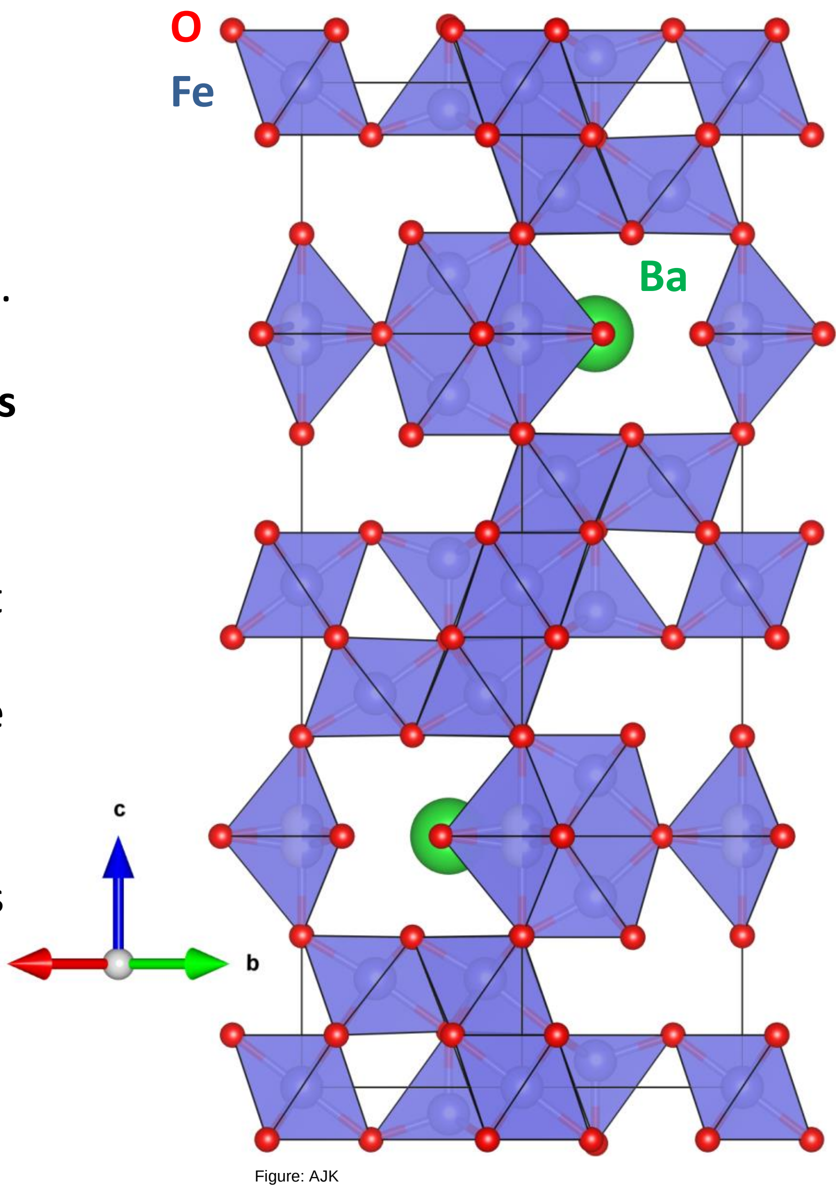


Figure: AJK

$P6_3/mmc$

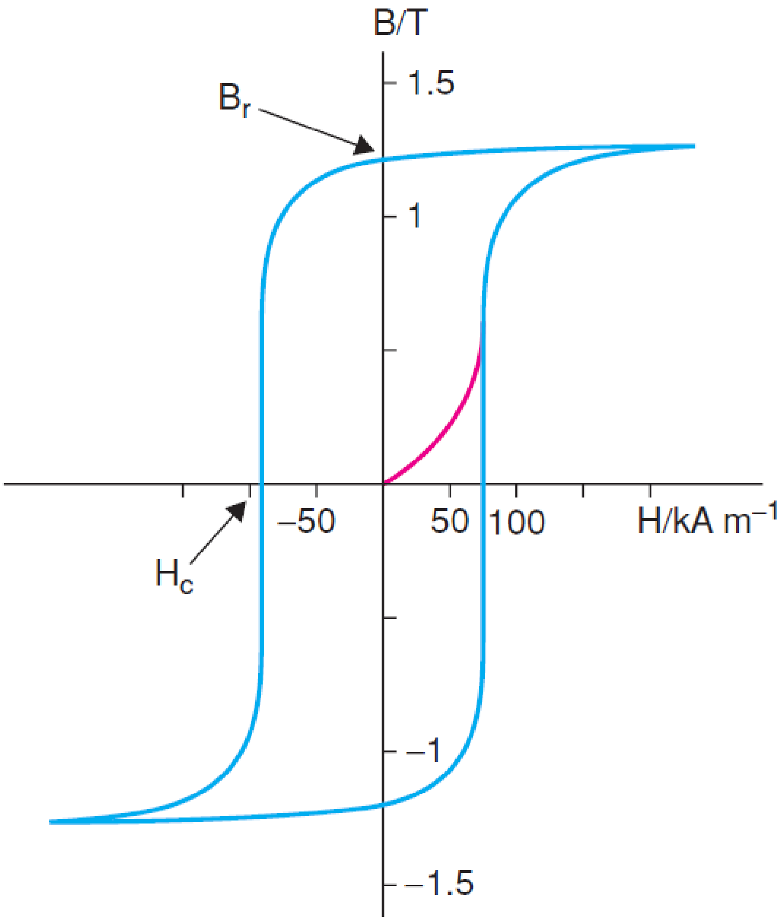
Ref: West p. 464

Multiferroics

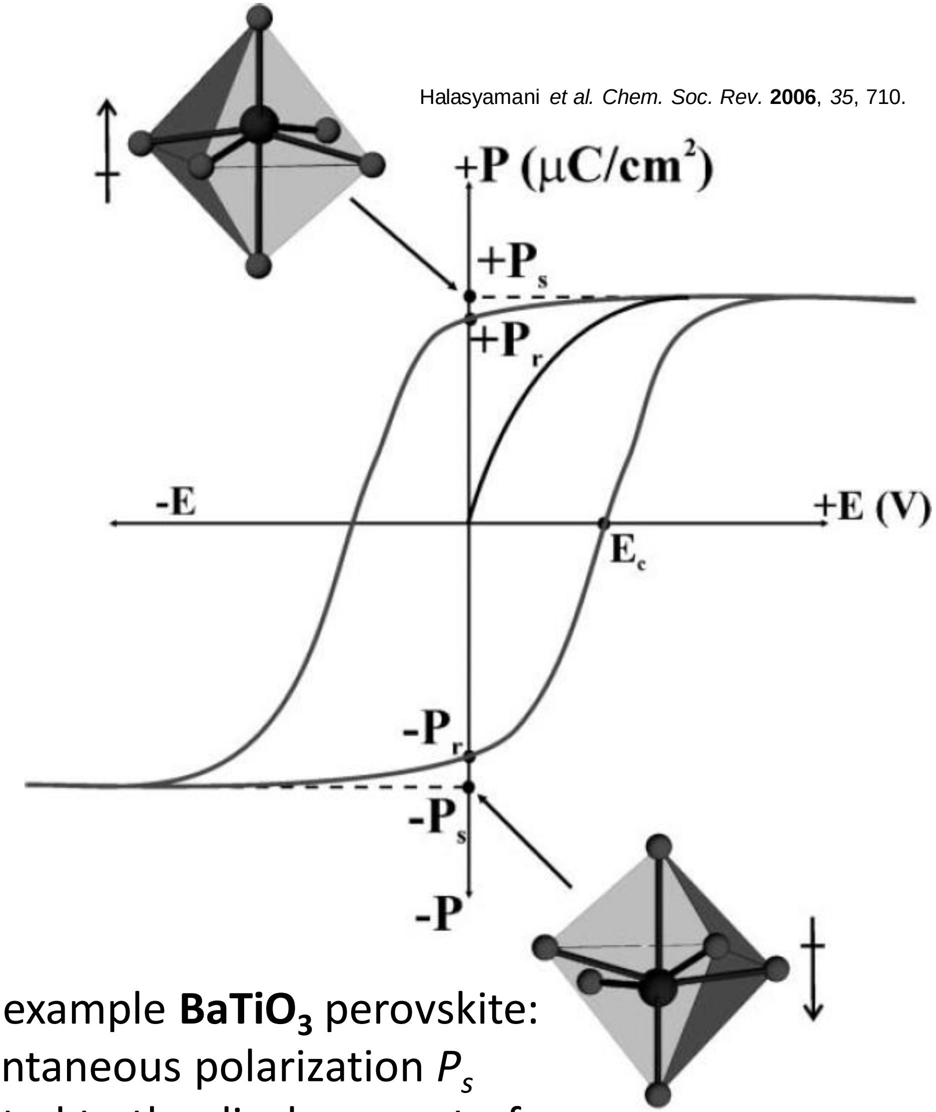
- Multiferroics are materials which exhibit more than one type of ferroic order (ferroelectricity, ferromagnetism, ferroelasticity)
- Of most interest are materials that couple ferromagnetic and ferroelectric order
- Multiferroics can be classified as follows:
    - **Type I** in which the ferroelectricity is largely independent of ferromagnetism
    - **Type II** in which the ferroelectricity can be stimulated by ferromagnetism
- Type II multiferroics give intrinsic magnetoelectric couplings and, therefore, are of more interest for practical applications in which magnetic properties can be switched in an applied electric field or vice versa.
- These compounds present opportunities for potential applications in **information storage**, the emerging field of **spintronics**, and **sensors**

Ref: West p. 469

Ferromagnetism and ferroelectricity



Rectangular hysteresis loop showing coercivity, H_c, and remanence, B_r.



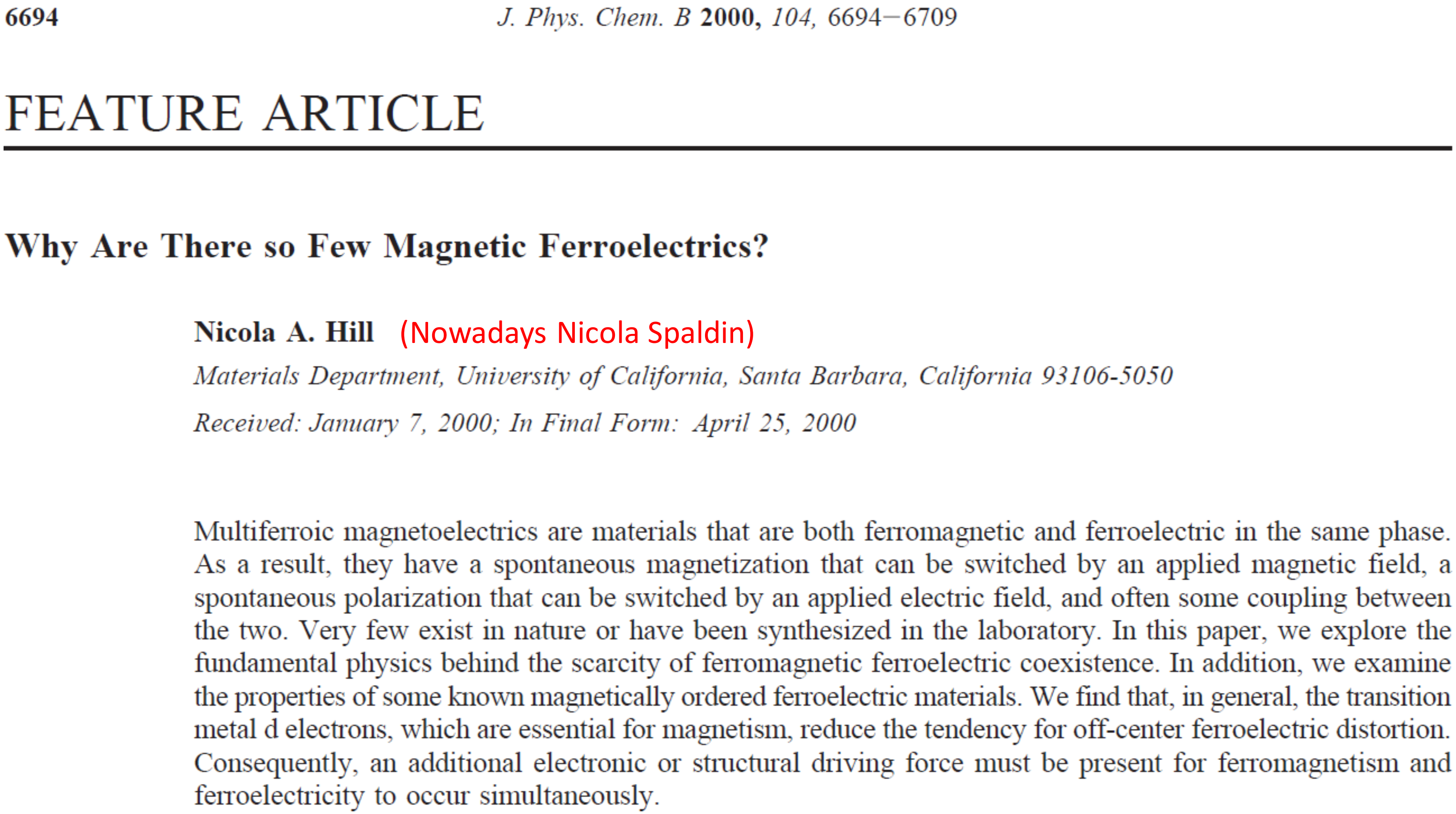
Halasyamani *et al. Chem. Soc. Rev.* **2006**, *35*, 710.

For example **$BaTiO_3$** perovskite: Spontaneous polarization P_s related to the displacement of the B atom (Ti)

Multiferroics are not easy to find

- Coupling ferromagnetism and ferroelectricity represents a significant challenge since the requirements for these two properties are fundamentally different.
- Ferroelectric materials should be electrical **insulators** and have non-centrosymmetric, **polar** crystal structures (e.g. polar cation-anion bonds)
  - Typically, ferroelectrics are transition metal-containing materials in which the transition metal ions have an empty *d* shell, such as Ti^{4+}, Nb^{5+} and Ta^{5+}.
- Most ferromagnetic materials are metallic conductors in which the cation–anion bonds do not exhibit a dipole moment
  - The magnetism requires **unpaired electrons** in *d* and *f* shells
  - Ferromagnetism is therefore favored in late 3*d* transition metal elements such as Mn, Fe, Co and Ni and their compounds.

Computational search for multiferroics



6694 *J. Phys. Chem. B* **2000,** *104,* 6694−6709

FEATURE ARTICLE

Why Are There so Few Magnetic Ferroelectrics?

Nicola A. Hill (Nowadays Nicola Spaldin)

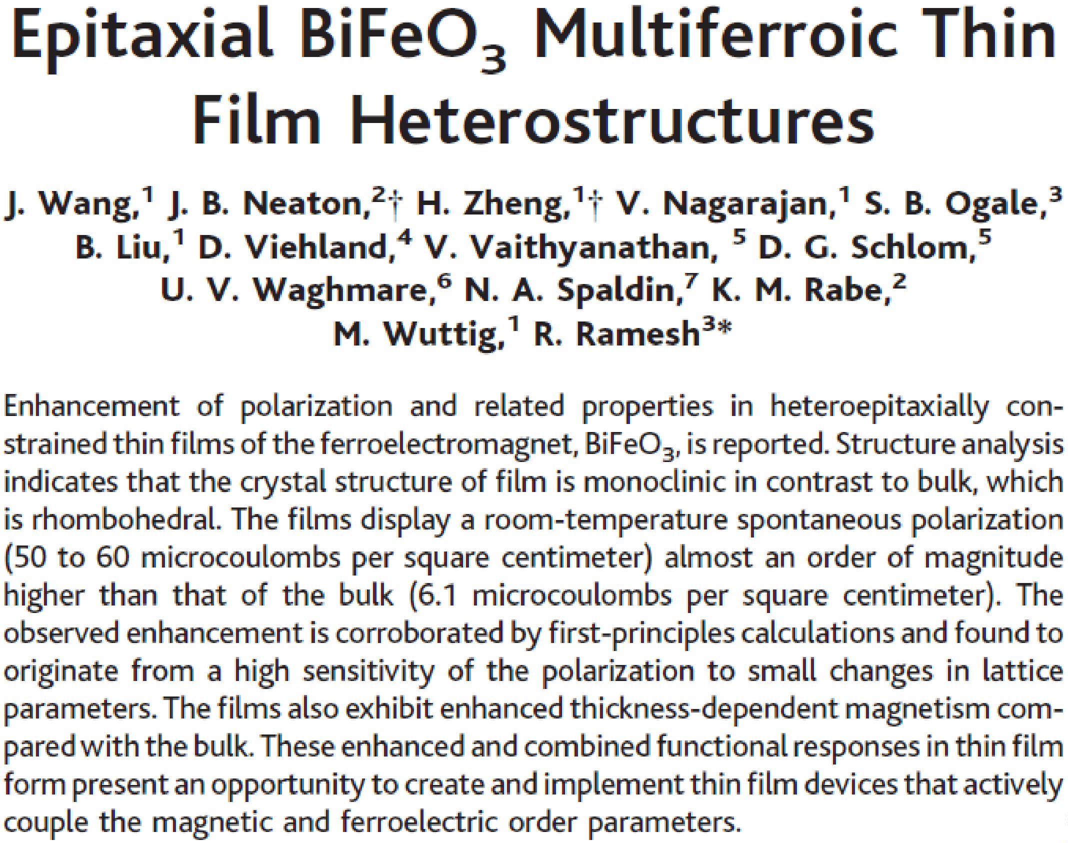
Materials Department, University of California, Santa Barbara, California 93106-5050

Received: January 7, 2000; In Final Form: April 25, 2000

Multiferroic magnetoelectrics are materials that are both ferromagnetic and ferroelectric in the same phase. As a result, they have a spontaneous magnetization that can be switched by an applied magnetic field, a spontaneous polarization that can be switched by an applied electric field, and often some coupling between the two. Very few exist in nature or have been synthesized in the laboratory. In this paper, we explore the fundamental physics behind the scarcity of ferromagnetic ferroelectric coexistence. In addition, we examine the properties of some known magnetically ordered ferroelectric materials. We find that, in general, the transition metal d electrons, which are essential for magnetism, reduce the tendency for off-center ferroelectric distortion. Consequently, an additional electronic or structural driving force must be present for ferromagnetism and ferroelectricity to occur simultaneously.

Multiferroic $BiFeO_3$

Science **2003**, *299*, 1719.



Epitaxial $BiFeO_3$ Multiferroic Thin Film Heterostructures

J. Wang,[1] J. B. Neaton,[2]† H. Zheng,[1]† V. Nagarajan,[1] S. B. Ogale,[3]
B. Liu,[1] D. Viehland,[4] V. Vaithyanathan, [5] D. G. Schlom,[5]
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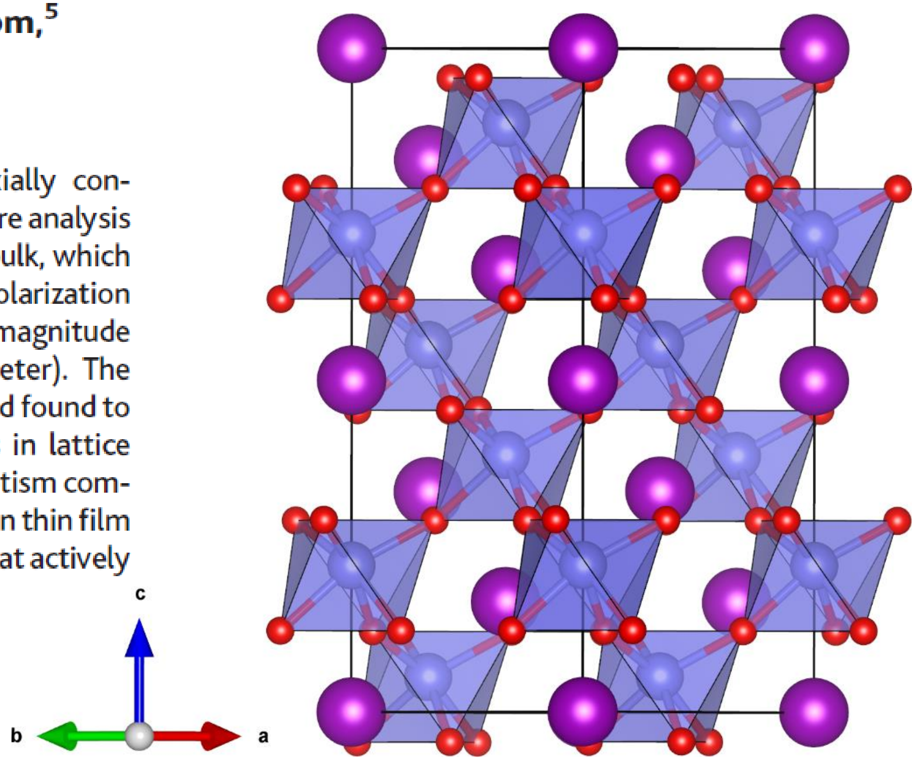
Enhancement of polarization and related properties in heteroepitaxially constrained thin films of the ferroelectromagnet, $BiFeO_3$, is reported. Structure analysis indicates that the crystal structure of film is monoclinic in contrast to bulk, which is rhombohedral. The films display a room-temperature spontaneous polarization (50 to 60 microcoulombs per square centimeter) almost an order of magnitude higher than that of the bulk (6.1 microcoulombs per square centimeter). The observed enhancement is corroborated by first-principles calculations and found to originate from a high sensitivity of the polarization to small changes in lattice parameters. The films also exhibit enhanced thickness-dependent magnetism compared with the bulk. These enhanced and combined functional responses in thin film form present an opportunity to create and implement thin film devices that actively couple the magnetic and ferroelectric order parameters.

$BiFeO_3$ has a distorted perovskite structure below T_c (space group $R3c$)



Bismuth ferrite $BiFeO_3$

- $BiFeO_3$ shows T_N of 643 K for **antiferromagnetic order** and T_c of 1100 K for **ferroelectric order**
- The ferroelectricity is associated with the Bi^{3+} cation and its $6s^2$ lone pair of electrons
  - Generates an asymmetric coordination environment for Bi, leading to a polar Bi–O bond
- The Fe^{3+} ions are responsible for the **antiferromagnetic order** through Fe–O–Fe exchange interactions.
  - The antiferromagnetism is complex since the spin interactions also incorporate a helimagnetic spiral spin structure.
- $BiFeO_3$ has perovskite structure, but in its ferroelectric polymorph below T_c, the structure undergoes a rhombohedral distortion in which there is spontaneous polarization parallel to the [111] direction of the high-temperature cubic unit cell
- Several other perovskite materials are also multiferroic, including $BiMnO_3$ and $PbVO_3$

Extra slides about spintronics and half-metals

(Maarit Karppinen)

SPINTRONICS

- **TRADITIONAL ELECTRONICS:** based on the charge of electrons
- **SPINTRONICS:** utilizes both the charge and the spin of electrons
- **FIRST-GENERATION SPINTRONIC DEVICES:**

  based on ferromagnetic multilayers (alloys of Fe, Co and Ni)
  with about 40 % spin-polarization

  - spin-valve (→ computer hard-disk read heads)
    - electron flow controlled by the direction of magnetization
    - based on giant magnetoresistance (GMR) effect
  - non-volatile magnetic random-access memory (MRAM)
    - based on magnetic tunnel junctions
    - supposed to replace dynamic random-access memory (DRAM)
- **NEW-GENERATION SPINTRONIC DEVICES:**

  based on materials with higher degree of spin-polarization

SPIN VALVE

- simplest magnetoresistance device
- two ferromagnetic (FM) layers separated by a metallic spacer
- one of the FM layers is pinned but the other is free to switch between parallel (low resistivity state) and antiparallel (high resistivity state) alignments