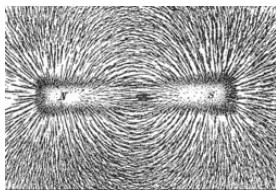


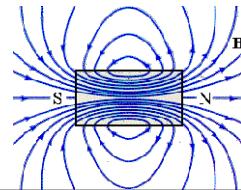
# **Chapter 8:**

## **Magnetic and Electrical Properties**





In solids, properties of individual atoms can interact *cooperatively* to produce effects not found in fluids.



### Magnetic Susceptibility:

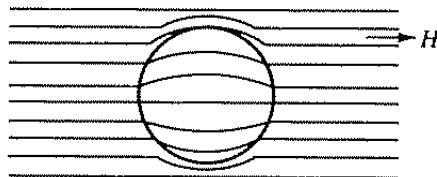
- magnetic field produces lines of force that penetrate the medium to which the field is applied.
- The density of the lines of force is known as the **magnetic flux density**.
- In a vacuum, the magnetic field and the magnetic flux density are related by the permeability of free space,  $\mu_0$ .  $B = \mu_0 H$
- If a magnetic material is placed in the field, it can increase or decrease the flux density.



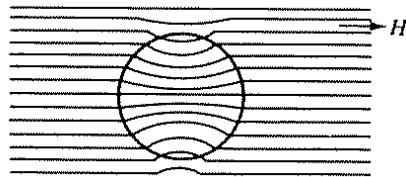
## Magnetic Descriptions of Atoms & Ions

**Diamagnetic** – Atoms or ions with a closed shell of electrons, all of the electrons are paired.

**Paramagnetic** - Atoms or ions with unpaired electrons, where the moment of an atom with unpaired electrons is given by the spin, **S**, and orbital angular, **L** and total momentum, **J**, quantum numbers.



**Diamagnetic materials:**  
reduce the density of the lines of force (flux density).



**Paramagnetic materials:**  
increase the density of the lines of force (flux density).

- The field of the sample in the applied field is known as its **magnetization, M**, where **H** is the **applied field**.

- The **magnetic flux density, B**, is given by:

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

$\mu_0$  is the permeability of free space,  $4\pi \times 10^{-7}$  H m<sup>-1</sup>  
where H is the symbol for henry

- $\mu_0H$  is the induction generated by the field alone
- $\mu_0M$  is the additional induction contributed by the sample
- Typically, the magnetization is discussed in terms of the **magnetic susceptibility,  $\chi$** :

$$\chi = M/H$$

### Magnetic Susceptibility vs. Temperature

Interplay of applied field and thermal randomization leads to temperature dependence described by the **Curie Law**,  $\chi = C/T$   
(where C is a constant known as the **Curie constant**, and T is in Kelvin)

**Paramagnetic** substances with localized, weakly interacting electrons obey the Curie-Weiss law.

$$\chi_m = C/(T+\theta)$$

where  $\chi_m$  is the molar magnetic susceptibility, C = Curie constant, and  $\theta$  = Weiss constant

A plot of  $1/\chi_m$  vs. temperature is known as a Curie-Weiss plot.  
Ideally, it should be linear if the C-W law is obeyed. From such a plot we can then extract the **Curie constant** from the inverse of the slope and the **Weiss constant** from the y-intercept.

$$1/\chi_m = (T+\theta)/C = (1/C)T + \theta/C$$

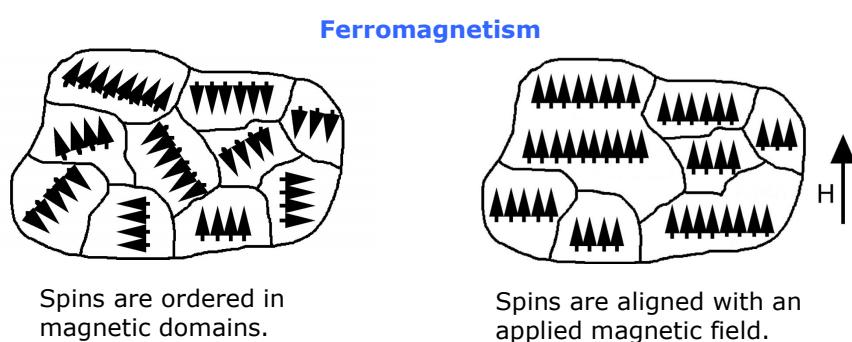
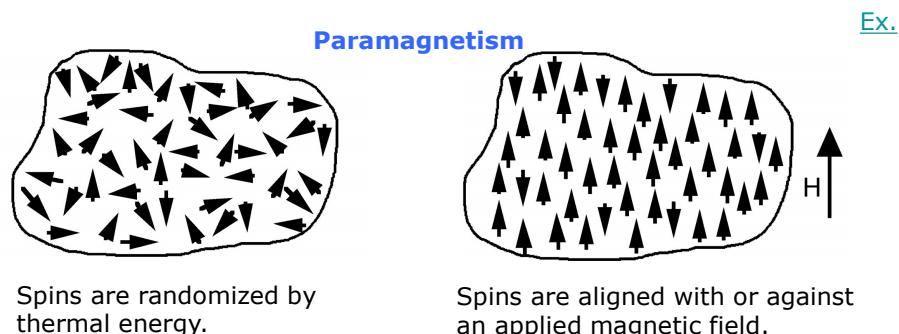
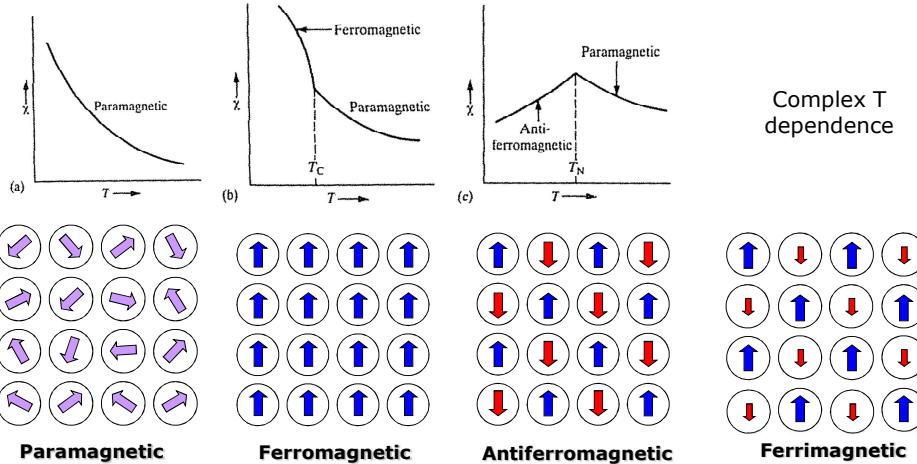
$$y = m \quad x + b$$

**Ferromagnetism** – magnetic moments of atoms align to produce a strong magnetic effect

- For ferromagnetism, the Curie Law becomes  $\chi = C/(T-T_c)$ , where  $T_c$  is the Curie Temperature.

**Antiferromagnetism** – magnetic moments of atoms align anti-parallel to produce a strong magnetic effect

- For antiferromagnetism, the Curie Law becomes  $\chi = C/(T+T_N)$ , where  $T_N$  is the Néel temperature.



### Characteristic Magnetic Properties

| Type                | Sign of $\chi$ | Typical $\chi$ (SI units) | Dependence of $\chi$ on H | Change of $\chi$ w/ inc. temp. | Origin  |
|---------------------|----------------|---------------------------|---------------------------|--------------------------------|---|
| Diamagnetism        | -              | $-(1-600) \times 10^{-5}$ | Independent               | None                           | Electron charge   |
| Paramagnetism       | +              | 0-0.1                     | Independent               | Dec.                           | Spin and orbital motion of electrons on atoms.                        |
| Ferromagnetism      | +              | $0.1-1 \times 10^{-7}$    | Dependent                 | Dec.                           | Cooperative interaction between magnetic moments of individual atoms. |
| Antiferromagnetism  | +              | 0-0.1                     | May be dependent          | Inc.                           |   |
| Pauli paramagnetism | +              | $1 \times 10^{-5}$        | Independent               | None                           | Spin and orbital motion of delocalized electrons.                     |

### Other Classes of Magnetism

- **Spin Glass** – A random orientation of frozen spin orientations (in a paramagnet the spin orientations are fluctuating.) Can occur when the concentrations of magnetic ions are dilute or the magnetic exchange interactions are frustrated.
- **Cluster Glass** – The spin orientations lock in with magnetic order in small clusters, but no order between the clusters (similar to a spin glass).
- **Metamagnet** – There is a field-induced magnetic transition from a state of low magnetization to one of relatively high magnetization. Typically the external field causes a transition from an antiferromagnetic state to a different type (such as a ferromagnet).
- **Superparamagnet** – A ferromagnet with a particle size that is too small to sustain the multidomain structure. Thus the particle behaves as one large paramagnetic ion.

## Paramagnetism in Metal Complexes

- The temperature dependence is the result of the thermal motion and by using the Curie Law the **Curie constant** (C) gives information about the **magnetic moment** ( $\mu$ ) of the ion.
- The dimensionless quantity  $\chi$  is the susceptibility per unit volume, so to obtain the size of the magnetic field for an individual complex:

$$\chi_m = \frac{N_A \mu_0}{3kT} \mu^2$$

where  $N_A$  is Avogadro's number,  $k$  is Boltzman's constant,  $\mu_0$  is the permeability of free space, and  $T$  is the temperature in Kelvin.

In SI units,  $\chi_m$  is in  $\text{m}^3/\text{mol}$  and the magnetic moment ( $\mu$ ) is  $\text{J/T}$ . Usually,  $\mu$  is reported in **Bohr magnetons** (B.M. or  $\mu_B$ )  $1 \mu_B = 9.274 \times 10^{-24} \text{ J/T}$

The **spin only magnetic moment** is given by:  $\mu_s = g\sqrt{S(S+1)}$

where  $S$  is the number of unpaired electrons (for each electron  $S = 1/2$ , the spin quantum number);  $g = 2.00023$  (the gyromagnetic ratio for a free electron); and  $\mu$  is in Bohr magnetons (units of  $\mu_B$   $9.2742 \times 10^{-24} \text{ J/T}$ ).

## Atomic Moments in Compounds

Unpaired electrons and paramagnetism are usually associated with the presence of either transition metal or lanthanide (actinide) ions. In many transition metal compounds the surrounding anions/ligands quench the orbital angular momentum and one needs only to take into account the **spin only** moment. Consider the following examples for *unpaired 3d electrons*:

| Ion              | e <sup>-</sup> Config. | S   | m <sub>s</sub> (m <sub>B</sub> ) | m <sub>s+L</sub> (m <sub>B</sub> ) | m <sub>obs</sub> (m <sub>B</sub> ) |
|------------------|------------------------|-----|----------------------------------|------------------------------------|------------------------------------|
| Ti <sup>3+</sup> | d <sup>1</sup>         | 1/2 | 1.73                             | 3.01                               | 1.7-1.8                            |
| V <sup>3+</sup>  | d <sup>2</sup>         | 1   | 2.83                             | 4.49                               | 2.8-3.1                            |
| Cr <sup>3+</sup> | d <sup>3</sup>         | 3/2 | 3.87                             | 5.21                               | 3.7-3.9                            |
| Fe <sup>3+</sup> | d <sup>5</sup> (HS)    | 5/2 | 5.92                             | 5.92                               | 5.7-6.0                            |
| Ni <sup>2+</sup> | d <sup>8</sup> (HS)    | 1   | 2.83                             | 4.49                               | 2.9-3.9                            |
| Cu <sup>2+</sup> | d <sup>9</sup>         | 1/2 | 1.73                             | 3.01                               | 1.9-2.1                            |

Deviations from the spin-only value can occur for the following reasons:

Orbital (L) Contribution

- Can arise for partially filled (not  $1/2$  full)  $t_{2g}$  orbitals

Spin-orbit Coupling

- Increases the moment for d<sup>6</sup>, d<sup>7</sup>, d<sup>8</sup>, d<sup>9</sup> ions
- Decreases the moment for d<sup>1</sup>, d<sup>2</sup>, d<sup>3</sup>, d<sup>4</sup> ions
- Increases for heavier metal ions.

## Magnetic Moment of Lanthanides

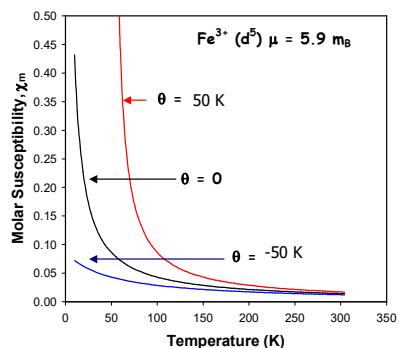
For lanthanides, magnetic moment depends on total electronic angular momentum  $J$ , where  $J = L + S$  where  $L$  is orbital angular momentum and  $S$  is the spin angular momentum.

$$\mu = g \sqrt{J(J+1)}$$

where  $g = 1 + \frac{J(J+1) + S(S+1) - L(L+1)}{2J(J+1)}$

| Rare Earth Elements |    |    |    |    |    |    |    |    |    |    |    |    |    |    |
|---------------------|----|----|----|----|----|----|----|----|----|----|----|----|----|----|
| La                  | Ce | Pr | Nd | Pm | Sm | Eu | Gd | Tb | Dy | Ho | Er | Tm | Yb | Lu |
| 57                  | 58 | 59 | 60 | 61 | 62 | 63 | 64 | 65 | 66 | 67 | 68 | 69 | 70 | 71 |
| Lanthanides         |    |    |    |    |    |    |    |    |    |    |    |    |    |    |
| H                   |    |    |    |    |    |    |    |    |    |    |    |    | He |    |
| Li                  | Be |    |    |    |    |    |    |    |    |    |    |    |    |    |
| Na                  | Mg |    |    |    |    |    |    |    |    |    |    |    |    |    |
| K                   | Ca |    |    |    | Sc | Ti | V  | Cr | Mn | Fe | Co | Ni | Cu | Zn |
| Rb                  | Sr |    |    |    | Y  | Zr | Nb | Mo | Tc | Ru | Rh | Pd | Ag | Cd |
| Cs                  | Ba |    |    |    |    |    |    |    |    |    |    | In | Sn | Sb |
| Fr                  | Ra |    |    |    |    |    |    |    |    |    |    |    | Te | I  |
|                     | An |    |    |    |    |    |    |    |    |    |    |    | Xe |    |
|                     | Lr |    |    |    |    |    |    |    |    |    |    |    |    |    |

## Curie-Weiss Plot



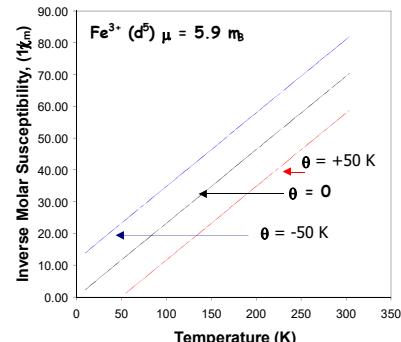
The Curie constant is equal to the inverse of the slope. It gives us the size of the moment per formula unit.

$$C = (N_A/3k)\mu^2$$

$$\mu = (3kC/N_A)^{1/2} = 2.84 C^{1/2}$$

$N_A$  = Avogadro's Number

$k$  = Boltzmann's constant



The Weiss constant is equal to the x-intercept. It's sign tells us about the short range magnetic interactions.

$\theta = 0 \rightarrow \text{Paramagnetic}$

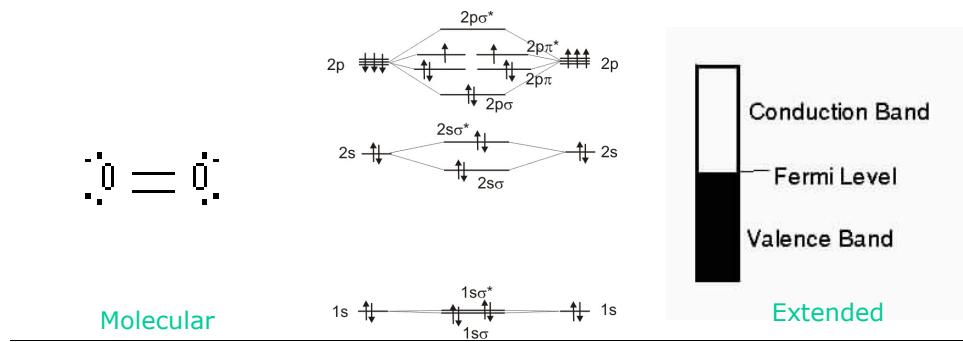
*Spins independent of each other*

$\theta > 0 \rightarrow \text{Ferromagnetic}$

*Spins tending to align parallel*

$\theta < 0 \rightarrow \text{Antiferromagnetic}$

*Spins tending to align antiparallel*



### Ferromagnetic metals

- Filling the **conduction band**, the electrons are implicitly placed into energy levels with **paired spins**, but even in the ground state of simple molecules it can be more favorable to have electrons in different orbitals with **parallel spins**, rather than the same orbital with paired spins. (e.g. molecular  $O_2$ )
- Occurs when **degenerate** or nearly degenerate levels exist.
- In a band, many degenerate levels exist as well as many levels close in energy to the highest occupied level – but unless the DOS is very high near the **Fermi Level**, a large number of electrons would have to be promoted to achieve a measurable number of unpaired spins.

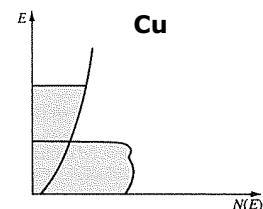
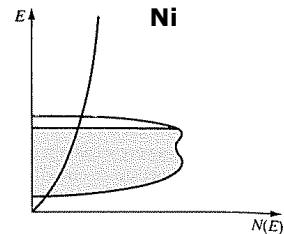
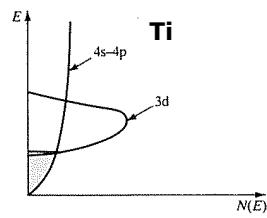
- In the **wide bands** of simple metals, the DOS is comparatively low, therefore in the absence of a magnetic field few electrons are promoted.

- When a magnetic field is applied, the electrons acquire extra energy term due to **interaction** of their spins with the field.

If the spins align **parallel** to the field, its magnetic energy is negative (electrons are at lower energy than they were in the absence of a field)

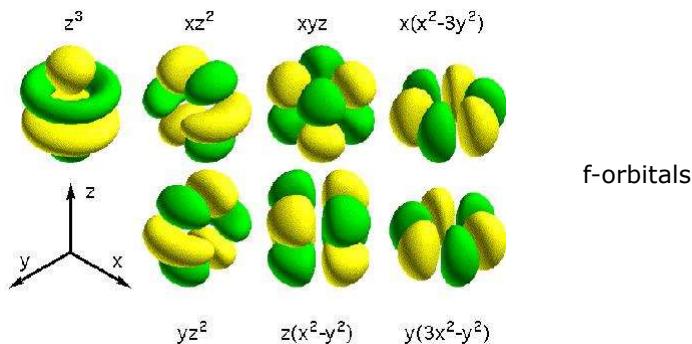
- If the spins align **anti-parallel** to the field, it may go to a higher energy state and change spin, as long as the promotion energy is not more than the gain in magnetic energy.

- This measurable imbalance of electron spins aligned with and against the field is weak effect known as **Pauli paramagnetism**.



## Lanthanide Alloys

Often contain a ferromagnetic element with a lanthanide ( $\text{SmCo}_5$ ,  $\text{NdFe}_{14}\text{B}$ ) and are among the most powerful magnets known.



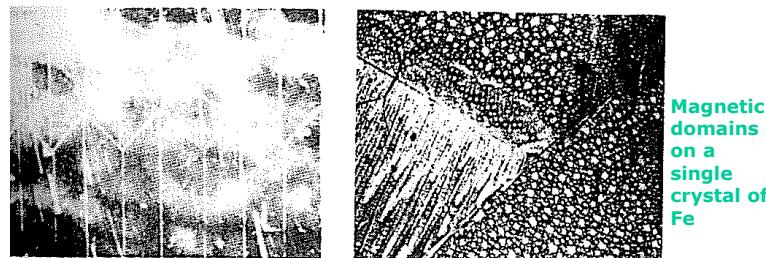
Usefulness of a particular ferromagnetic substance depends on factors such as: size of magnetization produced, how easily it can be magnetized and demagnetized, how readily it responds to an applied field.

## Ferromagnetic domains

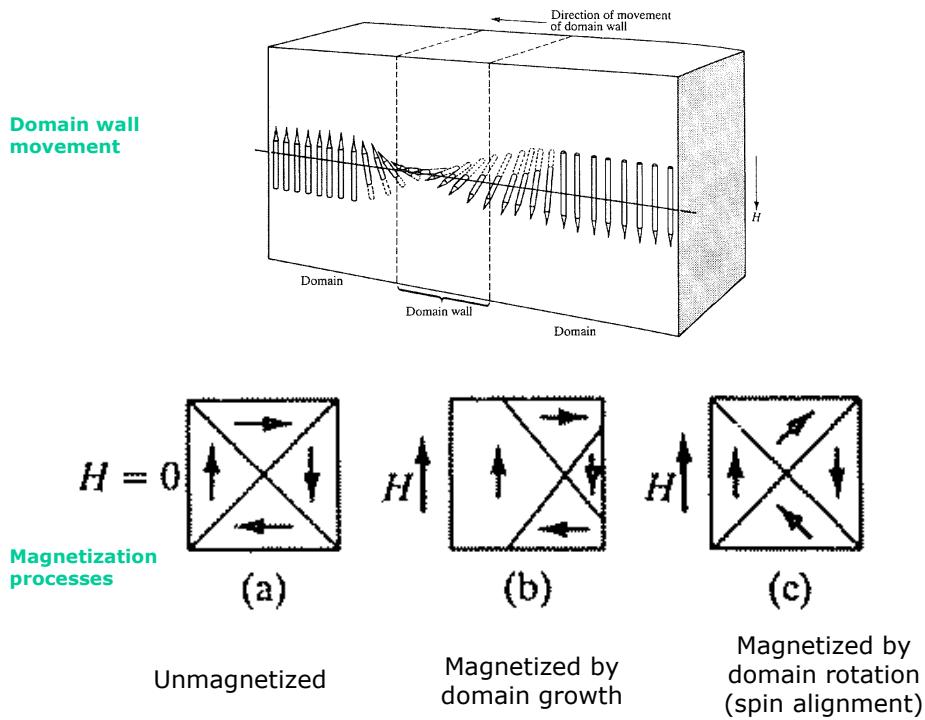
A **magnetic domain** describes a region which has uniform magnetization.

- Moments of the atoms are aligned within the domain, but different domains are aligned randomly w/r respect to each other.
- Spins tend to align parallel because of short-range **exchange interactions**, stemming from electron-electron repulsion.
- Longer-range **magnetic dipole interactions** also occur, tending to align the spins anti-parallel.
- Building a domain with few spins, short-range interactions dominate, but as more spins are added an individual spin will be exposed to a greater magnetic dipole interaction.
- Eventually, magnetic dipole interactions overcome exchange interaction.
- Regions separating magnetic domains are called domain walls where the magnetization rotates coherently from the direction in one domain to that in the next domain.

Domain patterns of Fe w/3.8%Si. White lines indicate boundaries between the domains.



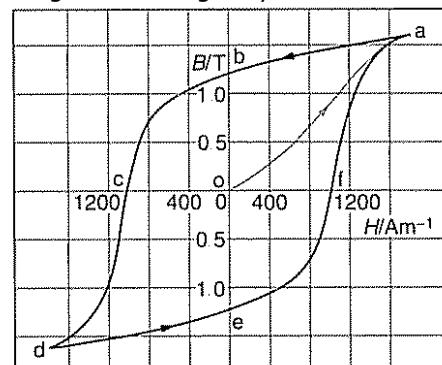
Magnetic domains on a single crystal of Fe



## Hysteresis Curves

Magnetic behavior of different ferromagnetic substances is demonstrated by **hysteresis curves**, a plot of **magnetic flux density** ( $B$ ) against **applied magnetic field** ( $H$ ).

- starting with a nonmagnetic sample (domains randomly aligned)  $B$  and  $H$  are zero, but as the field is increased the flux density also increases.
- Upon reaching the maximum value of magnetization all the spins are aligned in the sample, but when the applied field is reduced the flux density does not follow the initial curve, because of the difficulty of reversing processes where domains have grown through crystal imperfections.
- A sufficiently large magnetic field in the reverse direction must be applied before the magnetization process can be reversed.
- The magnetization where  $H$  is zero, but  $B$  is not zero is known as the **remnant magnetization**.
- The field that needs to be applied in the reverse direction to reduce magnetization to zero is the **coercive force**.



## Soft and hard magnetic materials

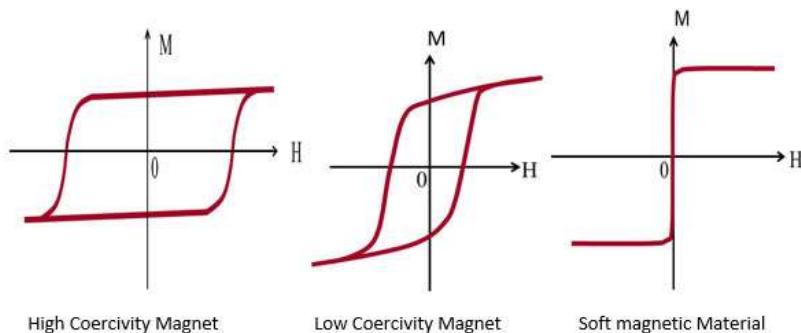
| Material                                  | Coercivity (kA/m) | Saturation magnetization (kA/m) | Curie Temperature (°C) |
|---|-------------------|---------------------------------|------------------------|
| $\gamma\text{-Fe}_2\text{O}_3$            | ~25               | ~370                            | 600                    |
| Co- coated $\gamma\text{-Fe}_2\text{O}_3$ | ~50               | ~370                            |                        |
| $\text{CrO}_2$                            | ~60               | ~500                            | 128                    |
| Fe powder                                 | ~120              | ~1700                           |                        |

Materials that are *magnetically soft* are those of low coercivity,  $H_c$

- Soft materials have low permeability and a hysteresis loop that is 'narrow at the waist' and of small area.

Materials that are *magnetically hard* are those of high coercivity,  $H_c$ , and a high  $M_r$  ( $B_r$ )

- Hard materials are not easily demagnetized, find use as permanent magnets.



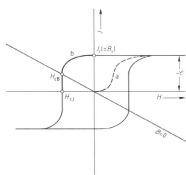
Typical hysteresis loops for (l to r) high coercivity permanent magnets, lower coercivity permanent magnets, and soft magnetic materials.

## Permanent Magnets

Solids used as permanent magnets need (1) a large coercive force, otherwise they would be easily demagnetized and (2) a large remnant magnetization and 'fat' hysteresis curve.

Alloys of Fe, Co, Ni form small crystals and include nonmagnetic areas, so that domain growth and shrinkage are difficult.

Magnets for electronic watches are made from samarium/cobalt alloys ( $\text{SmCo}_5$ ).



### KINETIC® ELECTRICALLY CHARGED EVERY TIME YOU MOVE YOUR BODY.

#### GENERATING UNIT

Transforms the movement of the wearer into electricity.



① OSCILLATING WEIGHT  
The everyday movement of your wrist rotates the oscillating weight.

② GEAR TRAIN  
This amplifies the rotational movement of the oscillating weight 100 fold and transfers it to the rotor.

③ ROTOR  
This is where the magic begins. Every movement of the oscillating weight is turned into magnetic charge. It can spin up to 100,000 RPM faster than a Formula One race car.

④ GENERATING COIL BLOCK  
Extremely high density coil transforms the magnetic charge into the electricity to power the watch.

#### CHARGING UNIT

Stores and supplies the generated electricity.



⑤ KINETIC ENERGY STORAGE UNIT  
The electrical energy is stored in this tiny technological marvel.

⑥ CIRCUIT BLOCK  
With the process, this electronic circuit controls voltage, amps and by quartz oscillator, produces a precise watch signal.

⑦ QUARTZ CRYSTAL OSCILLATOR  
When electricity is passed to it, it oscillates at a highly stable rate of 32,768 times a second.

#### STEP MOTOR UNIT

Converts electric signals into rotational motion to move the hands.

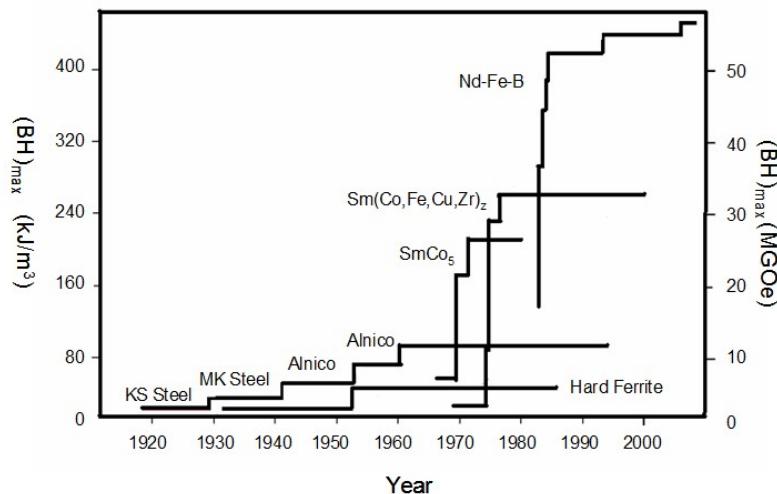


⑧ STEP MOTOR  
Finally, the electrical signal is converted into a precise rotational motion which is transmitted through the hands through the gear train.

⑨ GEAR TRAIN

⑩ HANDS

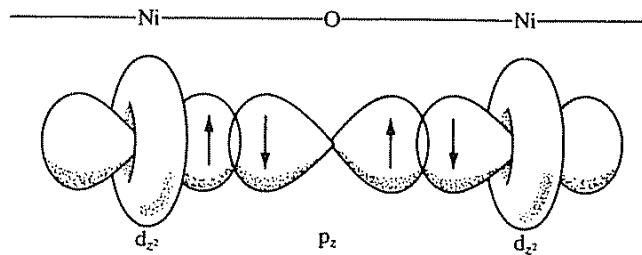
## Maximum Energy Product of Permanent Magnets



## Antiferromagnetism in Metal Oxides

Recall that VO and TiO have diffuse 3d orbitals and form delocalized bands (metallic conductors and Pauli paramagnetic)

- MnO, FeO, CoO, and NiO have **localized** 3d electrons and are *paramagnetic* at high temperatures, but on cooling become *antiferromagnetic* ( $T_N = 122\text{ K}$ ,  $198\text{K}$ ,  $293\text{K}$ ,  $523\text{ K}$  respectively)
- Antiferromagnetic materials show a drop in magnetic susceptibility at the onset of cooperative behavior, due to the canceling of magnetic moments.
- Magnetic interaction arises through the closed-shell oxide ions, a mechanism known as **superexchange**, where the pair of electrons in O must have opposite spin, thus adjacent Ni have opposite spins.

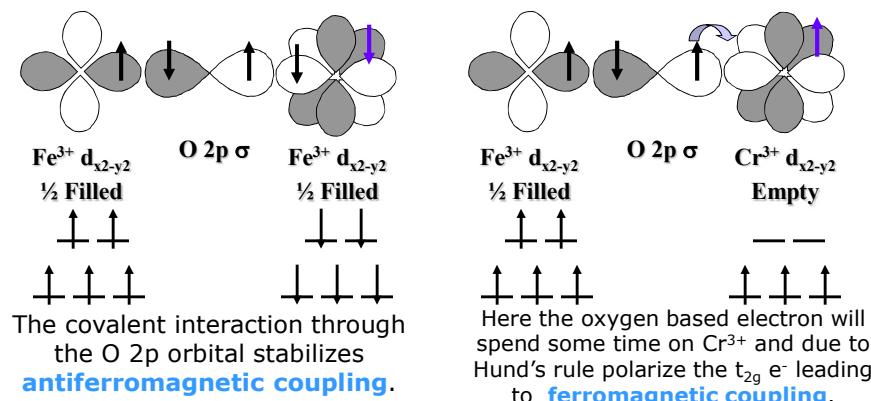


## Superexchange

In order for a material to be magnetically ordered, the spins on one atom must couple with the spins on neighboring atoms.

The most common mechanism for this coupling (particularly in insulators) is through the semicovalent superexchange interaction.

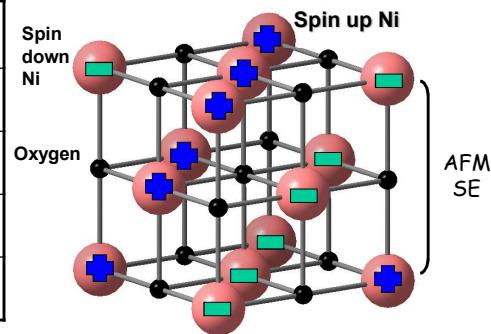
The spin information is transferred through covalent interactions with the intervening ligand (oxide ion).



## Magnetic Ordering in Rock Salt Oxides

In the rock salt structure the primary mechanism for magnetic exchange is the linear M-O-M superexchange interaction. In all of the compounds below the  $e_g$  orbitals are  $\frac{1}{2}$  filled, so the exchange interaction is AFM and overall magnetic structure is AFM as shown below.

|     |                | M-O Distance | T <sub>N</sub> (K) | Moment ( $\mu_B$ ) |
|-----|----------------|--------------|--------------------|--------------------|
| MnO | d <sup>5</sup> | 2.22 Å       | 122                | ~5                 |
| FeO | d <sup>6</sup> | 2.15 Å       | 198                | 3.3                |
| CoO | d <sup>7</sup> | 2.13 Å       | 293                | 3.5                |
| NiO | d <sup>8</sup> | 2.09 Å       | 523                | 1.8                |

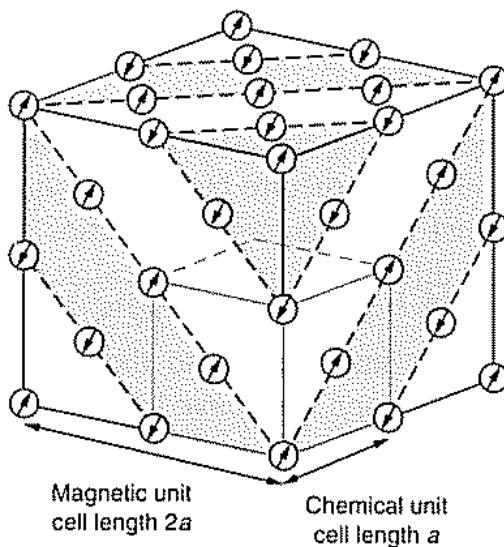


$$(\text{M-O distance} \downarrow) \rightarrow (\text{Covalency} \uparrow) \rightarrow (\text{Superexchange} \uparrow) \rightarrow (T_N \uparrow)$$

The moments given in this table were measured at low temperature using neutron diffraction. Under such circumstances the moment should nearly be equal to the number of unpaired electrons.

## Magnetic unit cell

Neutron diffraction, with a neutron beam that responds to nuclear positions *and* magnetic moments, is the primary experimental method used to determine the magnetic structure of a material.

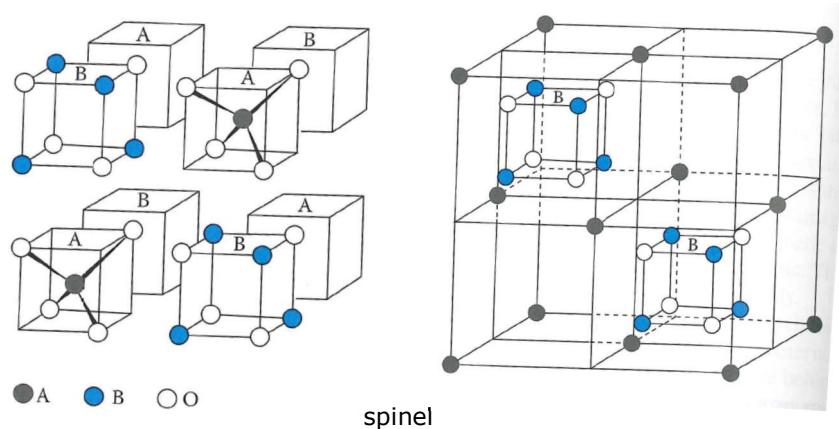


## Ferrimagnetism - Ferrites

Ferrites: the name given to a class of magnetic mixed oxides having an **inverse spinel** structure of  $AM_2O_4$ , where A is divalent ion and  $M^{3+}$  is a metal.

For an array of N atoms there are N octahedral holes and  $M^{3+}$  occupies half the octahedral sites, and  $A^{2+}$  occupies  $1/8^{\text{th}}$  of the  $2N$  tetrahedral sites.

*Inverse spinel structure* –  $A^{2+}$  occupies octahedral sites and  $M^{3+}$  cations are equally divided among the octahedral and tetrahedral sites.

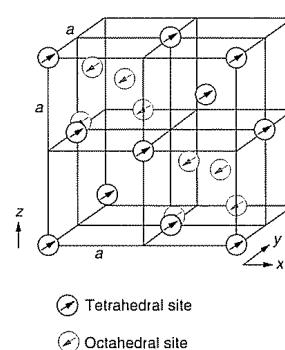
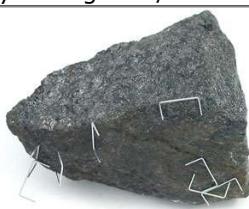


## Ferrimagnetism - Ferrites

Ions on the octahedral sites interact directly with each other and spins align parallel

- Ions on the octahedral sites interact with those on the tetrahedral site, but in this case interact through the oxide ions and the spins align antiparallel (like NiO).
- In  $AFe_2O_4$ ,  $Fe^{3+}$  on tetrahedral sites are aligned antiparallel to those on octahedral sites, so there is no net magnetization from these ions.
- The  $A^{2+}$ , if they have unpaired electrons, tend to align their spins with those of  $Fe^{3+}$  on adjacent sites (and with other  $A^{2+}$ ).
- This produces a net ferromagnetic interaction for ferrites in which  $A^{2+}$  has unpaired electrons.
- In magnetite ( $Fe_3O_4$ ), the interaction of ions on adjacent sites is particularly strong  $Fe^{2+}/Fe^{3+}$ .

Magnetite is the ancient lodestone used as an early compass.





## The Nobel Prize in Physics 2007

"for the discovery of Giant Magnetoresistance"



Photo: U. Montan

Albert Fert

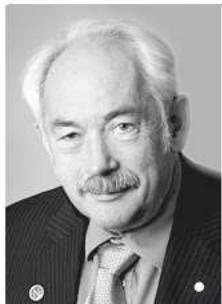
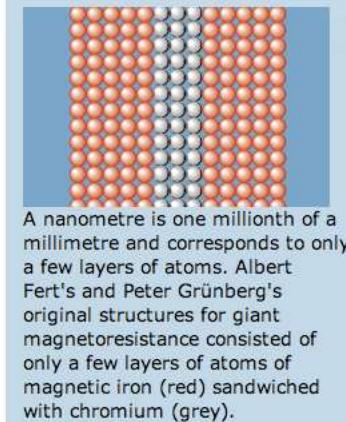


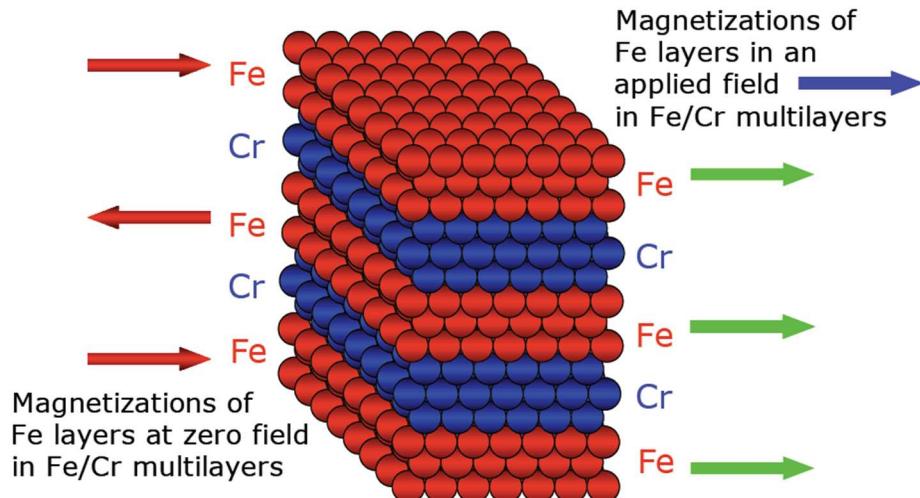
Photo: U. Montan

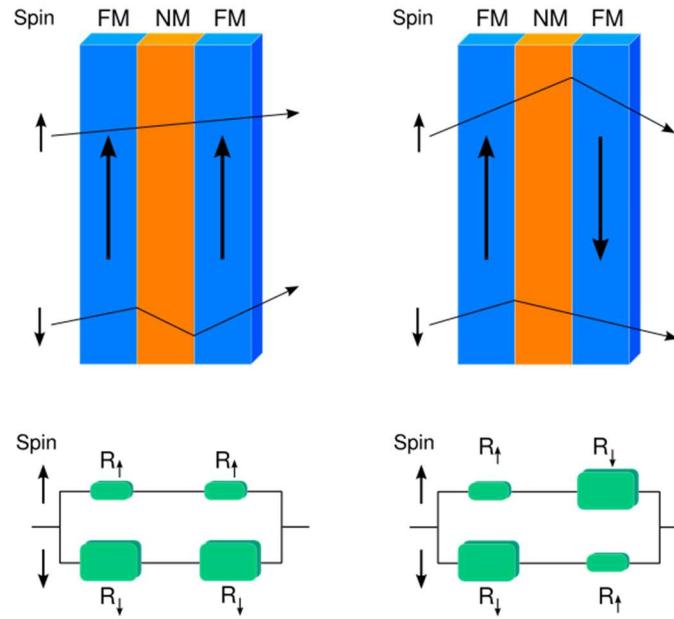
Peter Grünberg



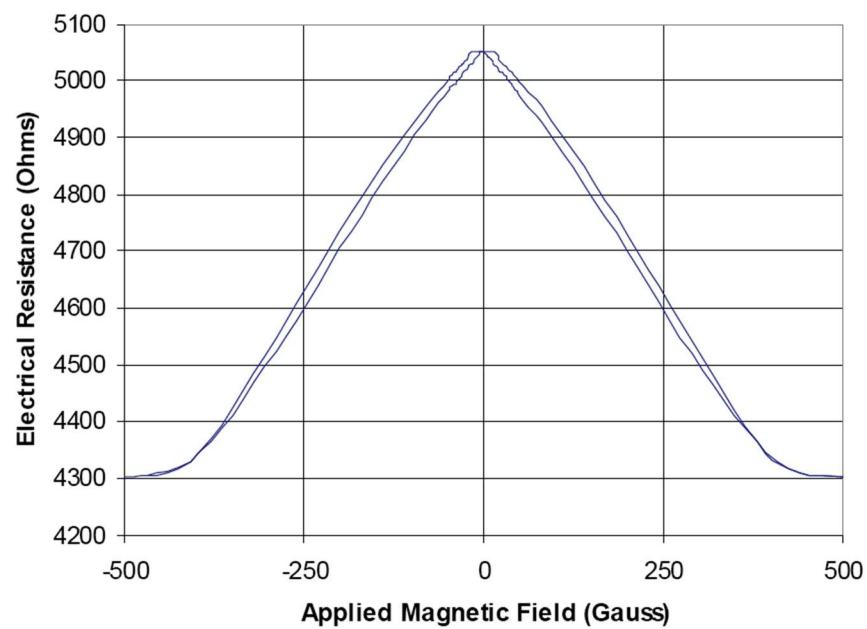
**Magnetoresistance** – the change in electric current flowing through a material as the result of applying a magnetic field.

## Giant, Tunnelling, and Colossal Magnetoresistance





Normally the resistance is higher  
in the anti-parallel case.

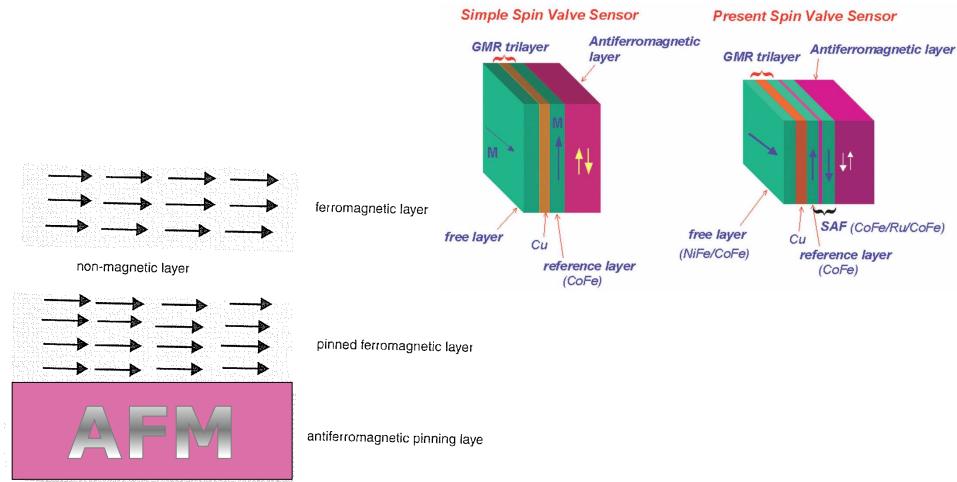


## Hard Disk Read Heads

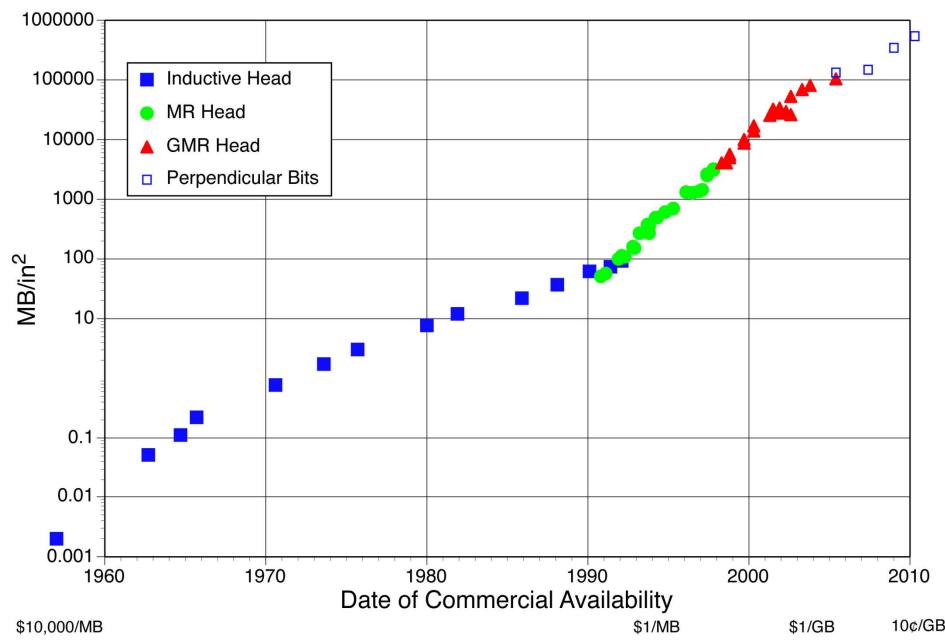
The top magnetic layer is free to change spin orientation with an applied field.

As the read head moves, magnetic fields on the disk cause the spins to align parallel or antiparallel to those in 1<sup>st</sup> layer. Information on the hard disk is coded as 0/1 and give rise to low/high current.

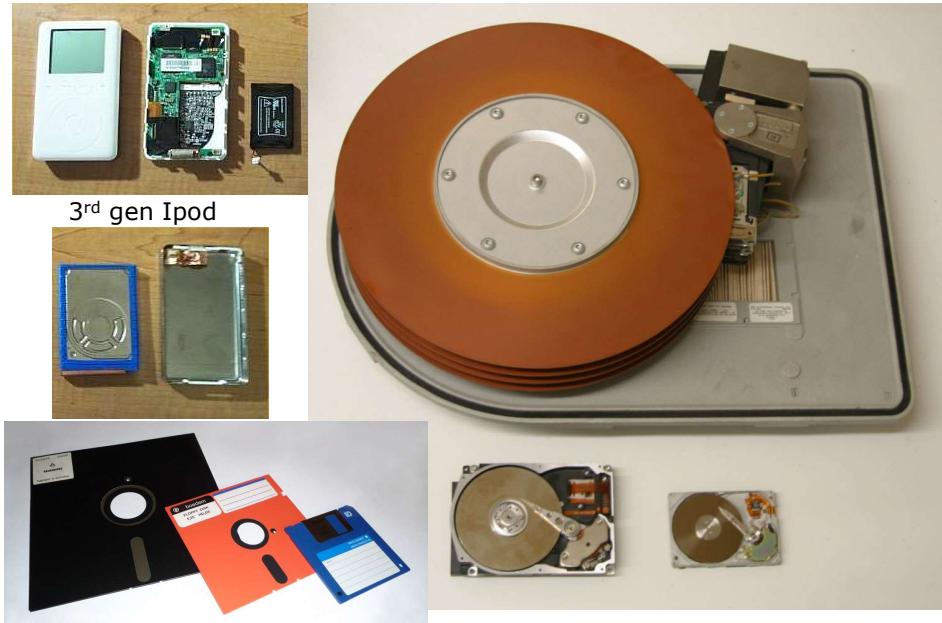
GMR can detect weak (small fields) giving rise to high capacity hard disks.



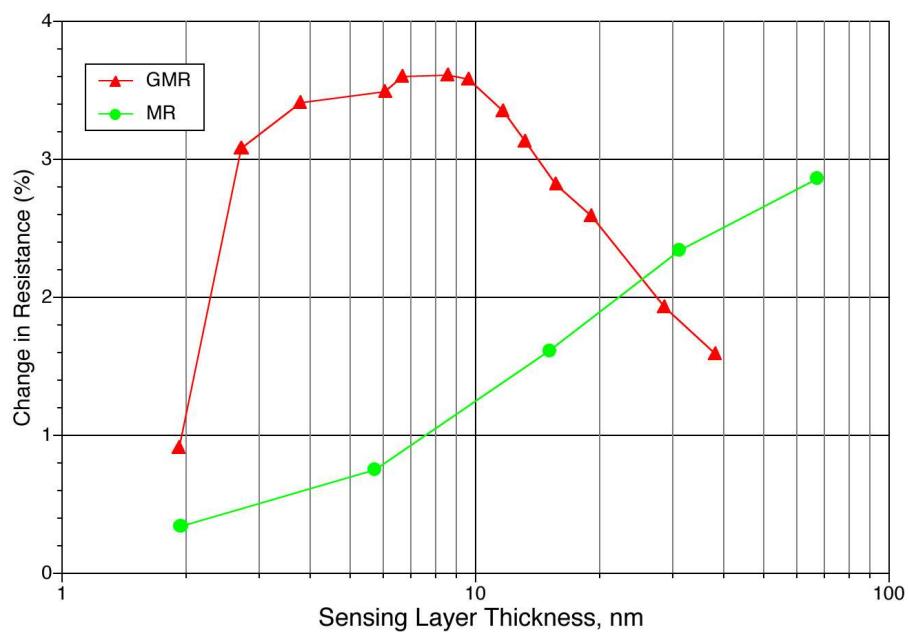
## Hard Disk Areal Density



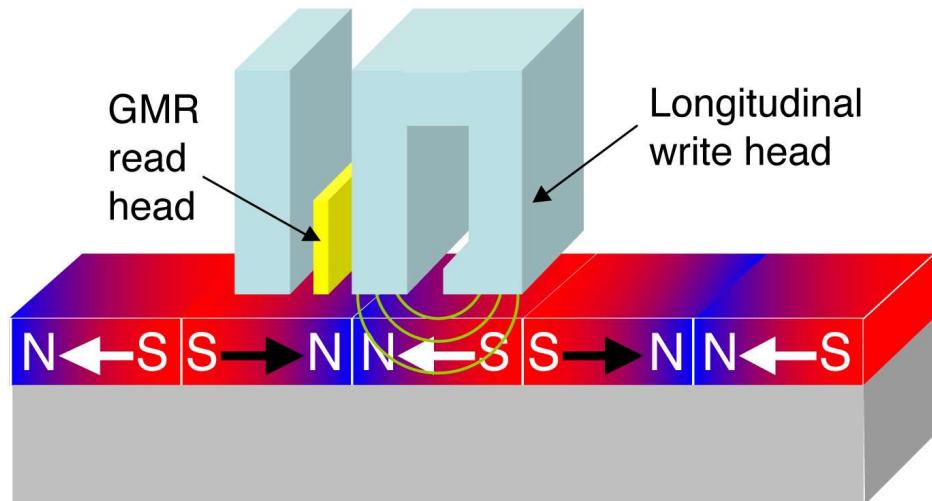
### Floppy and Hard Disk Size



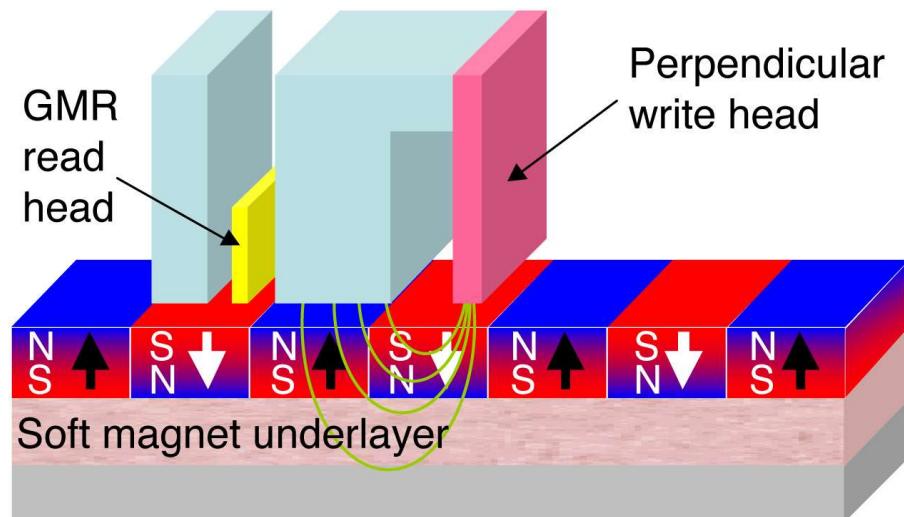
### Advantage of GMR



Longitudinal recording



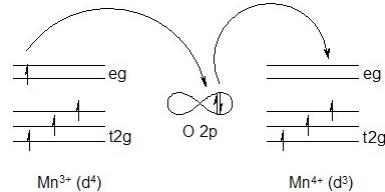
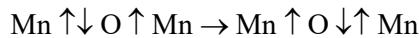
Perpendicular recording



## Tunneling and Colossal Magnetoresistance

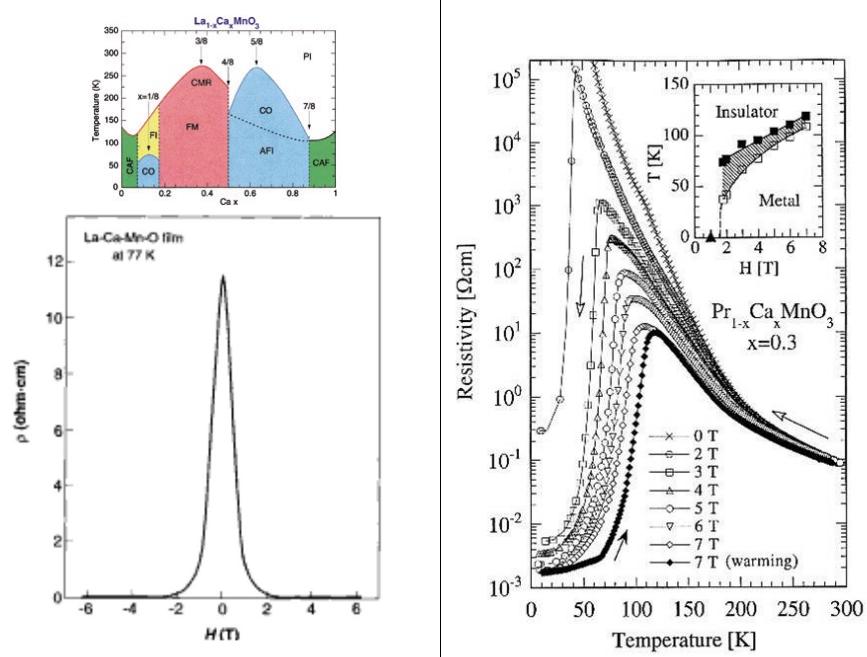
Tunneling Magnetoresistance (TMR) uses a thin insulating layer to separate two ferromagnetic layers

- electrons flow from one ferromagnetic layer to the next by quantum mechanical tunneling.
- Early 1990's, **Colossal Magnetoresistance** was observed for certain compounds (e.g.  $\text{La}_{1-x}\text{Ca}_x\text{MnO}_3$  or  $\text{RE}^{3+}_{1-x}\text{M}^{2+}_x\text{MnO}_3$  )
- A change in electrical resistivity, several orders of magnitude is found in large magnetic fields, greater than several tenths of a Tesla.
- The spin on the TM are coupled via the oxide ions.
- $\text{Mn}^{4+}$  couples antiferromagnetically via **superexchange**, and the coupling of  $\text{Mn}^{3+}$  can be ferro- or antiferro-magnetic.
- $\text{Mn}^{3+}$  ions couple to  $\text{Mn}^{4+}$  ions by **double exchange**, where a simultaneous hop of an electron from  $\text{Mn}^{3+}$  to an O 2p and from the O 2p to an  $\text{Mn}^{4+}$  takes place.

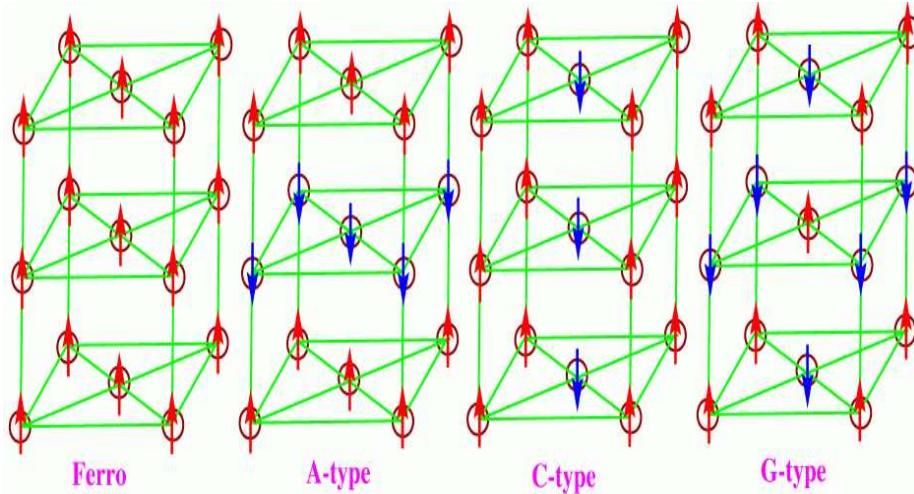


The CMR manganite phases can be described in terms of **band theory**.

- $e_g$  orbitals on manganese and the O 2p orbitals combine to form two bands, one for *spin-up* electrons and one for *spin-down* electrons.
- There is a large band gap between the two, so at low T one band is empty and one is partly full.
  - Known as **half-metals**, since only one type of spin is free to carry an electrical current.
- Ferromagnetism disappears at the Curie temperature.
  - above this temperature, the  $e_g$  electrons on manganese are better thought of as **localized** and the solid is **paramagnetic** with a much higher electrical resistance.
- As the ferromagnetic phase approaches the **Curie Point**, the electrical resistance rises as thermal energy starts to overcome the **double exchange**.
  - In this region the manganites exhibit Colossal Magnetoresistance, **CMR**.
- A strong magnetic field realigns the spins, restoring the half-metallic state and thus decreasing the resistivity.



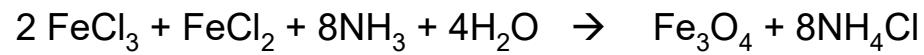
Double exchange is strong in manganites with  $x \approx 1/3$ , which form ferromagnetic phases at low T.



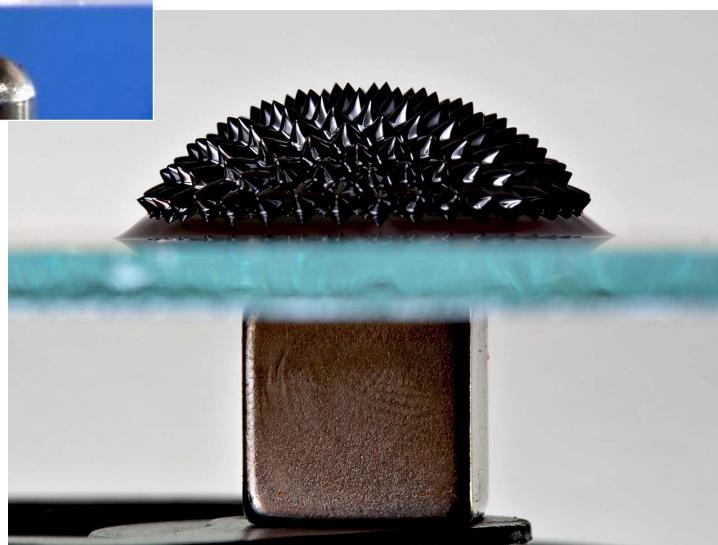
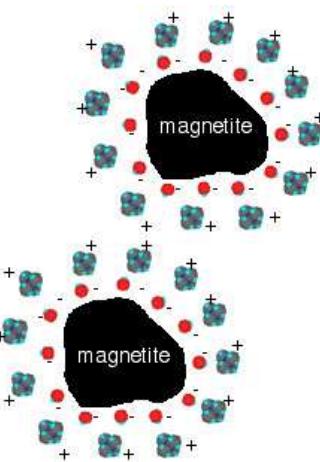
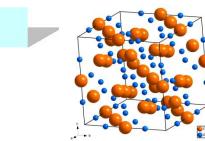
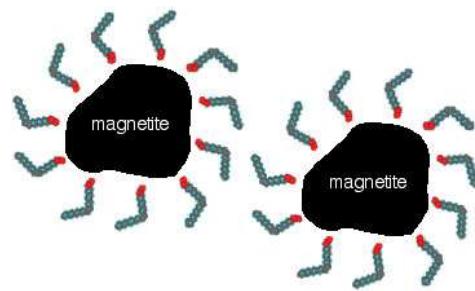
1. **A-type:** The intra-plane coupling is ferromagnetic while inter-plane coupling is antiferromagnetic.
2. **C-type:** The intra-plane coupling is antiferromagnetic while inter-plane coupling is ferromagnetic.
3. **G-type:** Both intra-plane and inter-plane coupling are antiferromagnetic.

## Ferrofluids

Precipitate magnetite

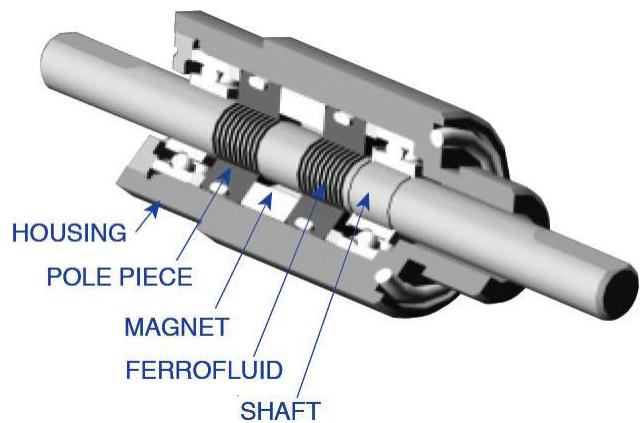


Add surfactant

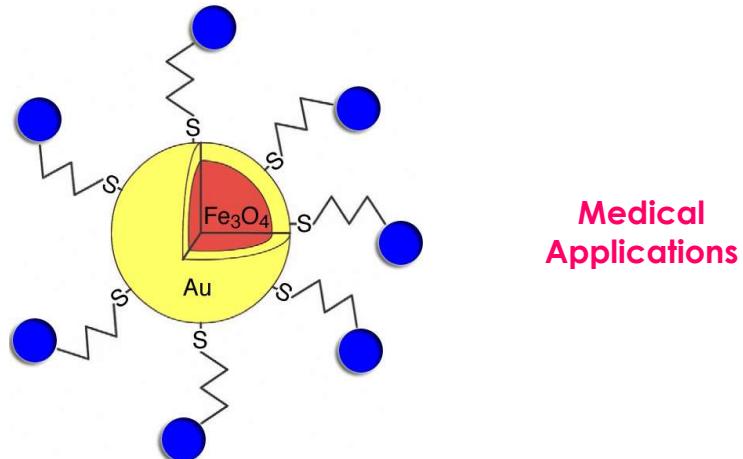




### Liquid O-ring Seals



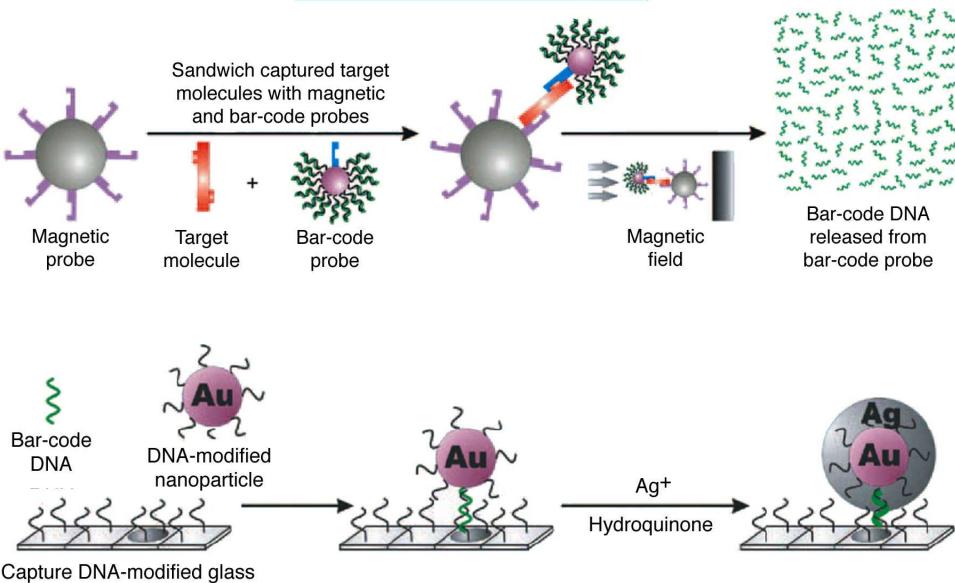
Coat with drugs, antibodies, peptides, or oligonucleotides



Use magnetic fields to position

- Deliver drugs to targets (especially for chemotherapy)
- "Tag and drag" removal (especially for toxins)

### Bar Code Assay



## Electrical Polarization

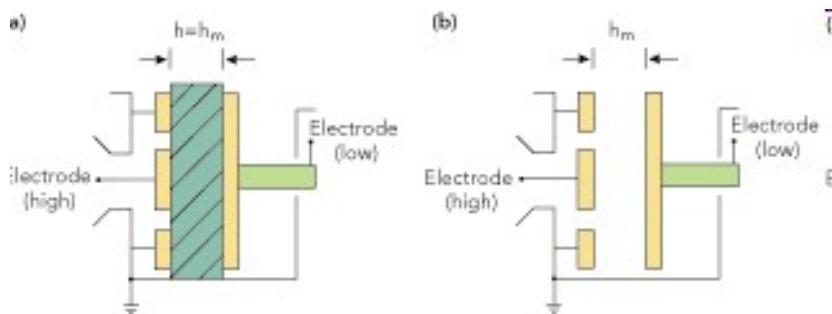
Most solids do not possess a net **dipole moment**.

- Even if composed of molecules with permanent dipole moments, the molecules tend to arrange (crystallize) in a way that the unit cell of the crystal has no net dipole moment.
- If a solid is placed in an electric field, a field is induced in the solid which opposes the applied field. There are two sources of the field.
  1. a distortion of the **electron cloud** of the atoms or molecules
  2. slight **movements of the atoms** themselves
- The average dipole moment per unit volume, induced in the solid, is the **electrical polarization**.

$$P = \epsilon_0 \chi_e E$$

where  $\epsilon_0$  is the permittivity of free space ( $8.85 \times 10^{-12} \text{ F m}^{-1}$ ),  $\chi_e$  is the dimensionless dielectric susceptibility, and  $E$  is the electric field.

- Susceptibility is often determined experimentally by determining the capacitance of an electric circuit with and without the solid.
  - The ratio of the two capacitances is the **relative permittivity**  $\epsilon_r$  (**dielectric constant**)
- $$\frac{C}{C_0} = \epsilon_r$$



The **dielectric constant** is related to the **dielectric susceptibility** by:

$$\epsilon_0 = 1 + \chi_e$$

If the experiment is performed using a high frequency alternating electric field, then the atoms cannot follow the changes in the field and only the effect due to the electron displacement is measured.

- Visible and ultraviolet light provides such a field and the refractive index of a material is a measure of the electron contribution to the dielectric constant.
- Substances with a high **dielectric constant** also tend to have high **refractive indices**.

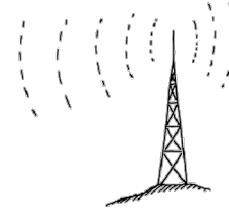
## Wireless Communications

Composed of passive elements that store, filter, and/or transfer electromagnetic energy with minimal loss

- Resonators, filters, circulators & isolators



$$f_0 \propto \frac{1}{D\sqrt{\epsilon}}$$



### Dielectric Constant (Permittivity)

A high dielectric constant allows components to be miniaturized

### Dielectric Loss

A low dielectric loss is needed to prevent energy dissipation and minimize the bandpass of the filter (more usable channels)

### Temperature Coefficient

For device stability the dielectric properties should be relatively insensitive to temperature

## Piezoelectric Crystals – $\alpha$ -quartz

A **piezoelectric crystal** is one that develops an electrical voltage when subject to mechanical stress, and conversely develops a strain when an electrical field is applied across it.

• Application of an **electric field** causes a *slight* movement of atoms in the crystal so that a dipole moment develops.

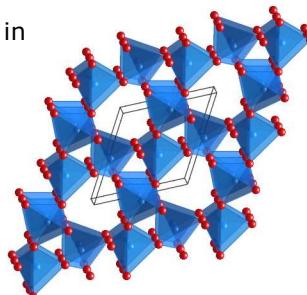
• For it to be piezoelectric, a crystal must be made up from units that are **non-centrosymmetric** (do not possess a center of symmetry)

• Of the 32 crystal classes, 11 possess a center of symmetry and 1 other cannot be piezoelectric because of other symmetry elements.

•  $\alpha$ -quartz is based on  $\text{SiO}_4$  tetrahedra, which do not have a center of symmetry, and are distorted in a way so that each unit has a net dipole moment

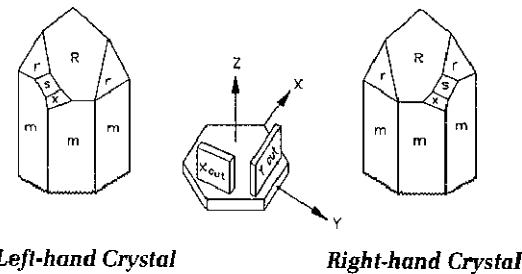
• External stress changes the Si-O-Si bond angles between tetrahedra, so that dipole moments no longer cancel and the crystal has a **net electrical polarization**.

• Effect is small in  $\alpha$ -quartz, output of electrical energy is only 0.01 of the input strain energy.





- $\alpha$ -quartz is useful where an oscillator of **stable frequency** is needed
- An electric field causes distortion of quartz and if an alternating field is applied, the crystal vibrates.
  - If the frequency of the electric field matches a natural vibration frequency of the crystal, a **resonance** occurs and a steady oscillation is set up with the vibrating crystal feeding energy back to the electrical circuit.
  - For some crystallographic cuts, the **natural frequency of the crystal is independent of temperature** and the crystal will oscillate at the same frequency, regardless of temperature.

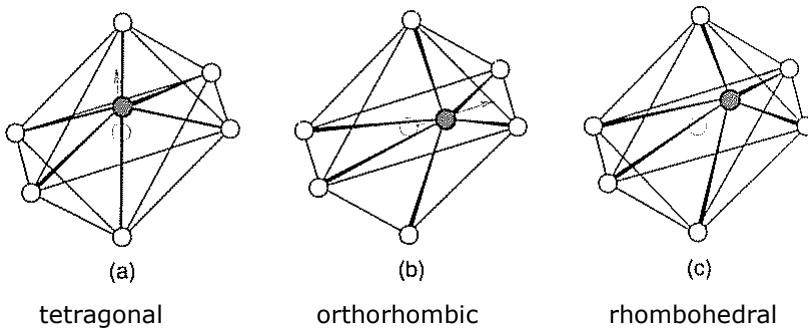


### Ferroelectric Effect

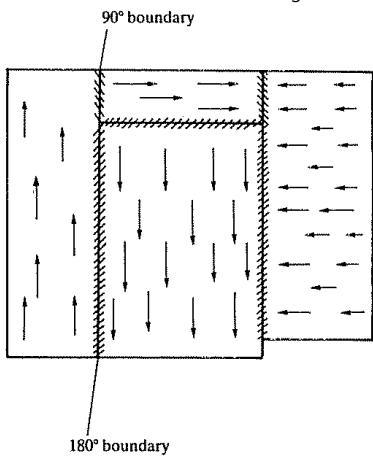


**Ferroelectric crystals** – possess domains of different orientation of electrical polarization that can be reoriented and brought into alignment by an electric field.

- The archetype ferroelectric is  $\text{BaTiO}_3$ , which has a large dielectric constant ( $\sim 1000$ ) and is widely used in capacitors.
- Above 393 K  $\text{BaTiO}_3$  is cubic, between 393 to 278 K it is tetragonal, between 278 to 183 K orthorhombic, and below 183 K it is rhombohedral.
- Distortions of the  $\text{TiO}_6$  octahedral occur and result in a net dipole moment.



### Domains in BaTiO<sub>3</sub>



Electric susceptibility and dielectric constant of ferroelectrics obey a Curie law dependence:

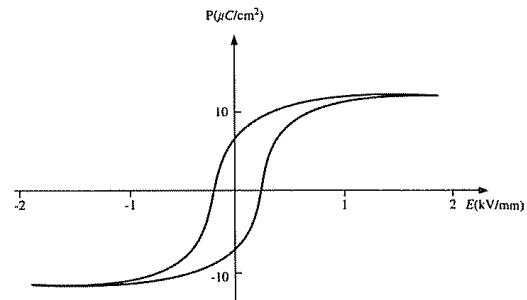
$$\epsilon_r = \epsilon_\infty + C/(T-T_c)$$

where  $\epsilon_\infty$  is the permittivity at optical frequencies and  $T_c$  is the Curie temperature.

- When an external field is applied, **domains** aligned favorably grow at the expense of others.

- The response to the field exhibits a **hysteresis**, similar to ferromagnets.

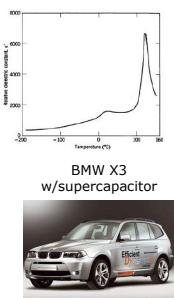
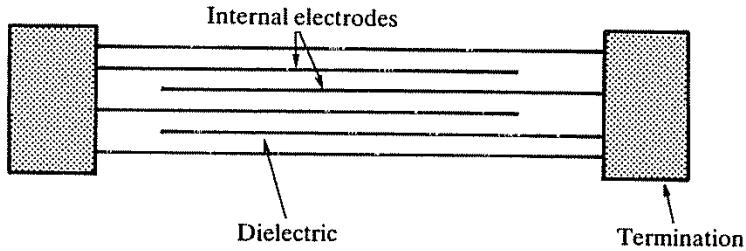
- Polarization grows until the whole crystal has its **dipole moments aligned**, this **polarization** remains while the field is reduced to zero and only declines as a field of opposite polarity is applied.



### Multilayer Ceramic Capacitors

**Capacitors** are used to store charge using an electric field to induce charge in the capacitor, which remains charged until a current is required.

- A high relative permittivity is needed to store a large amount of charge and retain a physically small capacitor.
- Near its Curie temperature, pure BaTiO<sub>3</sub> has a high permittivity ( $\sim 7000$ ), but rapidly drops when nearing room temperature.
- The dielectric properties are improved by chemically substituting elements (e.g. Zr<sup>4+</sup>, Sn<sup>4+</sup> in place of Ti<sup>4+</sup>), reducing the Curie temperature nearer room temperature and giving a flatter permittivity vs T curve.
- Other ferroelectric oxides include PZT ( $PbZr_{1-x}Ti_xO_3$ ), KH<sub>2</sub>PO<sub>4</sub>, Rochelle salt, and NaNO<sub>2</sub>.



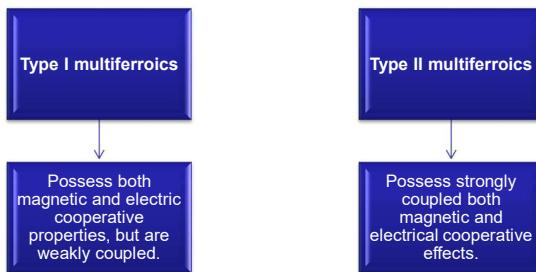
## Multiferroics

Materials that possess two or more cooperative properties:  
**ferromagnetism, ferroelectricity, and ferroelasticity**

Generally used to refer to materials that are ferroelectric *and* ferromagnetic *or* antiferromagnetic.

Apply a magnetic field to alter polarization, or apply an electric field (voltage) to change the spin.

- Potential applications: 1) computer memory written electrically, read magnetically; 2) Four logical states available for storage.
- Advantage: Writing using an electric field uses less energy



## BiFeO<sub>3</sub>

### Type I multiferroic

Thin films have a large remnant polarization  $T_N$  (Neel temperature), 643 K

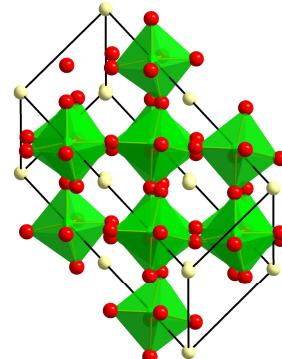
Ferroelectric transition temperature, 1100 K  
• Rare room temperature multiferroic

Lone pairs of Bi<sup>3+</sup> (6s<sup>2</sup>) give rise to cooperative offset arrangement and ferroelectric effect.

The Fe<sup>3+</sup> ions couple antiferromagnetically.

Little interaction between the polarization and magnetization, due to different ions.

- Effect of a magnetic field on the polarization, or the effect of an electric field on the magnetization is very small.



R3c (ferroelectric)

## Terbium Manganites: $\text{TbMnO}_3$ and $\text{TbMn}_2\text{O}_5$

### Type II multiferroics

#### $\text{TbMnO}_3$ (perovskite)

- Polarization is induced by spiral magnetism.
- Spins are cycloidal below 28 K, polarization along  $c$ -axis.
- $\text{Mn}^{3+}$  ( $d^4$ ) Jahn-Teller distortion
  - Ordering of  $e_g$  orbitals in  $ab$  plane
  - Spins couple ferromagnetically along the  $a$  and  $b$  axes, and antiferromagnetically along the  $c$ -axis.
- A magnetic field (5 T) applied along the  $b$ -axis causes electrical polarization to change from along  $c$ -axis to  $a$ -axis.
- Several other known solids with cycloidal spin arrangements produce a magnetoelectric effect:  $\text{CuO}$ ,  $\text{MnWO}_4$ ,  $\text{Ni}_3\text{V}_2\text{O}_8$

