



## Magnetism Intro

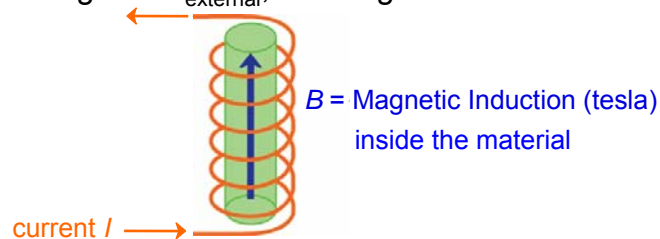
1. Magnetic properties of a substance depend on the number of unpaired electrons and how they interact with one another
2. Magnetic susceptibility measures the ease of alignment of electron spins in an external magnetic field
3. Magnetic response of electron to an external magnetic field is  $\sim 1000$  times that of even the most magnetic nuclei ( $m_e$  is 1000 times smaller)
4. Best definition of a magnet: a solid in which more electrons point in one direction than in any other direction

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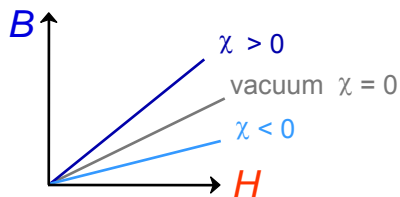


## Response to a Magnetic Field

- For a given  $H_{\text{external}}$ , the magnetic field in the material is  $B$



- Magnetic susceptibility,  $\chi$  (dimensionless)



$\chi$  measures the material response relative to a vacuum.

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## Magnetism: Definitions

The magnetic field inside a substance differs from the free-space value of the applied field:

$$\vec{H} = \vec{H}_0 + \Delta\vec{H}$$

inside sample      applied field      shielding/deshielding due to induced internal field

Usually, this equation is rewritten as:

$$\vec{B} = \vec{H}_0 + 4\pi\vec{M}$$

magnetic induction      magnetization (mag. moment per unit volume)

or  $\vec{B}/\vec{H}_0 = 1 + 4\pi\chi_v$   
where  $\chi_v$  = volume susceptibility,  
and  $B/H_0$  = permeability (mag. equiv. of dielectric const)

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## Magnetism Intro

1. Magnetic Properties correspond to  
number and distribution of unpaired  $e^-$ .
2. Mag. Effects of  $e^- \sim 10^3$  of nuclei.
3. Magnetic Susceptibility measures the ease of polarization of  $e^-$  density by magnetic field.

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## Magnetism: Definitions

$$\chi_g = \chi_v / \rho = \text{gram or mass magnetic susceptibility}$$

$$\chi_m = \chi_g / MW = \text{molar magnetic susceptibility}$$

$$\begin{aligned} \mu_{\text{eff}} &= (3 k / N \beta^2)^{1/2} (\chi_m T)^{1/2} = \text{effective magnetic moment} \\ &= 2.828 (\chi_m T)^{1/2} \quad \text{in units of Bohr magnetons} \end{aligned}$$

$$\beta = e h / 4 \pi m c = \text{Bohr magneton} = 0.93 \times 10^{-20} \text{ erg/Gauss}$$

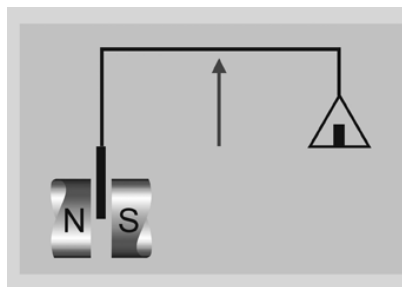
ICBST  $\chi$  is proportional to  $-(\partial E / \partial H_0) / H_0$

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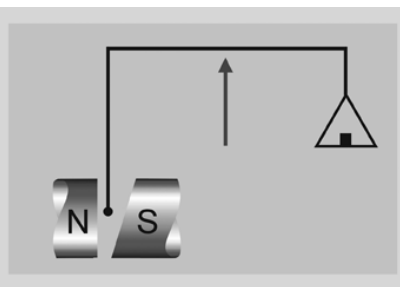
## Magnetism: Measurement

### Gouy Balance



Homogeneous magnetic field  
Magnetic force on sample =  $\chi_v H^2$   
Use calibration standard to find  $H^2$   
Weigh sample with and without field  
Need large samples, >100 mg

### Faraday Balance

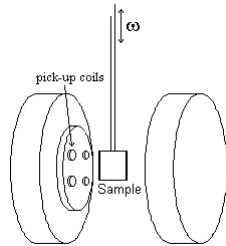


Inhomogeneous magnetic field  
Magnetic force =  $\chi_v V H \partial H / \partial x$   
Calibrate to find  $H \partial H / \partial x$   
Weigh sample with and without field  
Small samples, ~10 mg



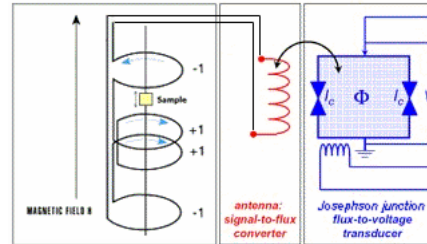
## Magnetism: Measurement

### Vibrating Sample Magnetometer



1. Sample size ~ 10 mg
2. Sample vibrates at ~50 Hz
3. Often uses supercon magnets
4. Sensitivity similar to Faraday
5. Easier to do variable temp

### SQUID: Superconducting Quantum Interference Device Magnetometer



1. Sample size < 1 mg, very sensitive
2. Key component is two supercon half-loops linked by an insulating barrier (Josephson junctions). The loop converts flux into a voltage

For both techniques, oscillation of sample induces a current in the pick-up coils. This current is either detected directly (VSM) or indirectly (SQUID).

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## Magnetism: Measurement

### Solution NMR technique – Evans' Method

Dissolution of a paramagnetic substance in a solvent shifts the solvent resonances from the shifts seen for the pure solvent

Experimental technique: a solution containing the paramagnetic substance is placed in NMR tube along with a second tube containing pure solvent. Best to use a solvent with a sharp singlet. The NMR spectrum will contain two peaks, one due to the pure solvent and another peak, shifted from the first, due to the solution.

$$\chi_g = 3\Delta\nu/2Q\pi\nu c + \chi_0 + \chi_0(d_0 - d_s)/c$$

$\Delta\nu$  = frequency shift of solvent resonance

$Q = 1$  for an electromagnet,  $= 2$  for a superconducting magnet

$\nu$  = NMR probe frequency

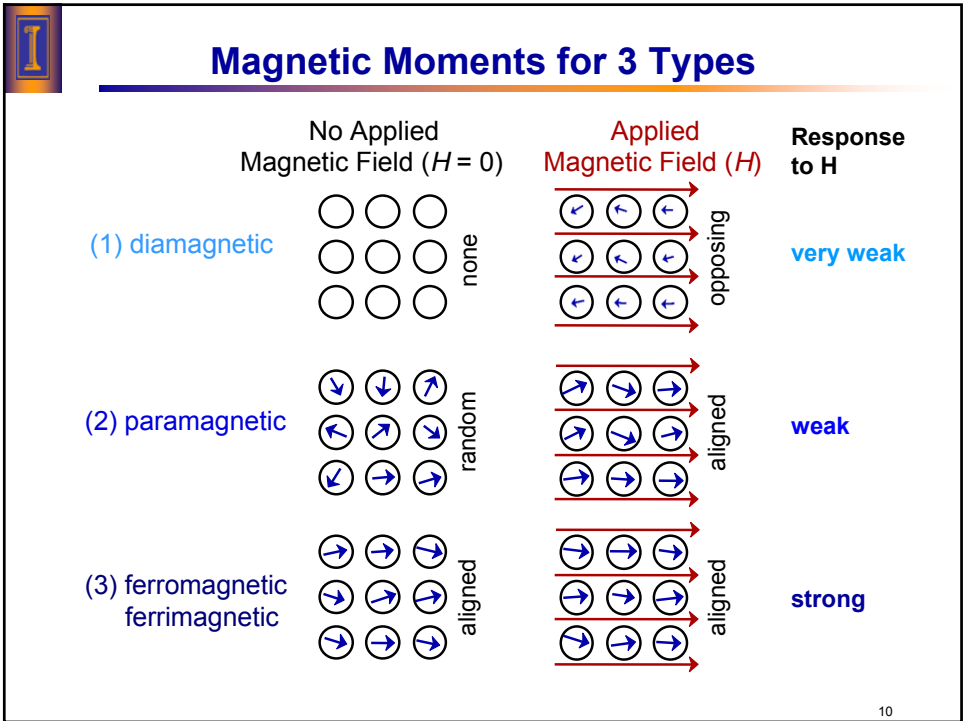
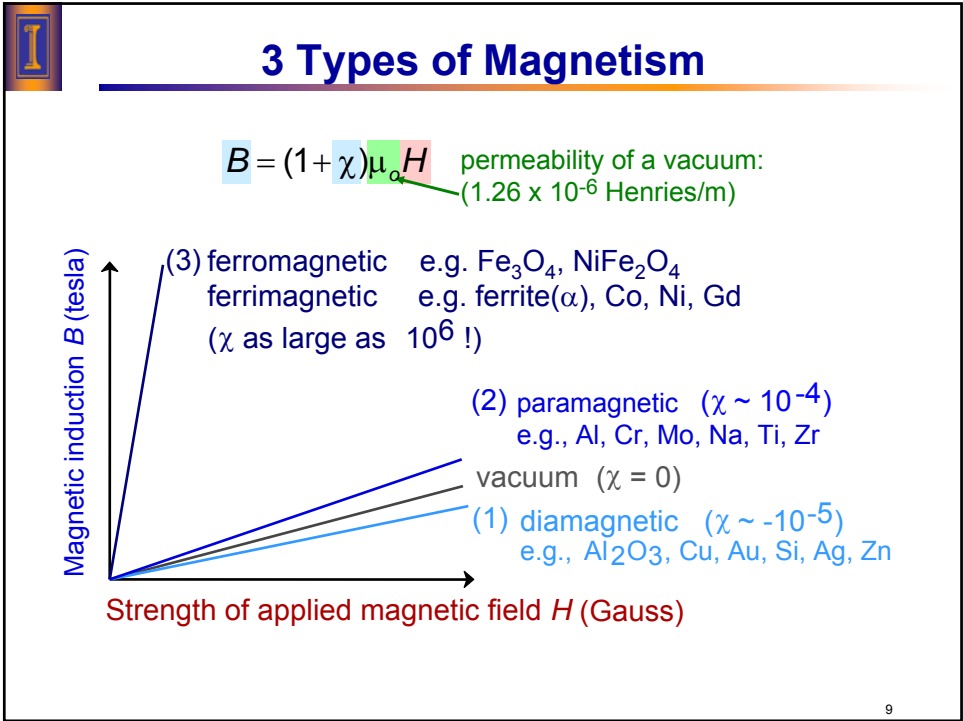
$c$  = concentration of sample (grams per  $\text{cm}^3$ )

$\chi_0$  = gram susceptibility of solvent

$d_0 - d_s$  = change in density of solvent vs solution



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## Diamagnetism

Diamagnetism of an atom:

$$\chi^{\text{dia}} = - N_{\text{avo}} e^2 \sum_i \langle r_i \rangle^2 / 6 m c^2$$

sum over all electrons in atom  
average orbital radius of i'th electron

Therefore, bigger atoms have a larger diamagnetism than smaller atoms

Note, bonding also influences  $\langle r_i \rangle$

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## Pascal's Approximation

The diamagnetic contribution of the paired electrons in a molecule is equal to the sum of the diamagnetic contributions from the constituent atoms and bonds

$$\chi_{\text{molecule}} = \sum_i \chi_{\text{atom } i} + \sum_j \chi_{\text{bond } j}$$

where  $\chi_{\text{atom } i}$  and  $\chi_{\text{bond } j}$  are empirically derived constants

Table of Pascal's constants (units of  $-10^{-6} \text{ cm}^3$ )

Ion	DC	Ion	DC
Na <sup>+</sup>	6.8	Co <sup>2+</sup>	12.8
K <sup>+</sup>	14.9	Co <sup>3+</sup>	12.8
NH <sub>4</sub> <sup>+</sup>	13.3	Ni <sup>2+</sup>	12.8
Hg <sup>2+</sup>	40	VO <sup>2+</sup>	12.5
Fe <sup>2+</sup>	12.8	Mn <sup>3+</sup>	12.5
Fe <sup>3+</sup>	12.8	Cr <sup>3+</sup>	12.5
Cu <sup>2+</sup>	12.8	Cl <sup>-</sup>	23.4
Br <sup>-</sup>	34.6	SO <sub>4</sub> <sup>2-</sup>	40.1
I <sup>-</sup>	50.6	OH <sup>-</sup>	12
NO <sub>3</sub> <sup>-</sup>	18.9	C <sub>2</sub> O <sub>4</sub> <sup>2-</sup>	34
ClO <sub>4</sub> <sup>-</sup>	32	OAc <sup>-</sup>	31.5
IO <sub>4</sub> <sup>-</sup>	51.9	pyridine	49.2
CN <sup>-</sup>	13	Me-pyr	60
NCS <sup>-</sup>	26.2	acac <sup>-</sup>	62.5
H <sub>2</sub> O	13	en	46.3
EDTA <sup>4-</sup>	~150	urea	33.4

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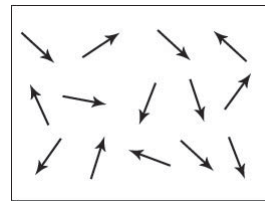
## Types of Magnetic Behavior

### Diamagnetism

- i) Substance repelled by external magnetic field ( $\chi < 0$ )
- ii) Due to presence of paired electrons (classically, Lenz's law: in a closed loop carrying current, an applied magnetic field will induce an opposing field in the loop)
- iii) Very weak magnetic response

### Paramagnetism: magnetic disorder

- i) Substance attracted by external magnetic field ( $\chi > 0$ )
- ii) Caused by spin and orbital angular moments of unpaired electrons
- iii) Temperature dependent magnetic behavior



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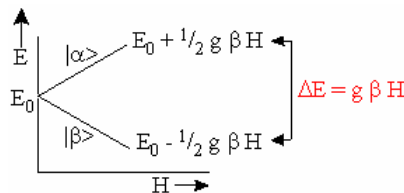


## Paramagnetism, e.g., $S = 1/2$

1. Magnetic moment  $\vec{\mu} = -g \beta \vec{S}$

where  $g$  = electron g-factor  
 $\beta$  = Bohr magneton  
 $S$  = spin angular momentum

2. In applied field,  $\hat{H} = -\vec{\mu} \cdot \vec{H} = g \beta \vec{S} \cdot \vec{H}$



3. There is a slight excess of spins aligned with H:

$$N_\alpha / N_\beta = e^{-g\beta H / kT} \quad (\text{Boltzmann})$$

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## Paramagnetism, e.g., $S = 1/2$

From last slide:  $N_\alpha/N_\beta = e^{-g\beta H / kT}$

It turns out that  $g\beta H \ll kT$  (even if  $T$  is small). By using the approximation  $e^x \sim (1 + x)$  if  $x \sim 0$ , we find:

$$N_\alpha/N_\beta = 1 - g\beta H / kT$$

If we define  $N = N_\alpha + N_\beta$ , then ICBST

$$N_\alpha = N(1 - g\beta H / 2kT) / 2$$

$$N_\beta = N(1 + g\beta H / 2kT) / 2$$

Now, net magnetization is:

$$M = \frac{1}{2} g \beta (N_\beta - N_\alpha) = Ng^2\beta^2H / 4kT$$

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## Paramagnetism, e.g., $S = 1/2$

From last slide:  $M = Ng^2\beta^2H / 4kT$

Remember that  $\chi = M/H$ , therefore  $\chi = Ng^2\beta^2 / 4kT$ , or

$$\chi = C / T \quad \text{where } C = Ng^2\beta^2 / 4k$$

This is the **Curie law**, which is usually a sign that the spin centers are acting completely independently

Empirically, it has been found that many substances obey a modified version of the Curie law, called the **Curie-Weiss** equation:

$$\chi = C / (T - \theta)$$

The Weiss constant,  $\theta$ , is non-zero when there are weak interactions between adjacent spin centers

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## Paramagnetism

For general case of spin-only magnetism, not just  $S = 1/2$ , we have:

$$\chi = Ng^2\beta^2 S(S + 1) / 3kT$$

Plugging this into the definition of eff. mag. moment:

$$\mu_{\text{eff}} = (3k / N\beta^2)^{1/2} (\chi T)^{1/2} \quad \text{or} \quad \mu_{\text{eff}} = g [S(S + 1)]^{1/2}$$

Ion	e <sup>-</sup> Config.	S	$\mu_S(\mu_B)$	$\mu_{S+L}(\mu_B)$	$\mu_{\text{obs}}(\mu_B)$
Ti <sup>3+</sup>	d <sup>1</sup>	1/2	1.73	3.01	1.7-1.8
V <sup>2+</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  $\frac{1}{2}$  full)  $t_{2g}$  orbitals

Spin-orbit Coupling

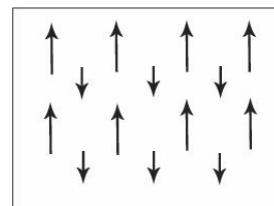
- Increases the moment for d<sup>6</sup>, d<sup>7</sup>, d<sup>8</sup>, d<sup>9</sup>
- Decreases the moment for d<sup>1</sup>, d<sup>2</sup>, d<sup>3</sup>, d<sup>4</sup>

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## Ferrimagnetism: A magnetically ordered state

- Anti-alignment of adjacent magnetic moments
- Spin cancellation is not complete, however, owing to different numbers of up and down spins
- Alignment persists even in absence of external field
- Very strong magnetic response to external magnetic field



Ferrimagnets become paramagnetic when heated. The change from a ferrimagnetic state at low temperature to a paramagnetic state at higher temperature is a phase transition.

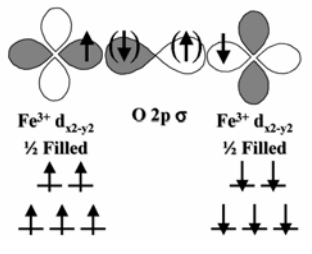
The transition temperature is called the Neél point.

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## Causes of ferrimagnetism

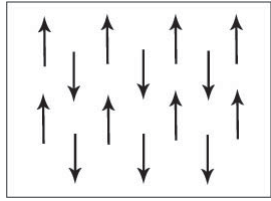
**Causes of ferrimagnetism:**

- a) Direct interaction (spin pairing, i.e., bonding)
- b) Superexchange (through-bond interaction) – diamagnetic bridging ligand is polarized by spins on magnetic neighbors



**Antiferromagnetism: a special case of ferrimagnetism**

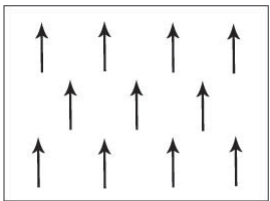
- i) In magnetically ordered state, there are equal number of spin up and spin down electrons
- ii) Diamagnetic below a certain temperature; paramagnetic above



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## Ferromagnetism

- i) Adjacent magnetic moments adopt a common (parallel) alignment
- ii) Moments remain aligned even in absence of external magnetic field
- iii) Macroscopic magnitude is immense
- iv) Field-dependent and temperature dependent magnetic behavior



**This is a magnetically ordered state too.**

**Ferromagnets will become paramagnetic when heated. The change from a ferromagnetic state at low temperature to a paramagnetic state at higher temperature is a phase transition.**

**The transition temperature is called the Curie point.**

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# Antiferromagnetism

- i) Anti-Alignment of Adjacent Mag. Momenta
- ii) Magnitude of coupling  $\sim$  that of Paramagnetism
- iii) Field and T dependent

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Causes:

- a) Direct Interaction (Spin Pairing, i.e. Bonding!)
- b) Super exchange (thru-bond interaction)

$1 \uparrow \text{---} (1 \downarrow) \text{---} 1 \downarrow$   
 interact  $\uparrow$  interact  
 spin paired atom w/ induced spin polarization

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# Temperature Effects on Magnetic Behavior

Temperature, K

Temperature, K

Temperature, K

Temperature, K

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## Magnetizing Ferro- and Ferri-Magnetic Materials

- As the applied field ( $H$ ) increases...  
--the magnetic moment aligns with  $H$ .

**“Domains” with aligned magnetic moment grow at expense of poorly aligned ones!**

Boundary between domains = “Bloch wall”

## Permanent Magnets: Hysteresis

- Process:
  1. initial (unmagnetized state)
  2. apply  $H$ , cause alignment
  3. remove  $H$ , alignment stays!  
=> permanent magnet!
  4. Coercivity,  $H_C$   
Negative  $H$  needed to demagnetize!
- Hard vs Soft Magnets
  - large coercivity  
good for perm magnets  
add particles/voids to make domain walls hard to move  
(e.g., tungsten steel:  $H_c = 5900$  amp-turn/m)
  - small coercivity--good for electric motors  
(e.g., commercial iron 99.95 Fe)

## Magnetic Storage

- Information is stored by magnetizing material.
- Head can...
  - apply magnetic field  $H$  & align domains (i.e., magnetize the medium).
  - detect a change in the magnetization of the medium.


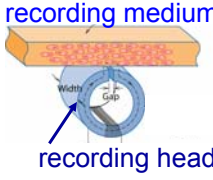
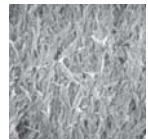


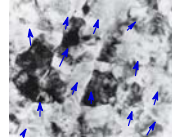
fig 1.1



- Two media types:
  - Particulate: needle-shaped  $\gamma\text{-Fe}_2\text{O}_3$ . +/- mag. moment along axis. (tape, floppy)
 



~2.5  $\mu\text{m}$
  - Thin film: CoPtCr or CoCrTa alloy. Domains are ~ 10 - 30 nm! (hard drive)
 



~120 nm

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## Other Kinds 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 whose particle size is too small to sustain the multidomain structure. Thus the particle behaves as one large paramagnetic ion.



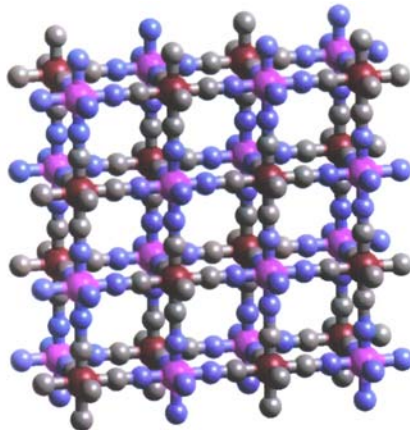
## Examples of Molecule-Based Magnetic Materials

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## General Structure of Prussian Blue

PB formula:  $\text{Fe}^{\text{III}}[\text{Fe}^{\text{II}}(\text{CN})_6]_{0.75} \cdot n\text{H}_2\text{O}$



C = gray spheres

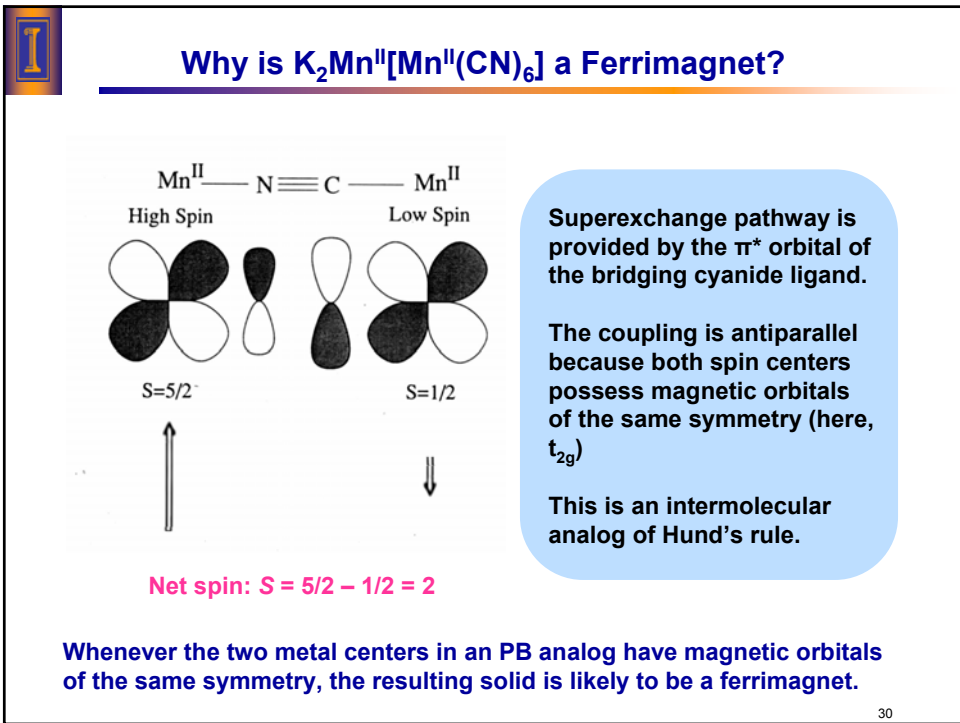
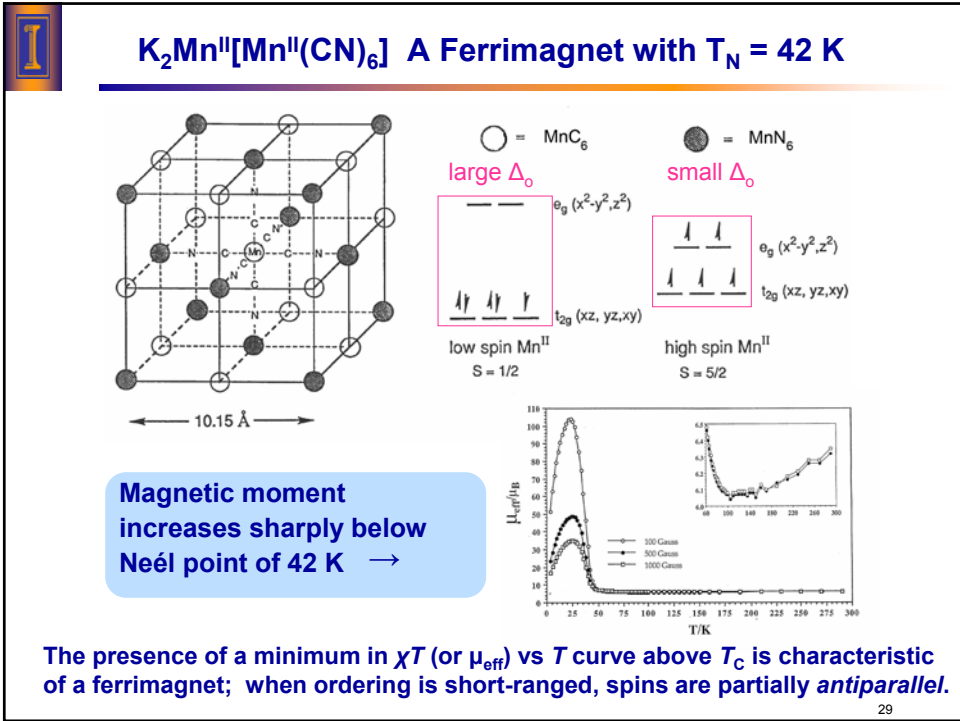
N = blue spheres

M = red/pink spheres

Structure is similar to that of perovskite (cubic  $\text{CaTiO}_3$ ) except cyanide (CN) replaces oxygen, and there are two different types of octahedral metal centers in alternating sites.

General synthetic route:  $\text{M}^{\text{m}+} + \text{M}(\text{CN})_6^{\text{n}-} \longrightarrow \text{PB Analog}$

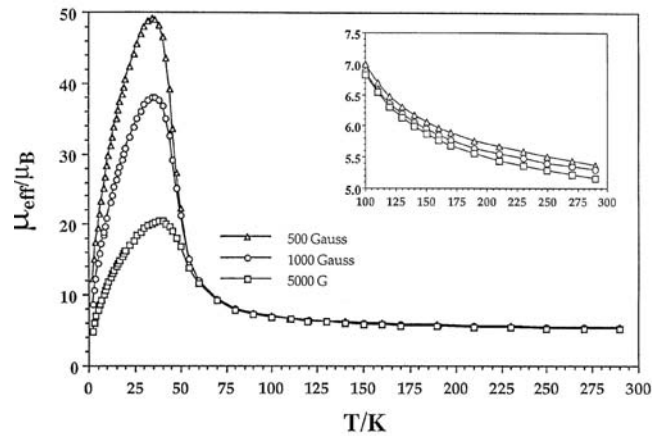
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## CsNi<sup>II</sup>[Mn<sup>III</sup>(CN)<sub>6</sub>·H<sub>2</sub>O: A Ferromagnetic Prussian Blue!

$T_C = 42\text{ K}$

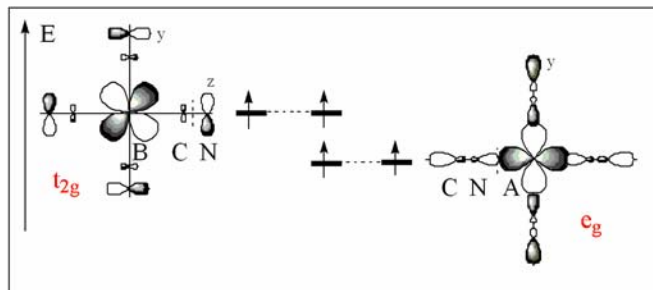
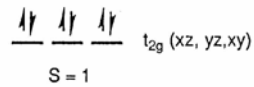
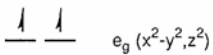
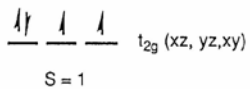
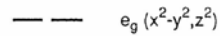


The absence of a minimum in  $\chi T$  (or  $\mu_{\text{eff}}$ ) vs  $T$  curve above  $T_C$  is characteristic of a ferromagnet; when ordering is short-ranged, spins are partially aligned.

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## Orbital Orthogonality Gives Rise to Ferromagnetism



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## Magnetic Data for Prussian Blue Analogues: What Correlates with $T_C$ ?

Compound	$T_C$ /K	Coupling
CsMn <sup>II</sup> [Cr <sup>III</sup> (CN) <sub>6</sub> ]•H <sub>2</sub> O	90	AF
Mn <sup>II</sup> <sub>3</sub> [Cr <sup>III</sup> (CN) <sub>6</sub> ] <sub>2</sub> •12H <sub>2</sub> O	66	AF
Fe <sup>II</sup> <sub>3</sub> [Cr <sup>III</sup> (CN) <sub>6</sub> ] <sub>2</sub> •12H <sub>2</sub> O	16	F
Co <sup>II</sup> <sub>3</sub> [Cr <sup>III</sup> (CN) <sub>6</sub> ] <sub>2</sub> •12H <sub>2</sub> O	23	F
Ni <sup>II</sup> <sub>3</sub> [Cr <sup>III</sup> (CN) <sub>6</sub> ] <sub>2</sub> •12H <sub>2</sub> O	53	F
CsNi <sup>II</sup> [Cr <sup>III</sup> (CN) <sub>6</sub> ]•2H <sub>2</sub> O	89	F
Cu <sup>II</sup> <sub>3</sub> [Cr <sup>III</sup> (CN) <sub>6</sub> ] <sub>2</sub> •12H <sub>2</sub> O	66	F
K <sub>2</sub> Mn <sup>II</sup> [Mn <sup>III</sup> (CN) <sub>6</sub> ]•H <sub>2</sub> O	41	AF
CsMn <sup>II</sup> [Mn <sup>III</sup> (CN) <sub>6</sub> ]•H <sub>2</sub> O	31	AF
Mn <sup>II</sup> <sub>3</sub> [Mn <sup>III</sup> (CN) <sub>6</sub> ] <sub>2</sub> •12H <sub>2</sub> O	37	AF
Co <sup>II</sup> <sub>3</sub> [Mn <sup>III</sup> (CN) <sub>6</sub> ] <sub>2</sub> •12H <sub>2</sub> O	16	F
CsNi <sup>II</sup> [Mn <sup>III</sup> (CN) <sub>6</sub> ]•H <sub>2</sub> O	42	F
Ni <sup>II</sup> <sub>3</sub> [Mn <sup>III</sup> (CN) <sub>6</sub> ] <sub>2</sub> •12H <sub>2</sub> O	30	F
Mn <sup>II</sup> [Mn <sup>IV</sup> (CN) <sub>6</sub> ]•H <sub>2</sub> O	49	AF
Fe <sup>III</sup> <sub>4</sub> [Fe <sup>II</sup> (CN) <sub>6</sub> ] <sub>3</sub> •15H <sub>2</sub> O	5.6	F
Mn <sup>II</sup> <sub>3</sub> [Fe <sup>III</sup> (CN) <sub>6</sub> ] <sub>2</sub> •12H <sub>2</sub> O	9	AF
Co <sup>II</sup> <sub>3</sub> [Fe <sup>III</sup> (CN) <sub>6</sub> ] <sub>2</sub> •12H <sub>2</sub> O	15	AF
Ni <sup>II</sup> <sub>3</sub> [Fe <sup>III</sup> (CN) <sub>6</sub> ] <sub>2</sub> •12H <sub>2</sub> O	23	F
Cu <sup>II</sup> <sub>3</sub> [Fe <sup>III</sup> (CN) <sub>6</sub> ] <sub>2</sub> •12H <sub>2</sub> O	21	F

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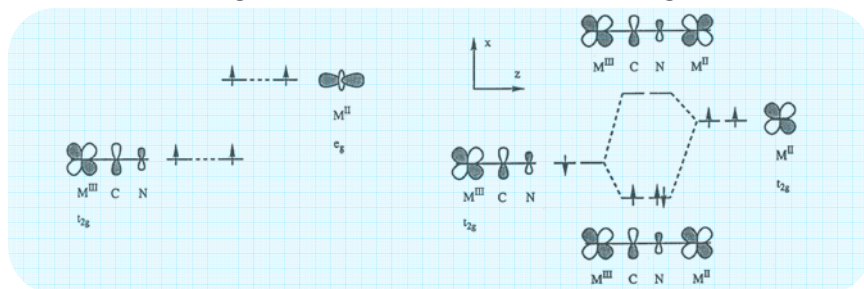


## The Superexchange Mechanism for Prussian Blues

$$J = J_{\text{ferromagnetic}} + J_{\text{antiferromagnetic}}$$

$$J_{\text{ferromagnetic}} > 0$$

$$J_{\text{antiferromagnetic}} < 0$$



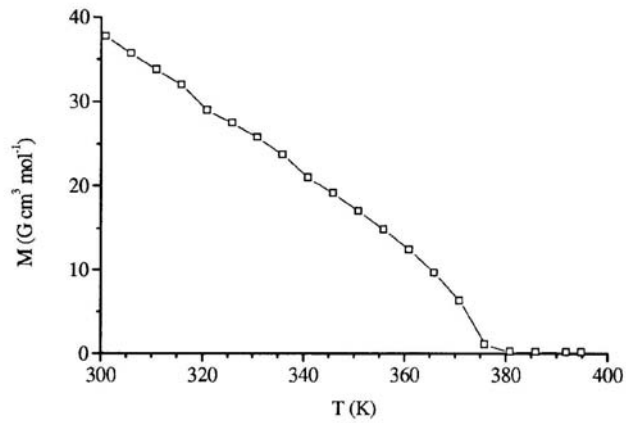
Our key insights: (1) Minimize competition between F and AF terms. Because all  $M(\text{CN})_6$  building blocks have spins only in the  $t_{2g}$  orbitals, pick a  $M'$  partner that has only  $t_{2g}$  (and no  $e_g$ ) magnetic orbitals also.

(2) Metal centers with high energy d-electrons should delocalize more strongly into the cyanide  $\pi^*$  orbital, thus bringing the spin density closer to the other metal center, and giving rise to higher  $T_C$ .

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## $KV^{III}[Cr^{III}(CN)_6] \cdot 2H_2O$ : A Ferrimagnet at 376 K (103 °C)

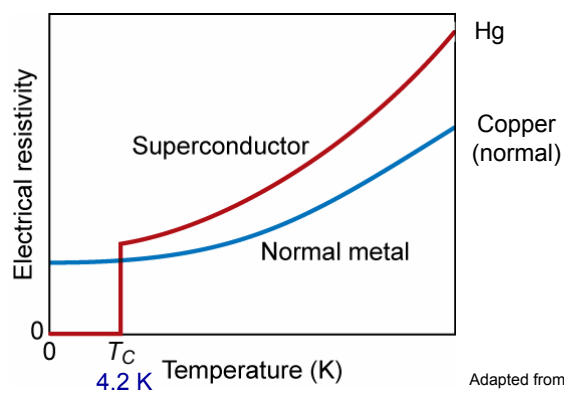


Holmes and Girolami, *J. Am. Chem. Soc.* 1999, 121, 5593

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## Superconductivity



Adapted from Fig. 20.26, Callister 7e.

- $T_c$  = temperature below which material is superconductive  
= critical temperature

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## Limits of Superconductivity

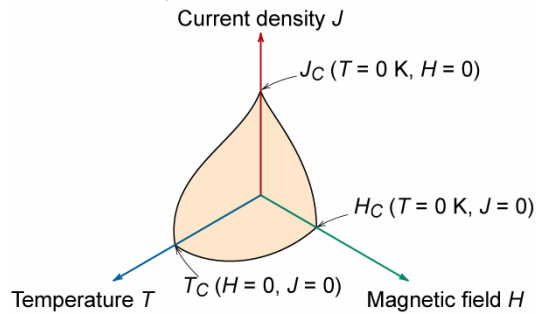
- 26 metals + 100's of alloys & compounds

- Critical Currents and Fields:

$J_c$  = critical current density if  $J > J_c$  not superconducting

$H_c$  = critical magnetic field if  $H > H_c$  not superconducting

$$H_c = H_0 (1 - (T/T_0)^2)$$



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## Advances in Superconductivity

- This research area was stagnant for many years.

Everyone assumed  $T_{c,max}$  was about 23 K

Many theories said you couldn't go higher

- 1987:  $T_c > 30$  K

ceramics of form  $Ba_{1-x} K_x BiO_{3-y}$

Started enormous race.

Y  $Ba_2Cu_3O_{7-x}$   $T_c = 90$  K

$Tl_2Ba_2Ca_2Cu_3O_x$   $T_c = 122$  K

tricky to make since oxidation state is quite important

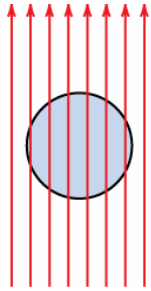
- Values now stabilized at ~120 K

38

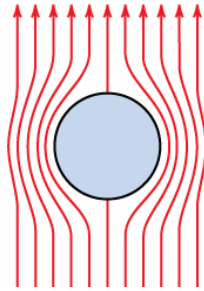


## Meissner Effect

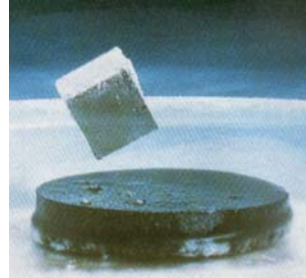
- Superconductors expel magnetic fields



normal



superconductor

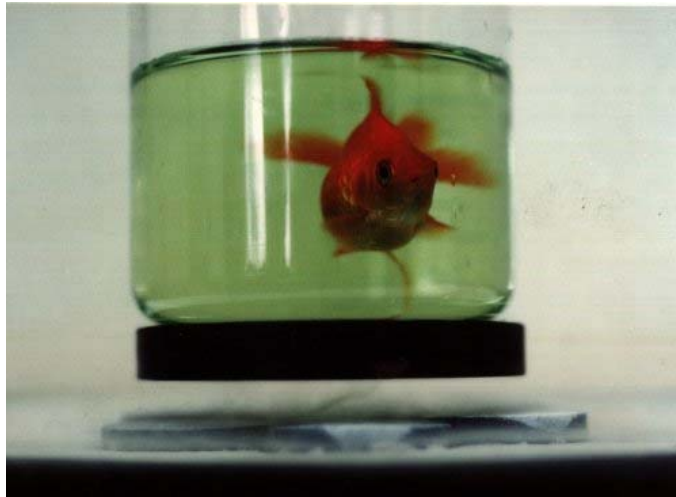


- This is why a superconductor will float above a magnet

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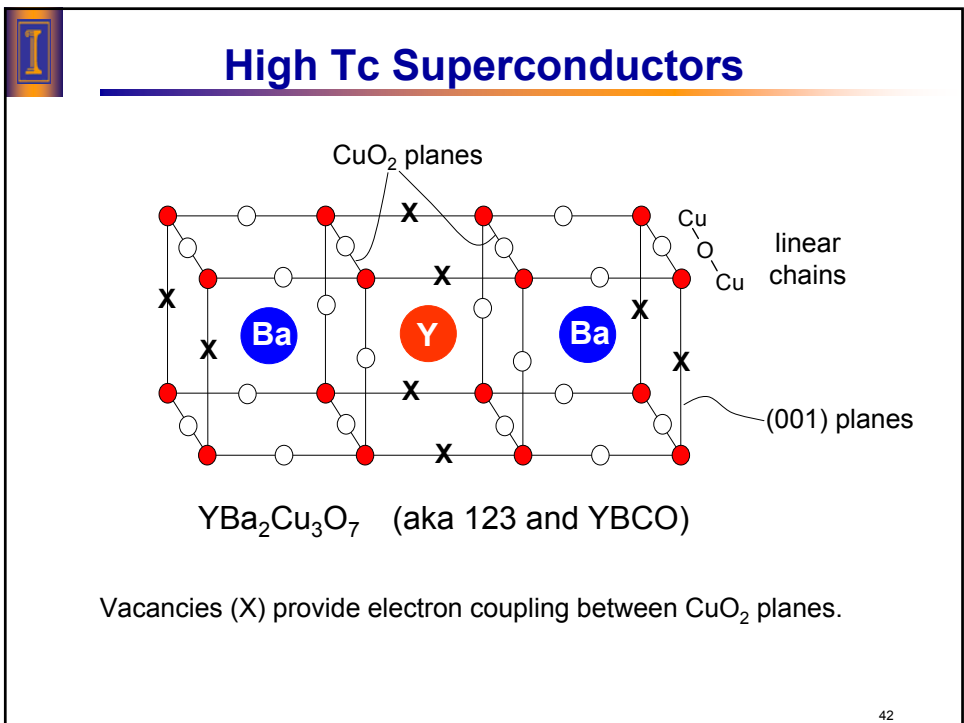
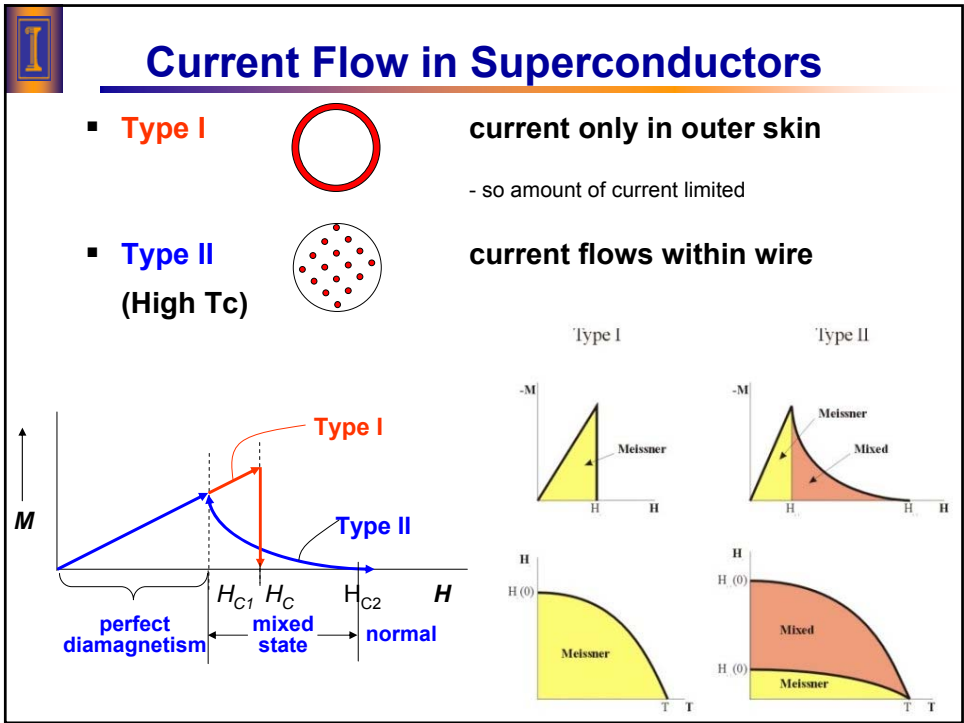


## Meissner Effect



**MLF: magnetically levitated fish**

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## High Tc Superconductors

YBa<sub>2</sub>Cu<sub>3</sub>O<sub>7</sub> (123, YBCO)

## High Tc Superconductors

YBa<sub>2</sub>Cu<sub>3</sub>O<sub>7</sub> (123)

(a) magnitude : 50,000

**SEM of crystal grains and spiral steps.**

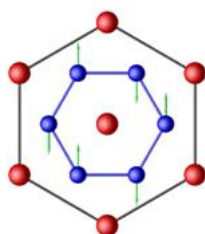
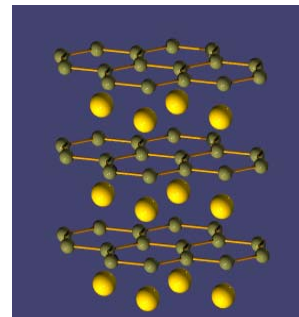
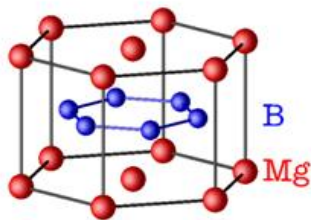
(b) magnitude : 150,000  
inclination of 40°

**SEM: tilt angle of 40° stack structure of spiral steps, each with the height of 4 to 5 nanometers.**



## High Tc Superconductors

MgB<sub>2</sub> T<sub>c</sub> = 39K  
highest T<sub>c</sub> metal



Vibrational normal mode  
of the boron atoms  
in a lattice oscillation mode  
that is essential for  
superconductivity in MgB<sub>2</sub>

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## Summary

- A magnetic field can be produced by putting a current through a coil.
- **Magnetic induction** is a change in magnetic moment from electrons; occurs when a material is subjected to a magnetic field.
- Types of material response to a field are:
  - ferri- or ferro-magnetic** (large magnetic induction)
  - paramagnetic** (poor magnetic induction)
  - diamagnetic** (opposing magnetic moment)
- **Hard magnets:** large **coercivity**.
- **Soft magnets:** small coercivity.
- **Magnetic storage media:**
  - particulate  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub> in polymeric film (tape or floppy)
  - thin film CoPtCr or CoCrTa on glass disk (hard drive)

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## Summary

### Magnetic Ordering in Solids

- **Diamagnetism:** No unpaired  $e^-$
- **Paramagnetism:** Unpaired  $e^-$ , disordered and fluctuating
- **Ferromagnetism:** All unpaired  $e^-$  spins aligned parallel
- **Antiferromagnetism:** Unpaired  $e^-$  aligned antiparallel
- **Ferrimagnetism:** Unpaired  $e^-$  aligned antiparallel but don't fully cancel out

### Magnetic Superexchange

- Unpaired electron spins couple through covalent interactions with intervening ligand
- $\frac{1}{2}$  filled metal orbital +  $\frac{1}{2}$  filled metal orbital, AFM SE
- $\frac{1}{2}$  filled metal orbital + empty metal orbital, FM SE
- Strength of superexchange interaction increases as covalency increases