

# PY3P04 Magnetic Properties of Solids

J. M. D. Coey

- 1 Introduction
- 2 Basic concepts
3. Magnetism of the electron
4. Magnetism of localized electrons on the atom
- 5 Paramagnetism
6. Ferromagnetism.
7. Miscellaneous Topics
8. Magnetic Applications



Comments and corrections please: [jcoey@tcd.ie](mailto:jcoey@tcd.ie)

# Magnetic Properties of Solids

## Condensed Matter II

PY304

J.M. D. Coey

12 lectures + Tutorials

### Recommended books

- J M D Coey: *Magnetism and Magnetic Materials*, Cambridge 2010:

A detailed advanced text. Selected sections only required for PY3PO4

- Stephen Blundell *Magnetism in Condensed Matter*, Oxford 2001

A readable treatment of the basics.

- J. Crangle; *The Magnetic Properties of Solids*, Arnold 1977: 1990

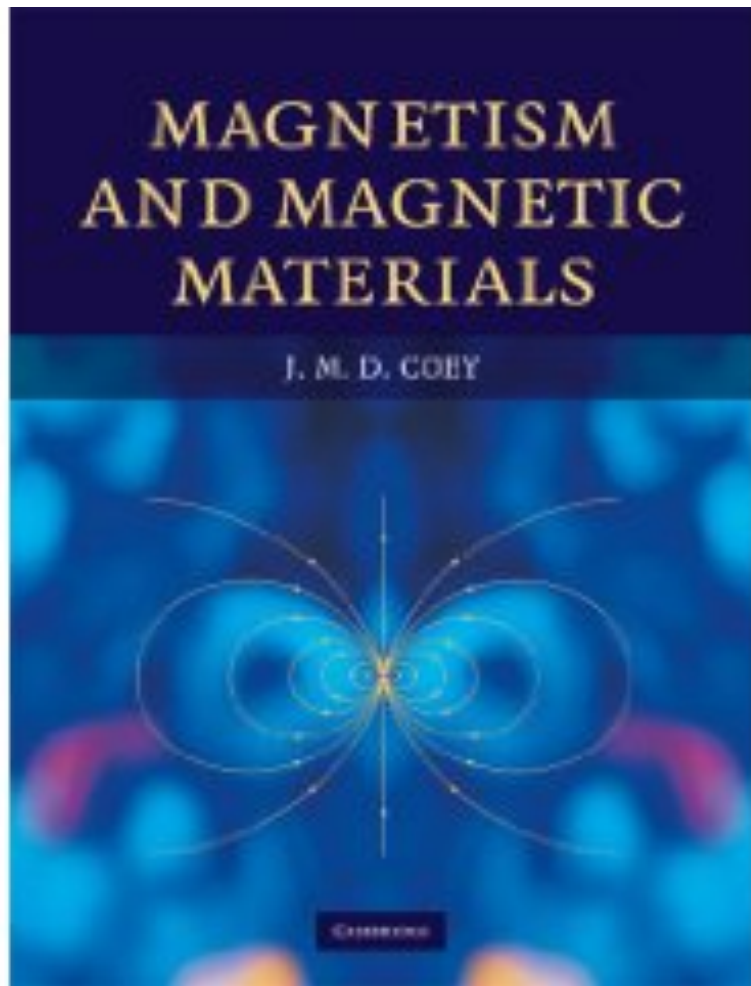
A short book which treats the material at an appropriate level.

- David Jiles *Introduction to Magnetism and Magnetic Materials*, Chapman and Hall 1991; 1997; 2015

A more detailed introduction, written in a question and answer format.

*Mondays at 15.00; Tuesdays at 16.00, Thursdays at 15.00*





638 pages. Published March 2010

Order from [Amazon.co.uk](https://www.amazon.co.uk) for just £48 !

[www.cambridge.org/9780521816144](http://www.cambridge.org/9780521816144)

- 1 Introduction
  - 2 Magnetostatics
  - 3 Magnetism of the electron
  - 4 The many-electron atom
  - 5 Ferromagnetism
  - 6 Antiferromagnetism and other magnetic order
  - 7 Micromagnetism
  - 8 Nanoscale magnetism
  - 9 Magnetic resonance
  - 10 Experimental methods
  - 11 Magnetic materials
  - 12 Soft magnets
  - 13 Hard magnets
  - 14 Spin electronics and magnetic recording
  - 15 Other topics
- Appendices, conversion tables.

# 1.1 Course overview

## 1 Introduction

- 1.1 Historical background.
- 1.2 Magnetization and hysteresis; Overview

## Lecture 1

6-27

## 2 Basic concepts

- 2.1 Moments and Magnetization
- 2.2 Two fields  $B$  and  $H$
- 2.3 Energy and Force
- 2.4 Units and Dimensions

## Lectures 2,3

25-55

## 3. Magnetism of the electron

- 3.1 Spin and Orbital moment
- 3.2 Electrons in a Field
- 3.3 Magnetism of electrons in solids.
- 3.4 Localized and delocalized electrons
- 3.5 Theory of the electronic magnetism

## Lectures 4,5

56-71

## 4. Magnetism of localized electrons on the atom

- 4.1 The hydrogenic atom and angular momentum.
- 4.2 The many-electron atom.
- 4.3 Addition of angular momenta
- 4.4 Zeeman interaction
- 4.4 Ions in solids

## Lectures 6,7

72-109

## 5 Paramagnetism

- 5.1 Classical Theory
- 5.2 Quantum theory
- 5.3 Paramagnetism of metals

## Lecture 8

110-122

## 6. Ferromagnetism.

- 6.1 Mean field theory
- 6.2 Exchange Interactions.
- 6.3 Ferromagnetic domains
- 6.4 Magnetic measurements
- 6.5 Hard and soft ferromagnets

## Lecture 9,10

123-151

## 7. Miscellaneous Topics

- 7.1 Antiferromagnetism
- 7.2 Ferrimagnets.
- 7.3 Other forms of magnetic order
- 7.4 Spin waves
- 7.5 Magnetic neutron scattering

## Lecture 11

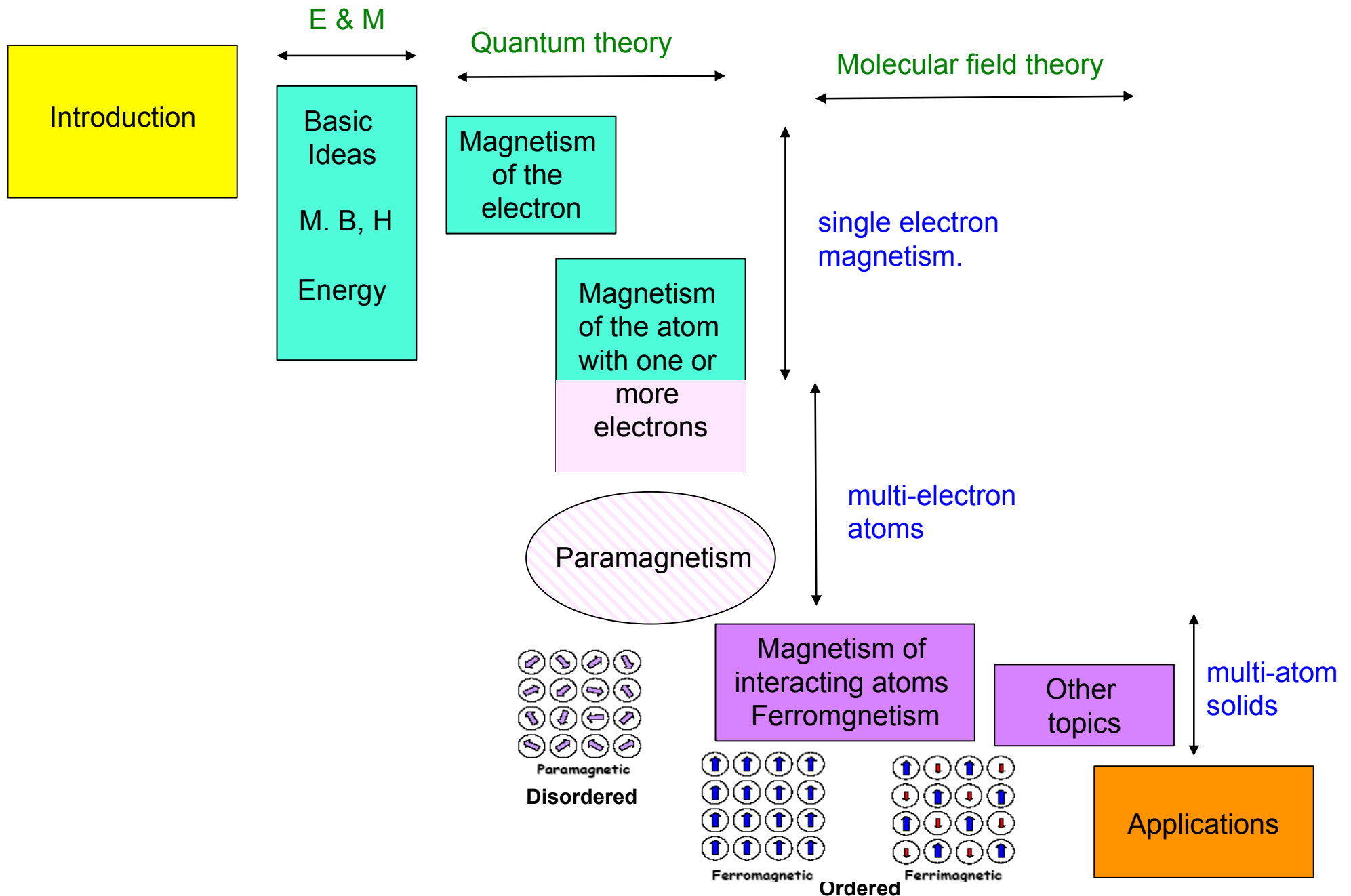
152-172

## 8. Magnetic Applications

- 8.1 Hard magnets
- 8.2 Soft magnets
- 8.3 Magnetic recording
- 8.4 Spin electronics

## Lecture 12

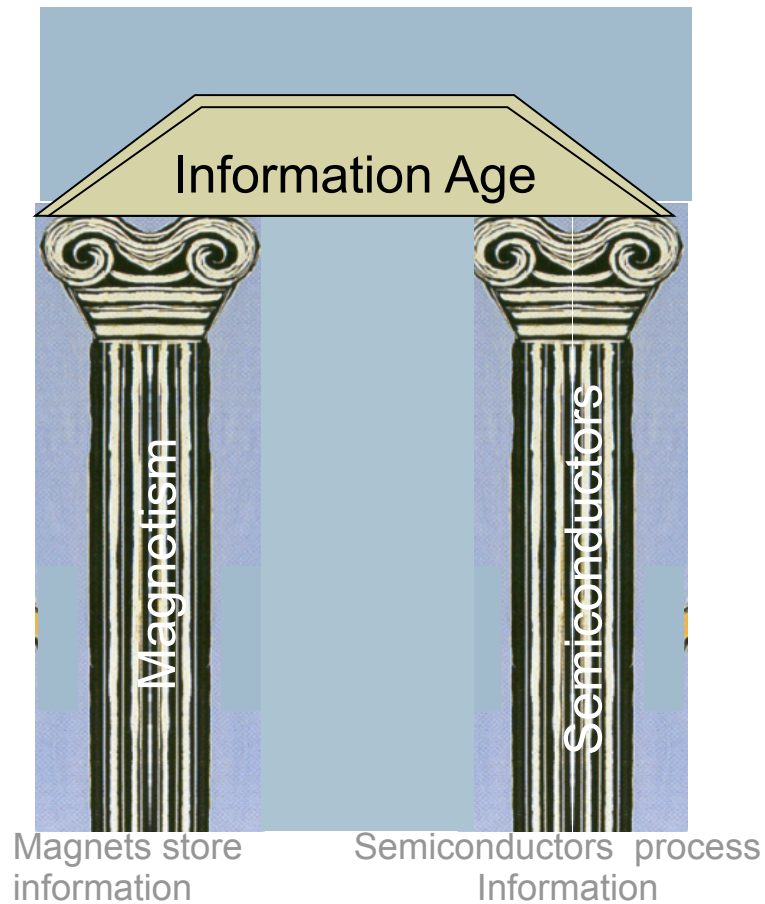
173-201



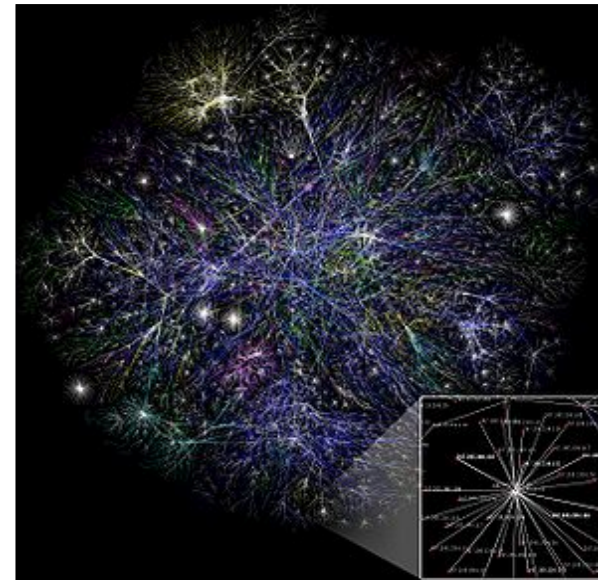
# **I. Introduction**

Condensed Matter II presents the basic concepts behind magnets and semiconductors.

Magnetism and semiconductor physics are the two pillars supporting information technology



$10^{21}$  bytes of information are stored every year. *Magnetically*

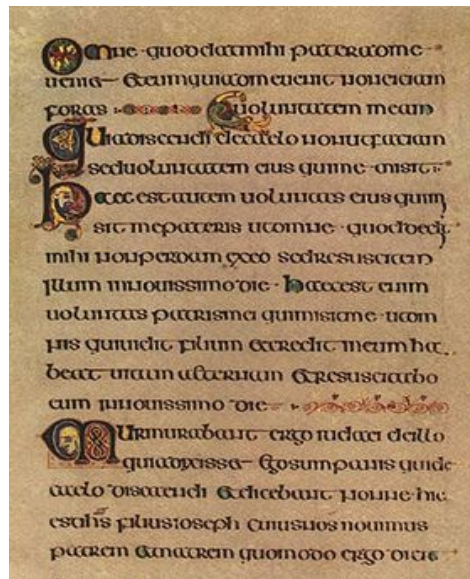


Every year we make more transistors and magnets in our fabs than we grow grains of wheat and rice in our fields.

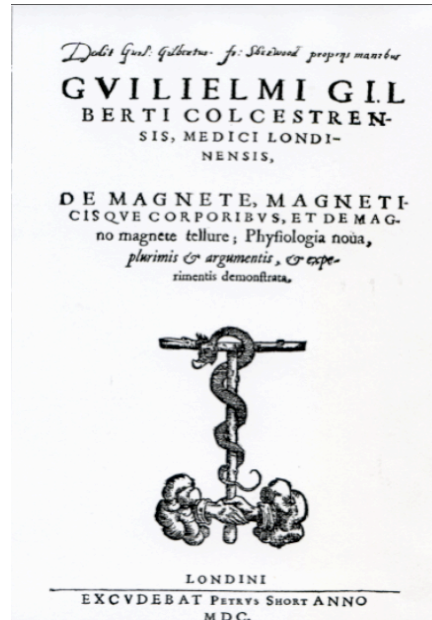
INTEL make  $5 \times 10^9$  transistors per second. ( $20 \times 10^6$  pp/a)



# The cost of a copy

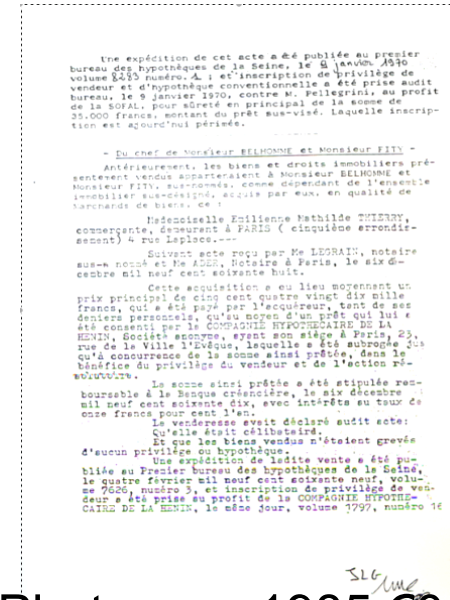


800; €2,000



Gilbert 1600 €1

Gutenberg  
1455 €20



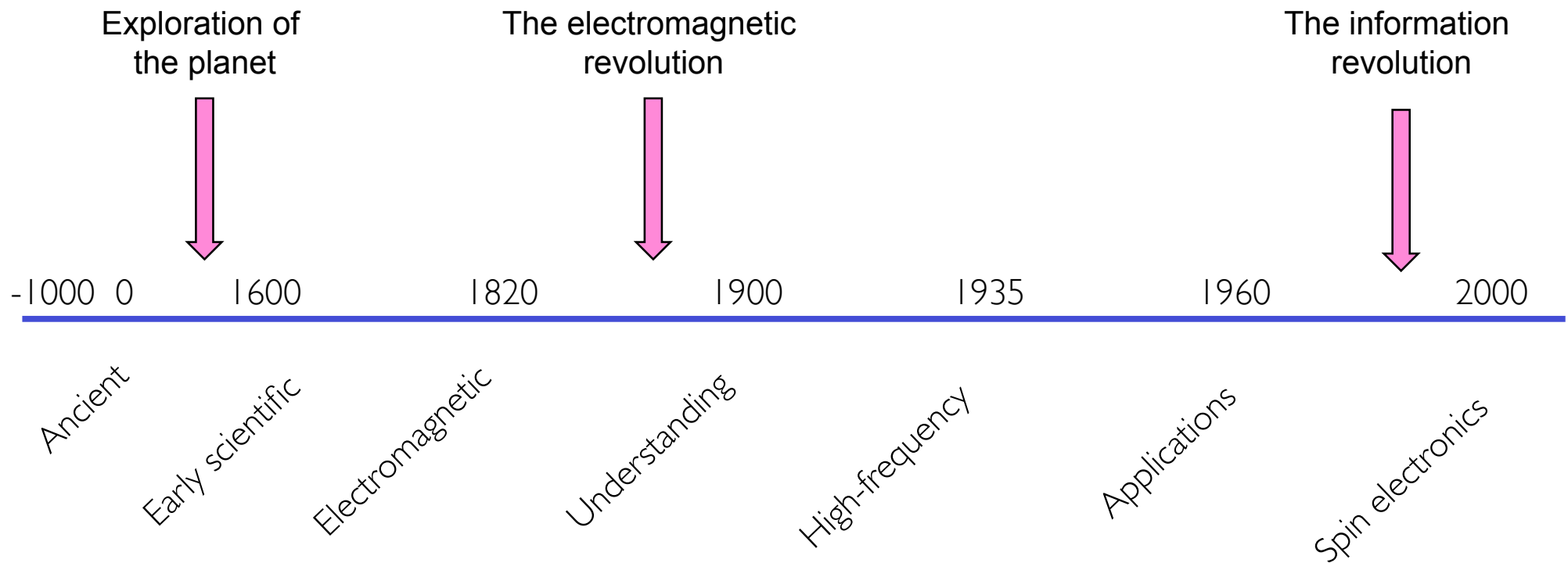
Photocopy 1985 €0.05



PDF 2008 €0.002

## 1.1 A little history

*Magnetism has changed the world three times*



*Seven ages of Magnetism*

[www.tcd.ie/Physics/Magnetism/Guide/magmoments/php](http://www.tcd.ie/Physics/Magnetism/Guide/magmoments/php)

# The Three Magnetic Revolutions

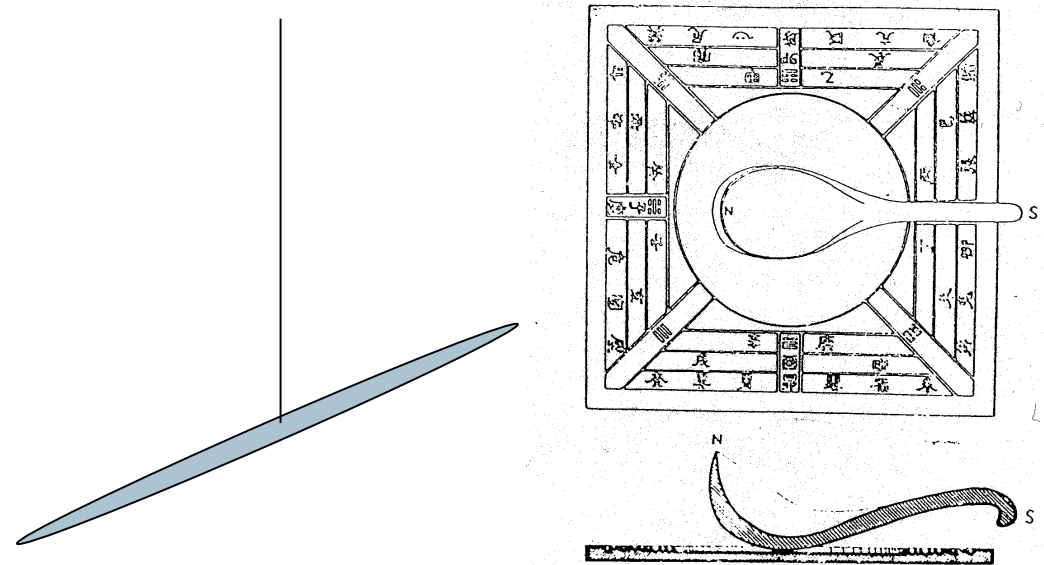
## 1 - The Compass

*Printing, gunpowder and the compass: These three have changed the whole face and state of things throughout the world; the first in literature, the second in warfare, the third in navigation; whence have followed innumerable changes, in so much that no empire, no sect, no star seems to have exerted greater power and influence in human affairs than these mechanical discoveries.*

Francis Bacon *Novum Organum* 1620



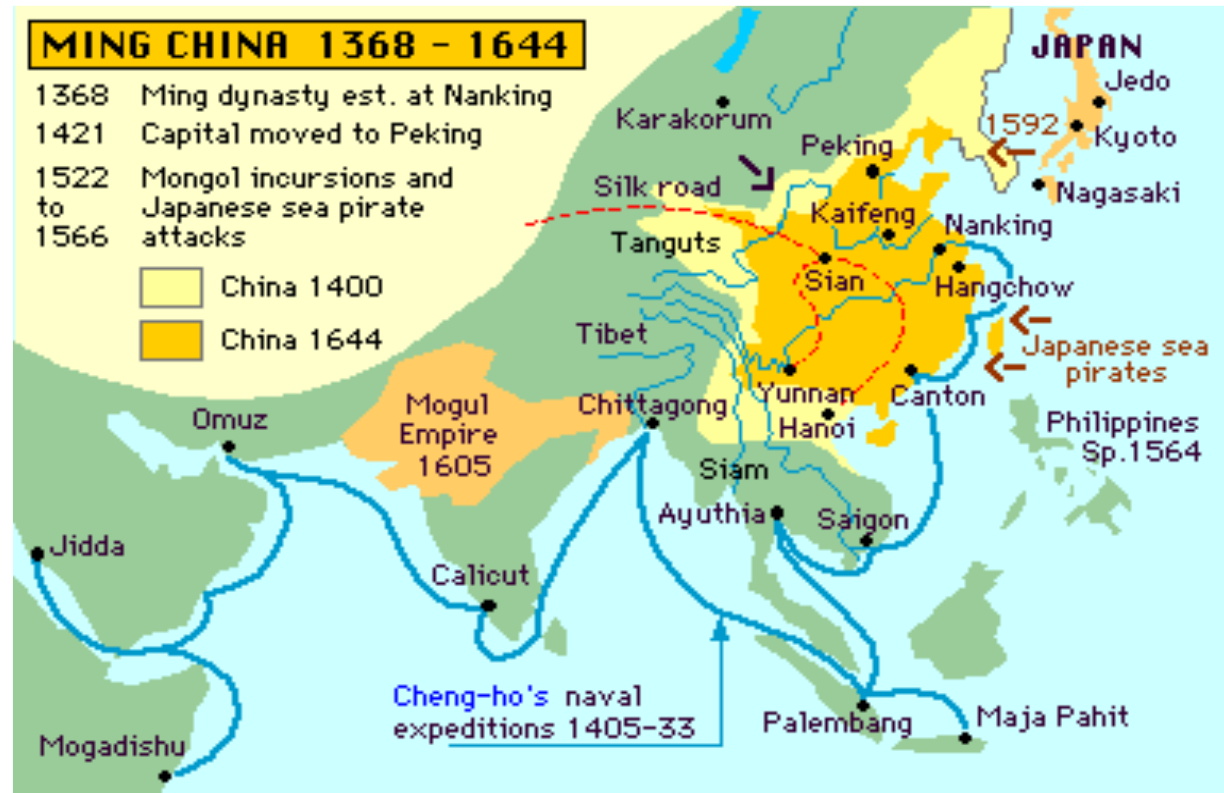
## The suspended compass



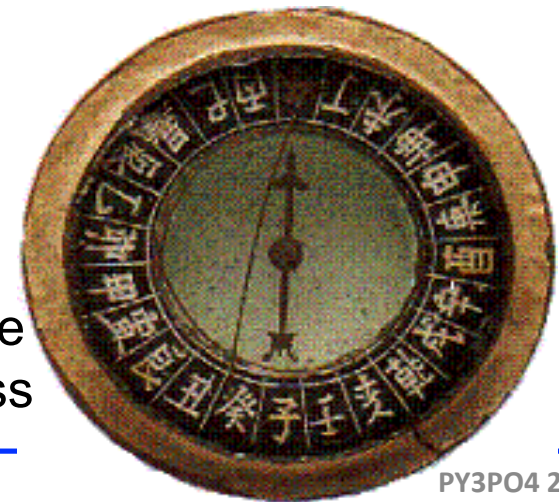
Shen Kua (沈括) reported how to make magnetized iron needles in 1060, and described the suspended needle compass in 1088. *Thermoremanence* and *induced magnetization* were discovered in China. The English monk Alexander Neckham, working at the University of Paris, gives the first European account of the compass in 1190.



Zheng He 郑和 1371-1432



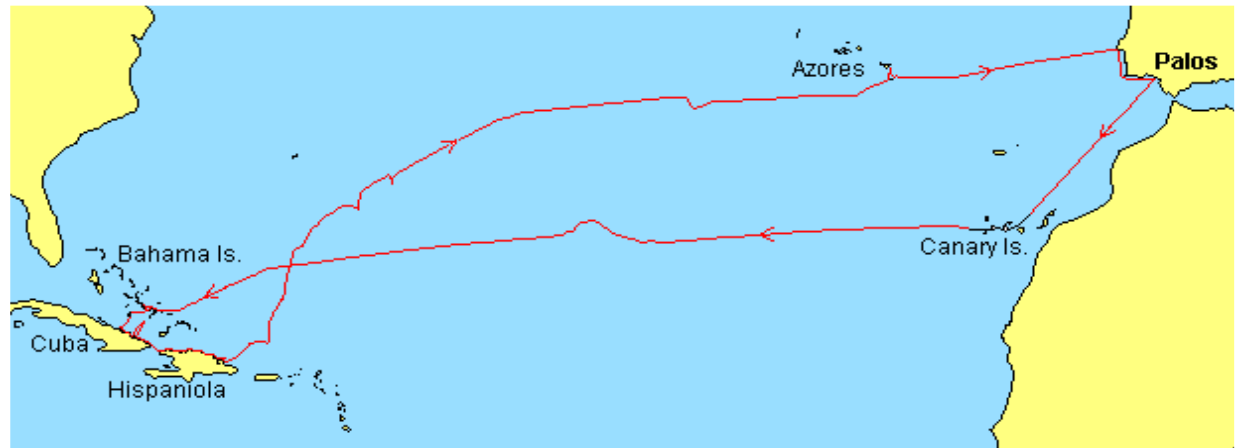
Chinese compass



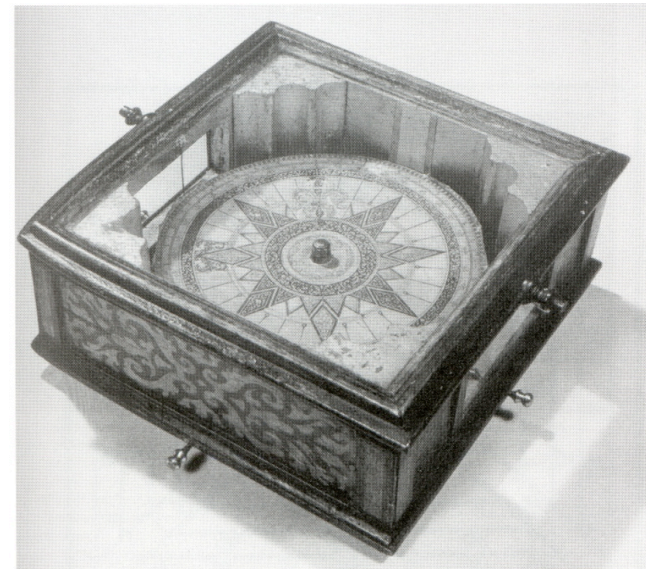




Christopher Columbus  
1452 - 1506



1492



Portuguese compass

# The Three Magnetic Revolutions

## 2 - The Electromagnetic Revolution

*From a long view of the history of mankind, there can be little doubt that the most significant event of the 19th century will be judged as Maxwell's discovery of the laws of electrodynamics.*

Richard Feynmann 1970

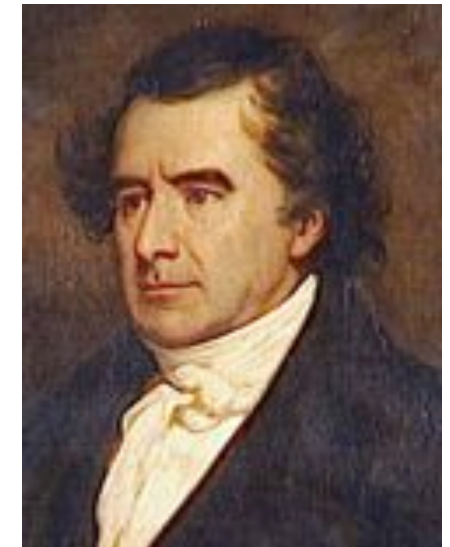
## *The electromagnetic revolution; 1820 to 1905*



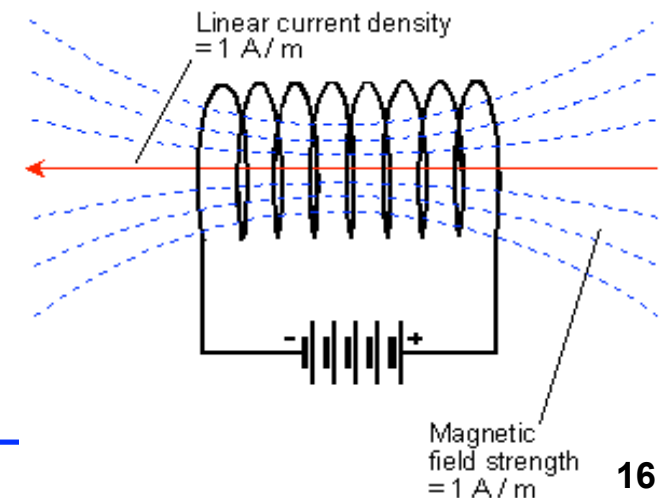
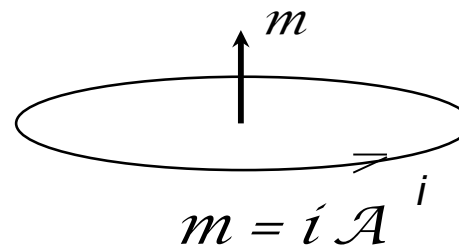
Oersted's famous 1820 experiment showed that a current-carrying conductor created a field everywhere *perpendicular* to the wire



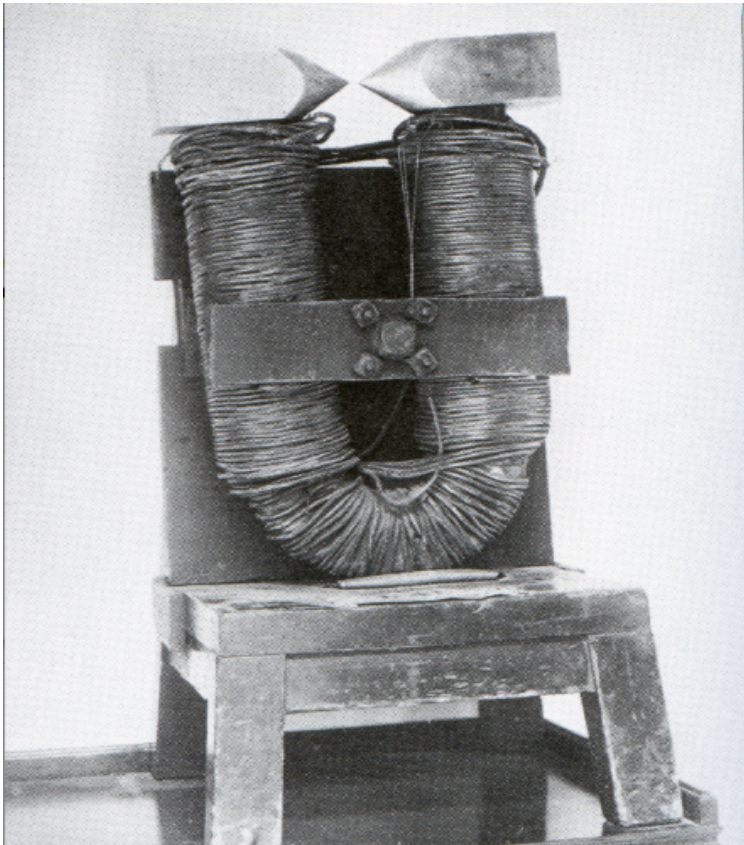
Within a week of the news reaching Paris in August 1820, Ampère and Arago showed that a current acts as a magnet, especially when wound into a solenoid. Ampère measured the force between conductors, and proposed that huge internal electric currents were responsible for the magnetism of iron.



Laplace  
Poisson  
Fresnel  
Fourier  
Biot  
Savart



It was a field day for experimentalists. The most intuitive and talented of all was Michael Faraday, who made a simple motor, discovered electromagnetic induction in 1831 and found a connection between magnetism and light.



Faraday's electromagnet

## A torrent of discoveries ensued:

1820 Oersted discovers the magnetic effect of electric currents

1821 Ampere attributes the magnetism of matter to 'molecular' currents

1821 Faraday builds a primitive electric motor

1825 Sturgeon invents the first practical electromagnet

1831 Faraday discovers electromagnetic induction

1833 Gauss and Weber build a telegraph more than 1 km long, with a galvanometer as the receiver

1845 Faraday discovers paramagnetism and diamagnetism

1847 Helmholtz states the conservation of energy in a general form

1858 The first transatlantic telegraph cable

1864-73 Maxwell formulates the theory of electromagnetism

1869 Gramme invents a practical dynamo

1879 Swan invents a practical incandescent bulb

1881 First public electric railway demonstrated in Berlin

1882 First hydroelectric power station

1885 Morse code

1887 Hertz generates and detects radio waves

1887 Michelson and Morley fail to detect the motion of the aether

1888 Tesla invents a practical AC motor

1890 Ewing describes hysteresis

1895 Curie describes the temperature variation of paramagnetic susceptibility

1896 Marconi patents the radio; transmits radio signals across the Atlantic in 1901

1898 Valdemar Poulsen invents magnetic recording





Me



High speed train; 200 km/h 1900

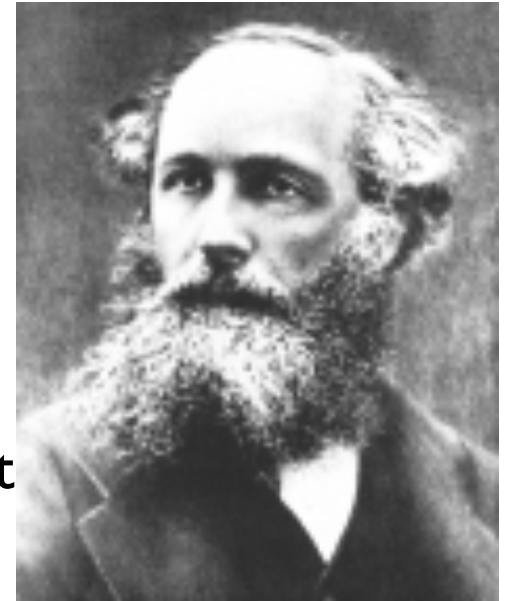


Trams

## Maxwell's equations

$$\begin{aligned}\nabla \cdot \mathbf{B} &= 0 \\ \epsilon_0 \nabla \cdot \mathbf{E} &= \rho \\ (1/\mu_0) \nabla \times \mathbf{B} &= \mathbf{j} + \epsilon_0 \partial \mathbf{E} / \partial t \\ \nabla \times \mathbf{E} &= -\partial \mathbf{B} / \partial t\end{aligned}$$

$$\begin{aligned}\nabla \cdot \mathbf{D} &= \rho \\ \nabla \times \mathbf{H} &= \mathbf{j} + \partial \mathbf{D} / \partial t\end{aligned}$$



Written in terms of two fields  $\mathbf{E}$  (N C<sup>-1</sup>) and  $\mathbf{B}$  (N (Am)<sup>-1</sup>), they are valid in *free space*.  
(Tesla)

They relate these fields to the charge density  $\rho$  (C m<sup>-3</sup>) and the current density  $\mathbf{j}$  (A m<sup>-2</sup>) at a point.

$$c = (\epsilon_0 \mu_0)^{-1/2}$$

$$c = 2.998 \times 10^8 \text{ m s}^{-1}$$

Also, the force on a moving charge  $q$ , velocity  $\mathbf{v}$

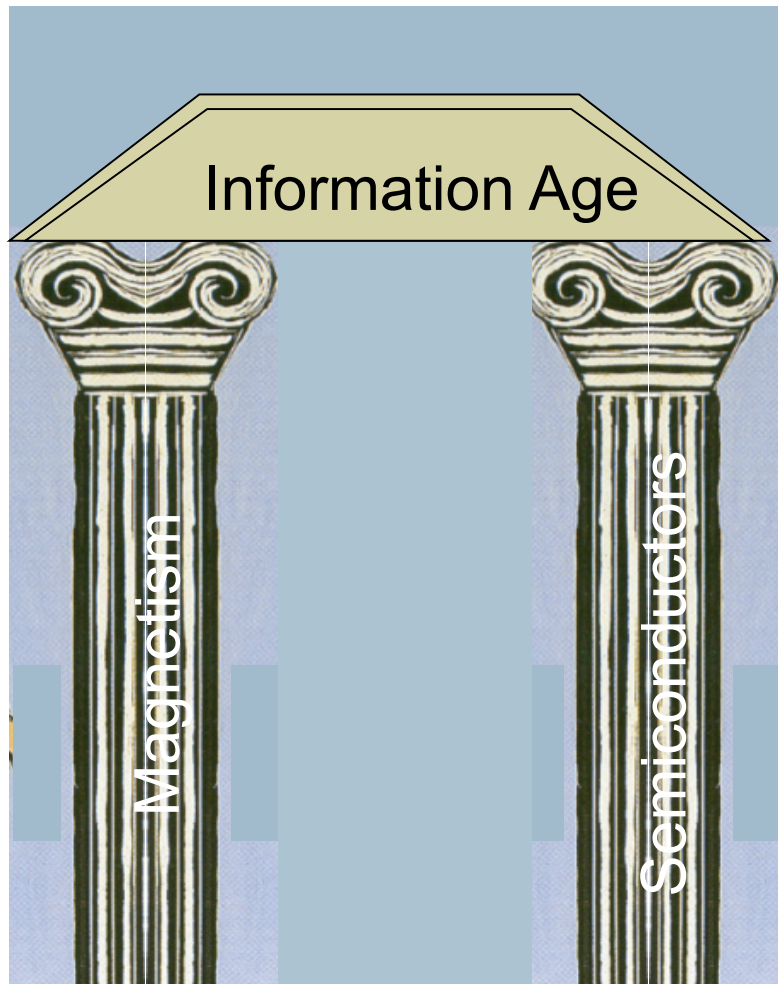
$$\mu_0 = 4\pi \times 10^{-7} \text{ T m A}^{-1}$$

$$\mathbf{f} = q(\mathbf{E} + \mathbf{v} \times \mathbf{B})$$

$$\epsilon_0 = 8.85 \times 10^{-12} \text{ C V}^{-1} \text{ m}^{-1}$$

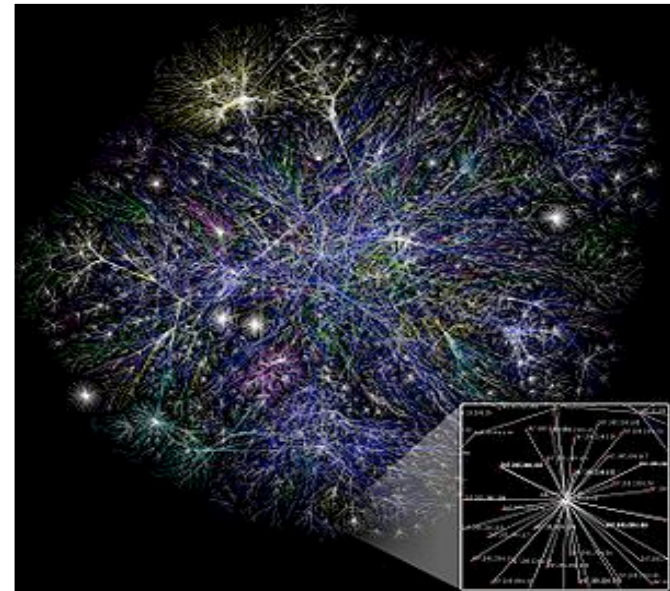
# **The Three Magnetic Revolutions**

## **3. The Information Revolution**



$>10^{21}$  bytes of information are stored every year.

$4 \cdot 10^{20}$  bytes of new capacity



Each year we store more information than in all previous human history!

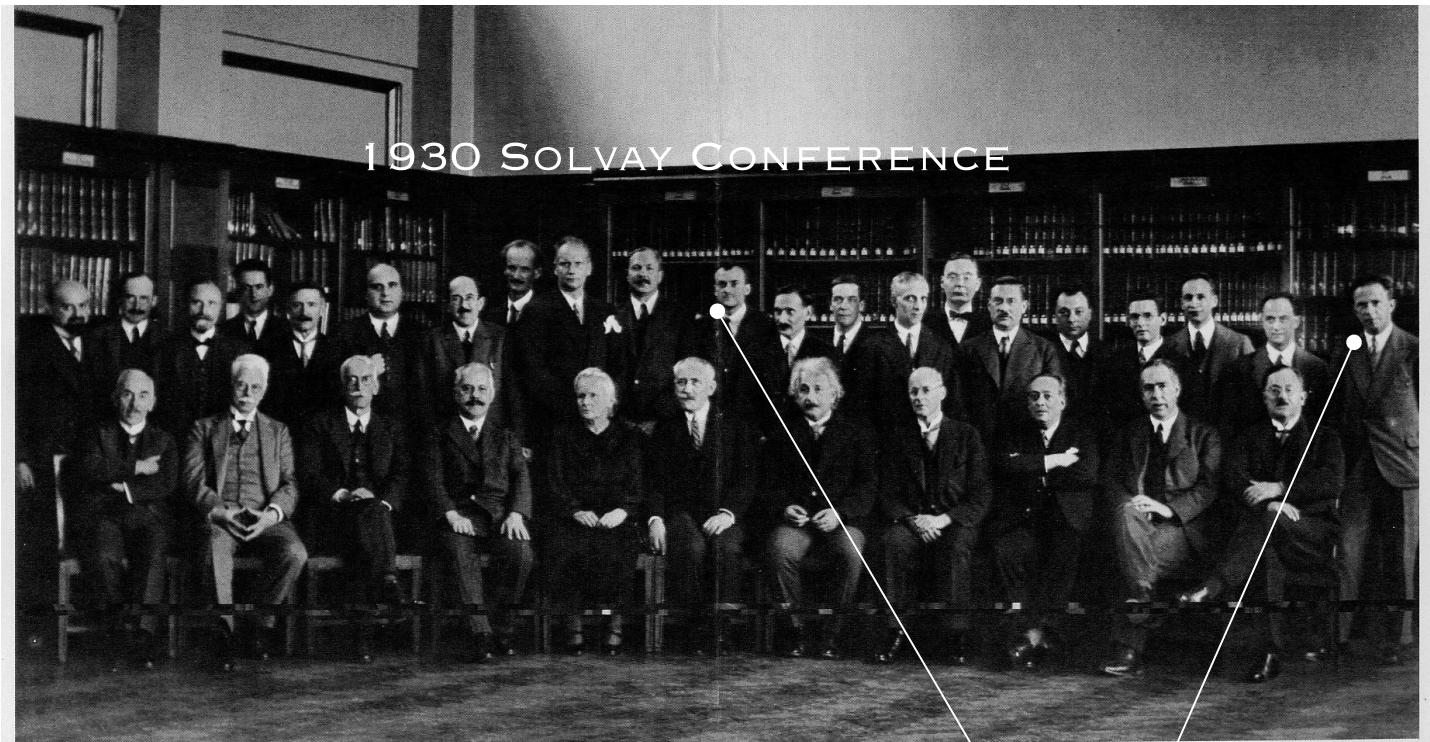


*The 1930 Solvay conference consecrated our physical understanding of magnetism in terms of quantum mechanics (exchange) and relativity (spin)*

*The  $m$  -  $J$  paradigm:*

$m$  represents the magnetic moment, mainly localized on the *atoms*

$J$  represents the exchange coupling of electron *spins*.



Dirac Heisenberg

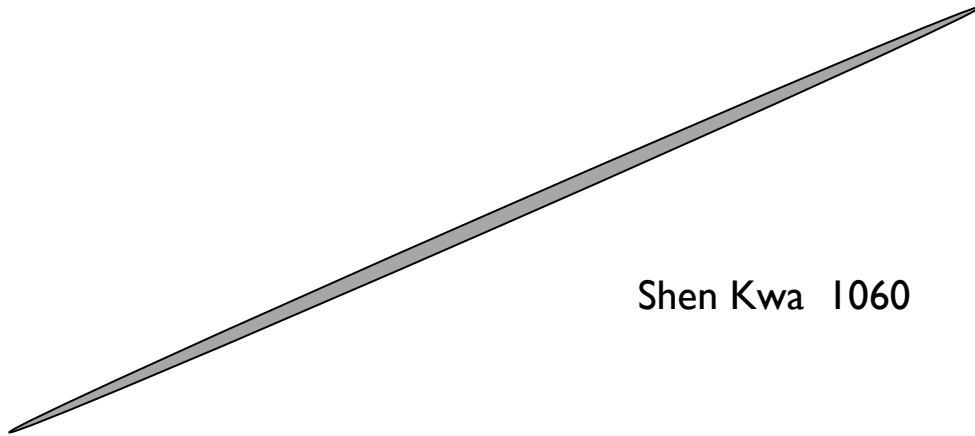
*At this point it seems that the whole of chemistry and much of physics is understood in principle. The problem is that the equations are much too difficult to solve.....*

*P.A. M. Dirac*

## The shape barrier broken: 1954



Daniel Bernouilli 1743



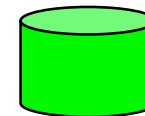
Shen Kwa 1060



Mishima 1930



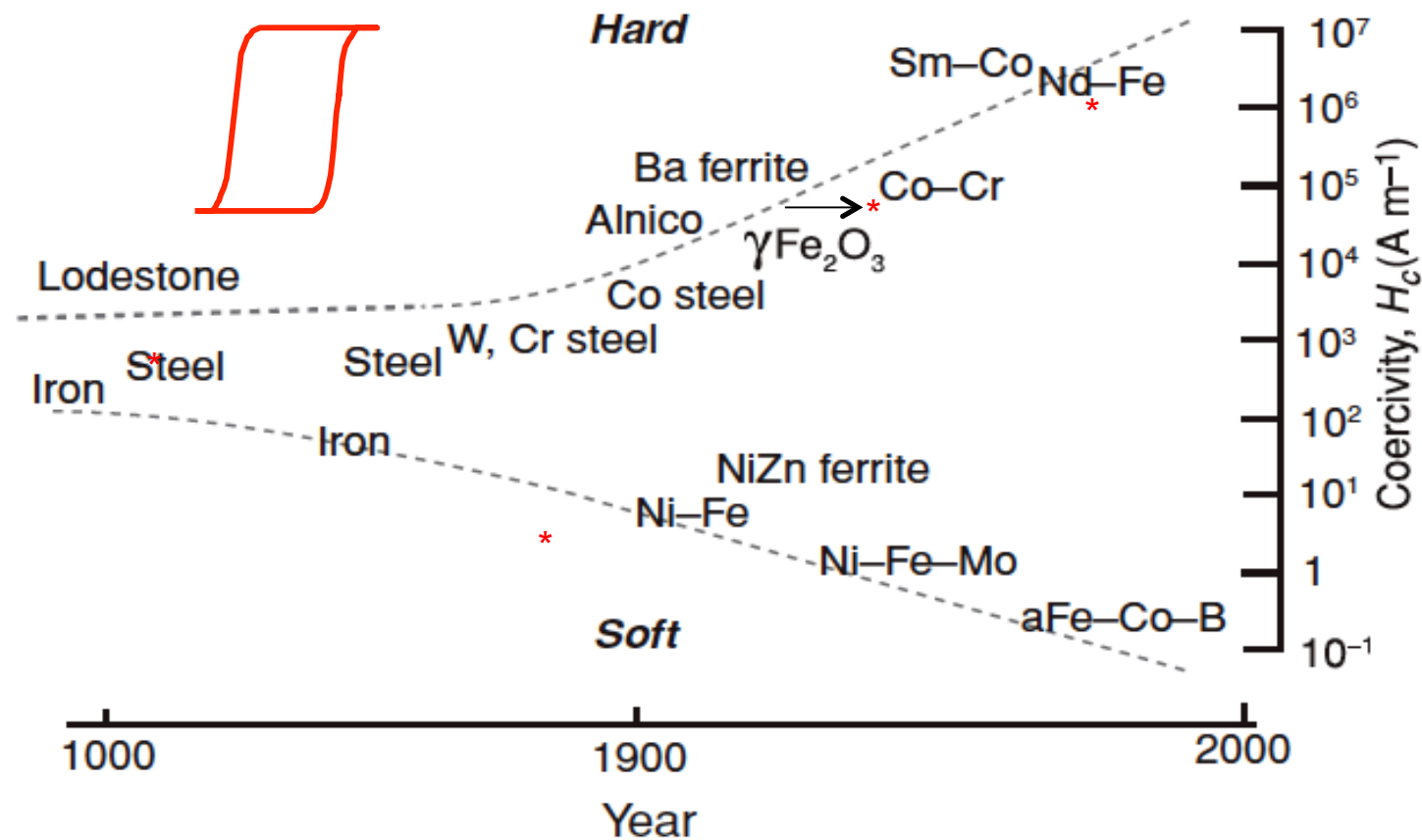
Gowind Knight 1760



Philips 1954

For centuries, magnets had to be made in awkward shapes, to avoid demagnetization.

## Coercivity



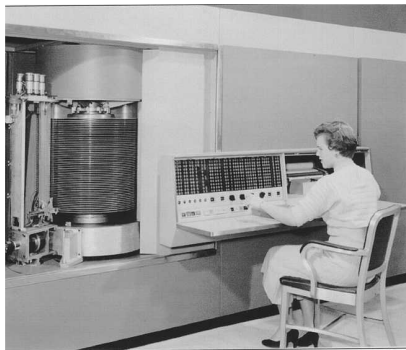
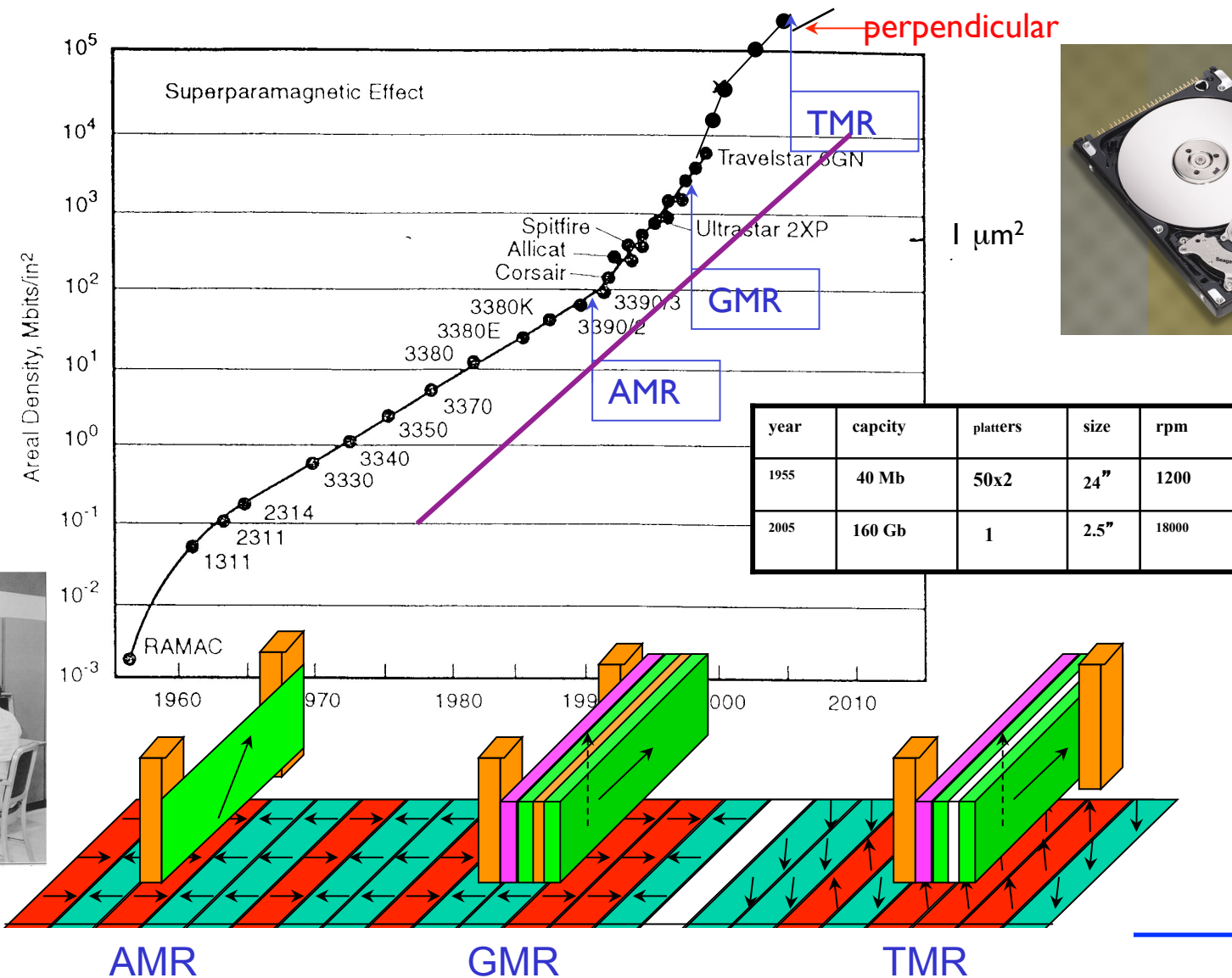
The story of magnetic materials in the 20th century was the story of mastery of coercivity

1900:  $10^3 < H_c < 10^5 \text{ A m}^{-1}$

2000:  $1 < H_c < 2 \cdot 10^7 \text{ A m}^{-1}$

Magnetic recording is the partner of semiconductor technology in the information revolution. It provides the permanent, nonvolatile storage of information for computers and the internet. ~

1 exabit ( $10^{21}$  bits) of data is stored





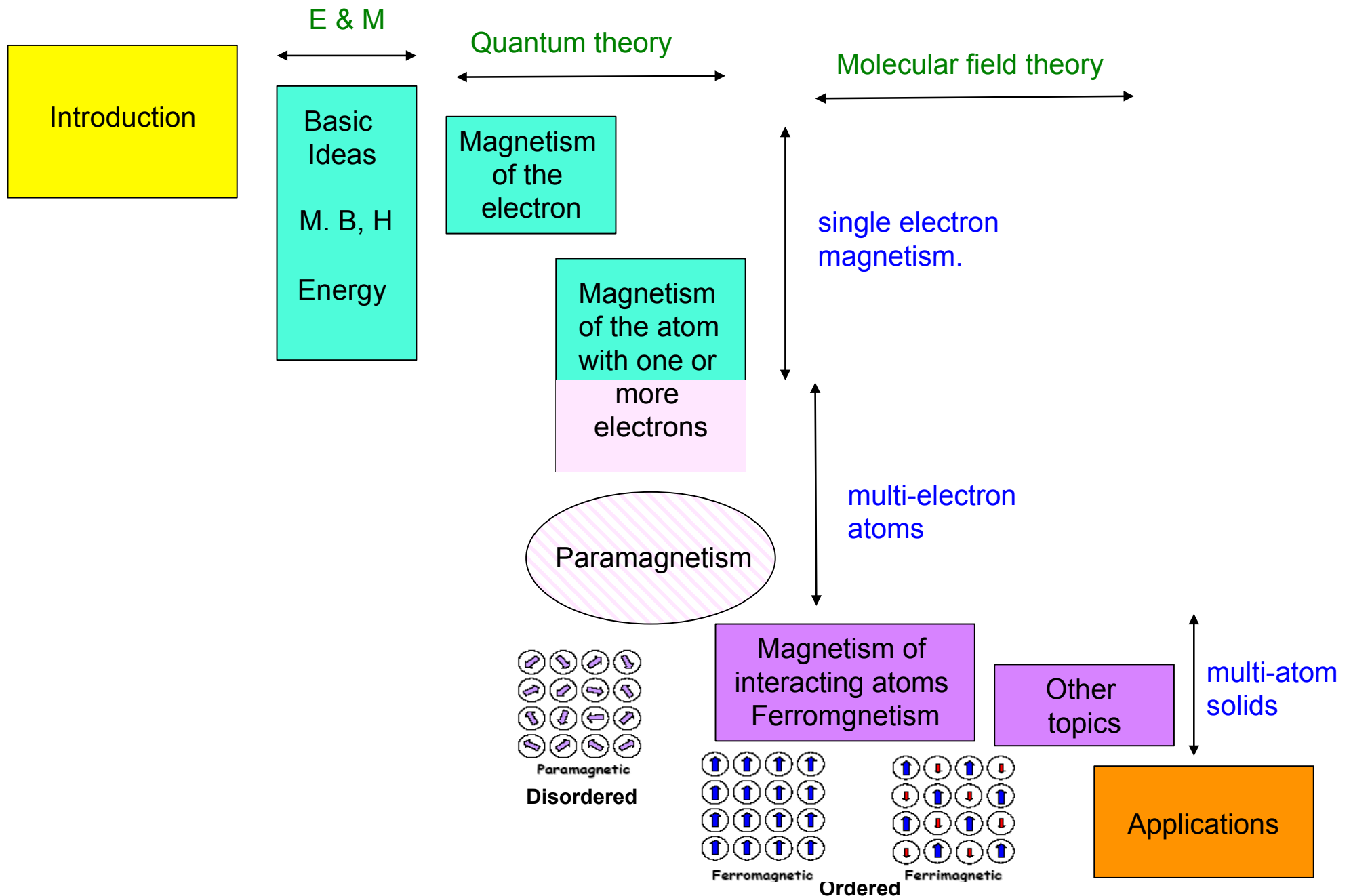


125 \$/kg in 2013

A Server;  
Facebook have  
30,000 of them

*All* the information  
accessed with  
web browsers is  
stored as  
magnetic records  
on hard discs in  
servers.

This is what the  
cloud *looks* like

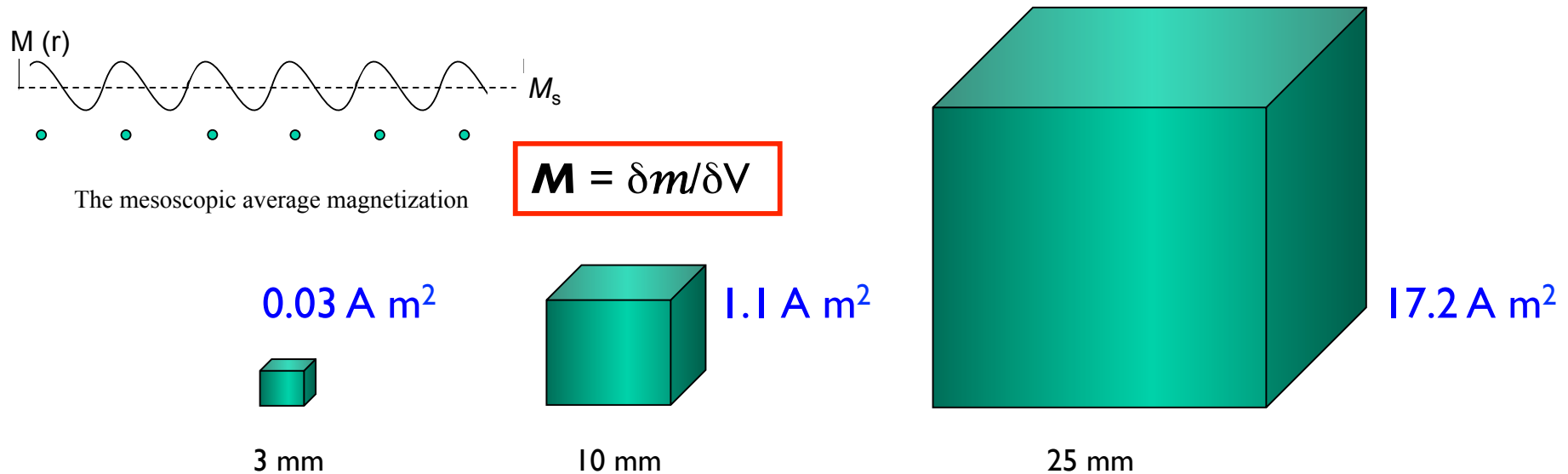


## 2. Basic concepts

This section introduces the magnetization  $\mathbf{M}$  and the two magnetic fields  $\mathbf{B}$  and  $\mathbf{H}$ . These are vectors which are defined at every position  $\mathbf{r}$  in a solid.

Units and dimensions in magnetism are discussed.

## 2.1 Magnets and magnetization



$m$  is the magnetic (dipole) moment of the magnet. It is proportional to volume

$$m = MV$$

magnetic moment      magnetization      volume

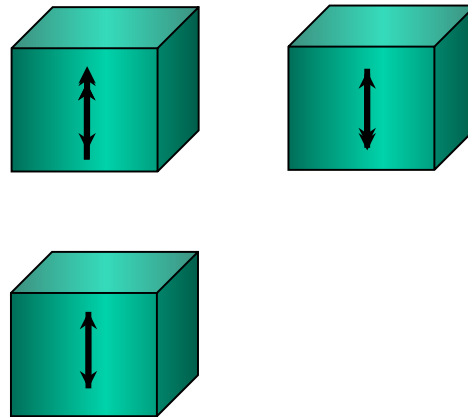
Suppose they are made of  
 $\text{Nd}_2\text{Fe}_{14}\text{B}$   
 $(M \approx 1.1 \text{ MA m}^{-1})$

What are the moments?

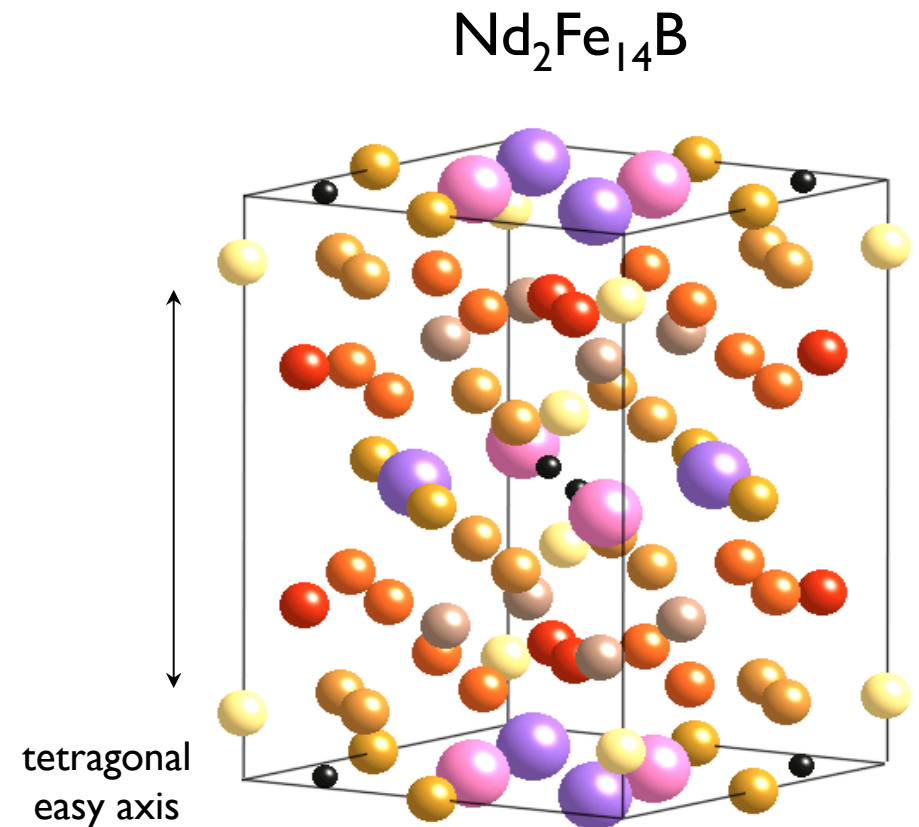
Magnetization is the property of the material;  
 Magnetic moment is a property of a particular magnet.

## Magnetic moment – a polar vector

Each magnet creates a field around it. This acts on *any* material in the vicinity but strongly with another magnet. The magnets attract or repel depending on their mutual orientation



↑ ↑	Weak repulsion
↑ ↓	Weak attraction
← ←	Strong attraction
← →	Strong repulsion

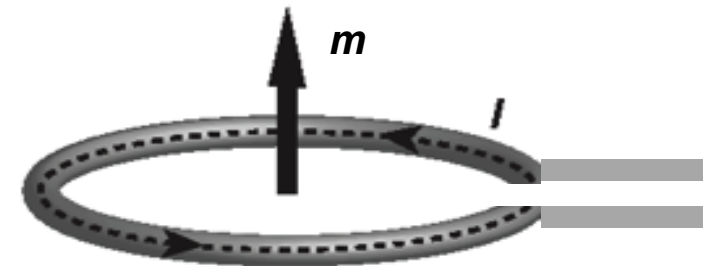


# Units

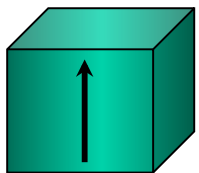
What do the units mean?

$$m - A \text{ m}^2$$

$$M - A \text{ m}^{-1}$$



Ampère, 1821. A current loop or coil is equivalent to a magnet.

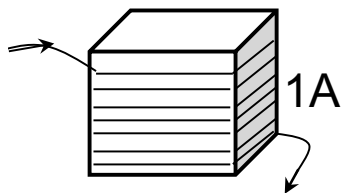


$$1 A \text{ m}^2$$

$\equiv$

$$m = I \mathcal{A}$$

area of the loop



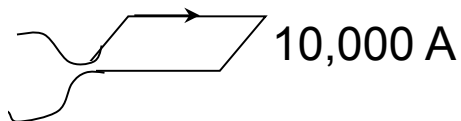
10,000 turns

$\equiv$

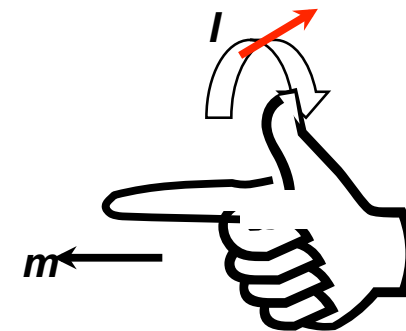
Permanent magnets  
win over electro-  
magnets at small  
sizes

$$m = n / \mathcal{A}$$

number of turns

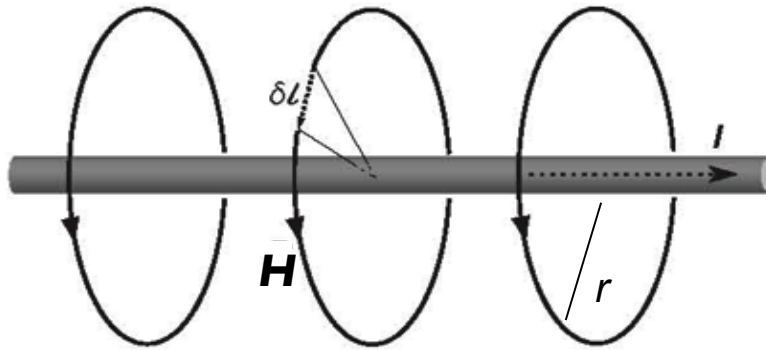


10,000 A



Right-hand corkscrew

## Magnetic field $H$ due to a current $I$



In free space  $\mathbf{B} = \mu_0 \mathbf{H}$



The relation between electric current and magnetic field was discovered by Hans-Christian Ørsted, 1820.

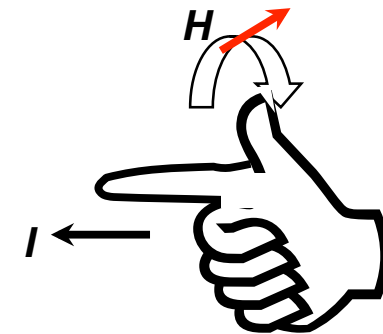
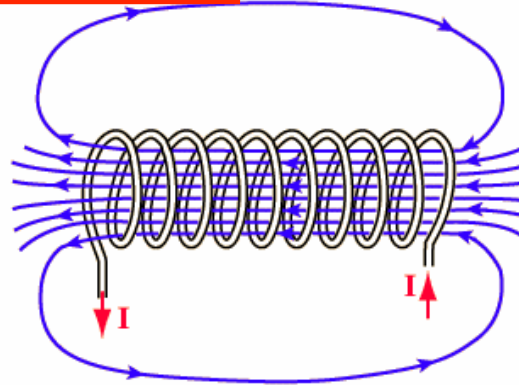
$$H = I / 2\pi r$$

$$\text{If } I = 1 \text{ A, } r = 1 \text{ mm}$$

$$H = 159 \text{ A m}^{-1}$$

Earth's field  $\approx 40 \text{ A m}^{-1}$

$$\oint \mathbf{B} d\mathbf{l} = \mu_0 I \quad \text{Ampère's law}$$

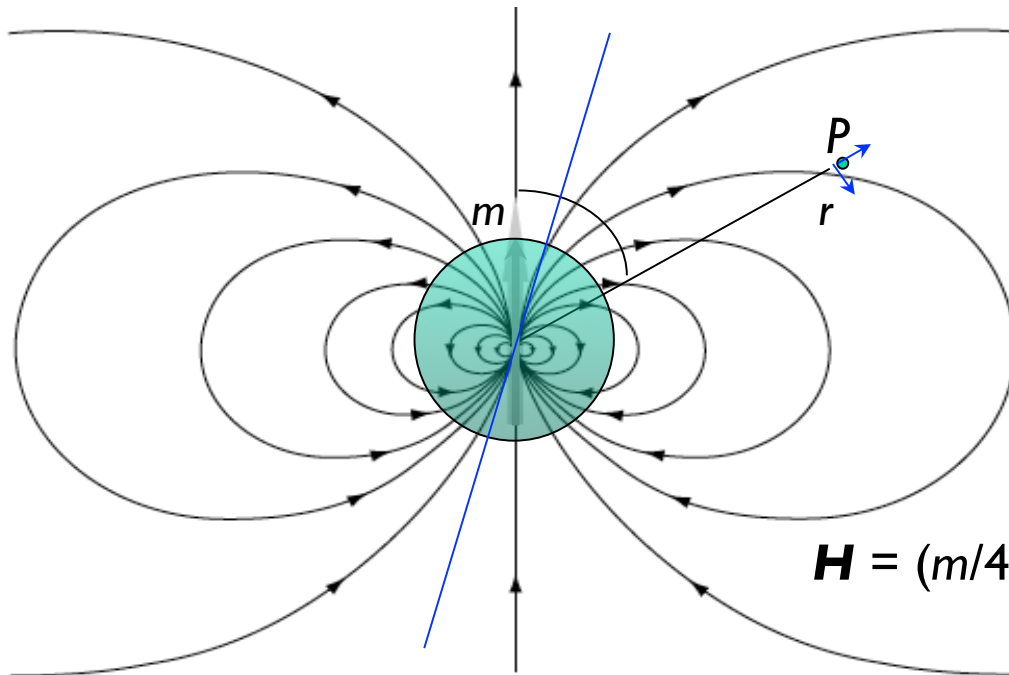


Right-hand corkscrew

long solenoid with  $n'$  turns  $\text{m}^{-1}$   $H = n' I$



## Magnetic field due to a moment $\mathbf{m}$ ; Scaling



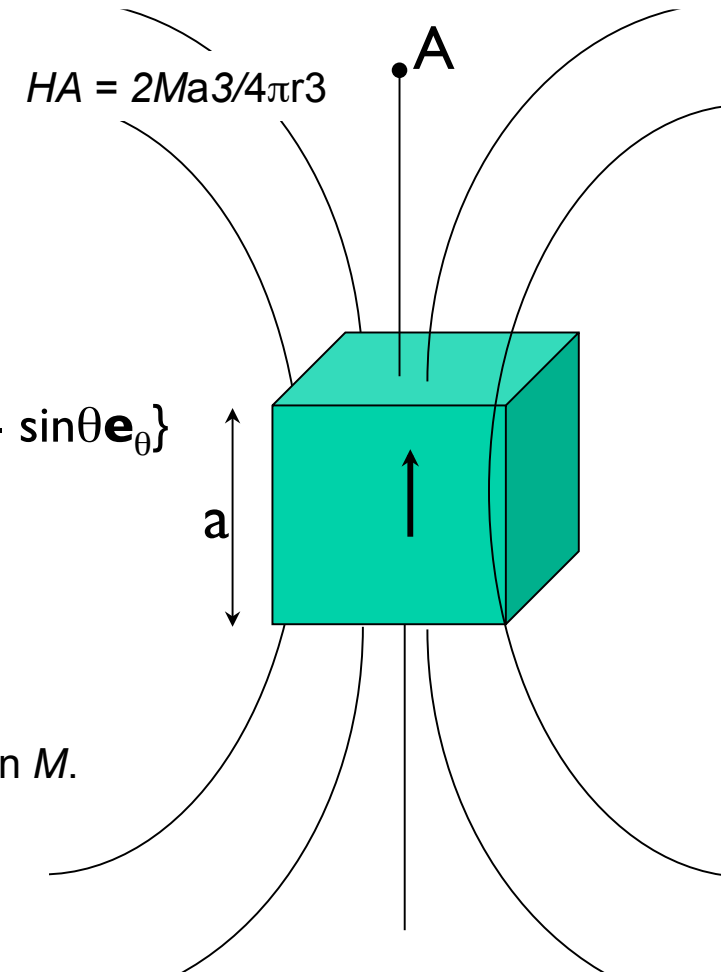
Just like the field of an electric dipole

Estimate the average magnetization of the Earth;  $r_e = 6400$  km

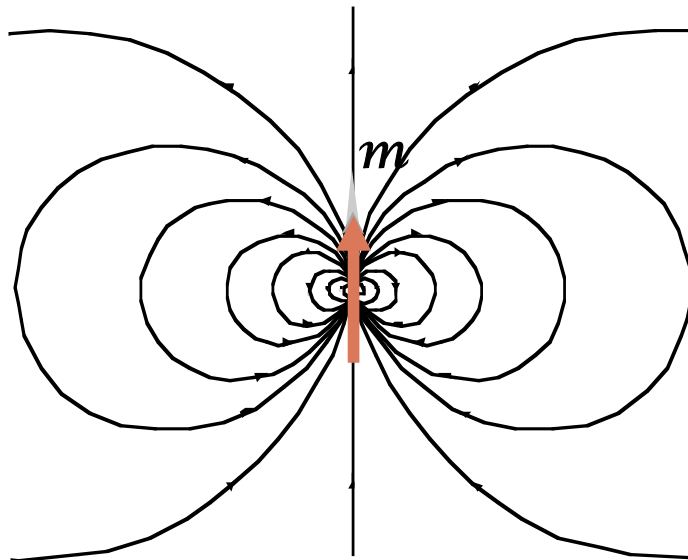
If  $a = 0.01$  m,  $r = 2a$ ,  $M = 1$  MA m<sup>-1</sup>  
 $H_A = 2M/16\pi = 40$  kA m<sup>-1</sup>

Magnet-generated fields just depend on  $M$ .  
 They are *scale-independent*

Why does magnetism lend itself to miniaturization ?



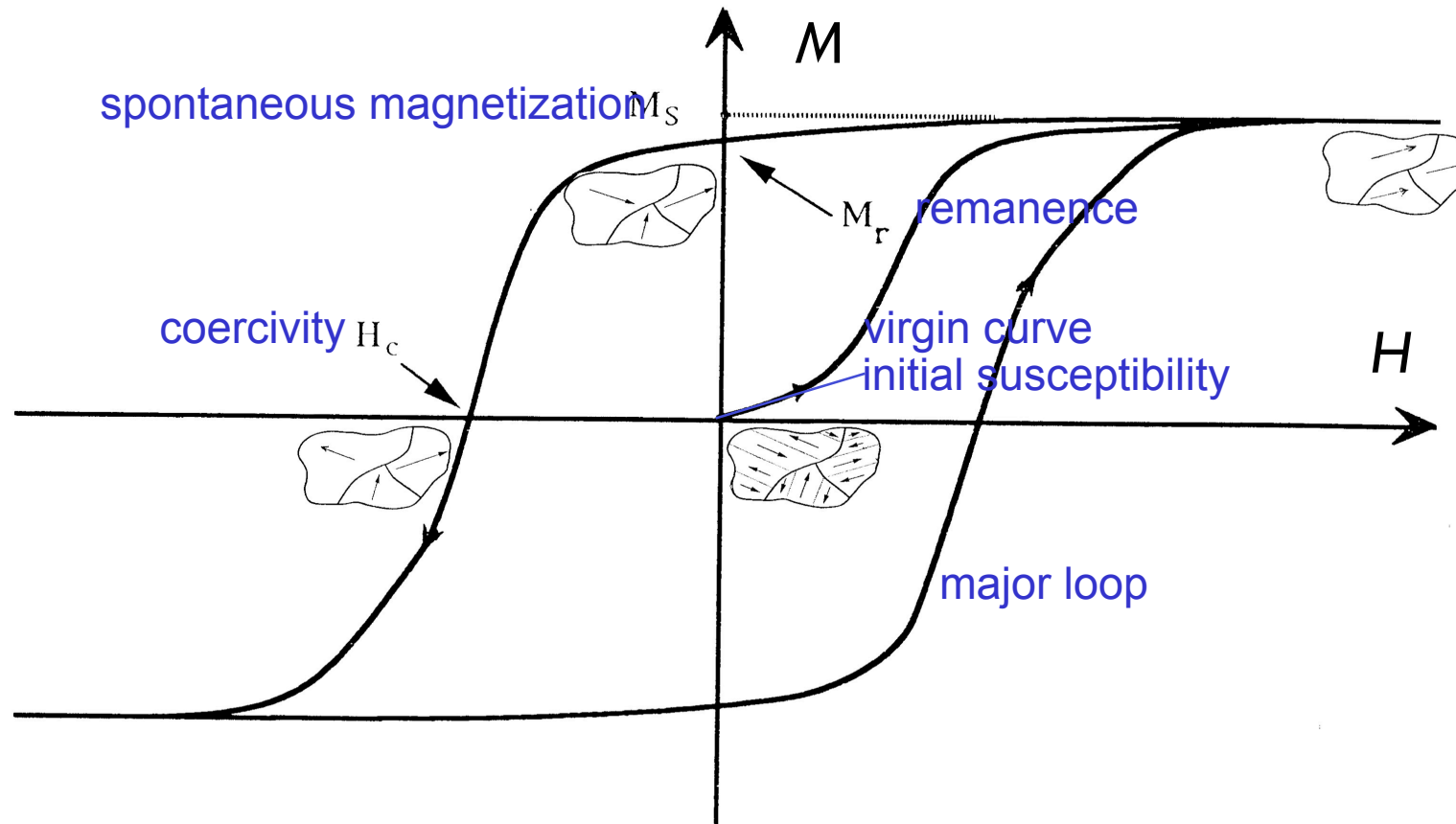




Dipole field

$$\mathbf{B}(\mathbf{r}, \theta) = (\mu_0 m / 4\pi r^3) [2\cos\theta \mathbf{e}_r + \sin\theta \mathbf{e}_\theta]$$

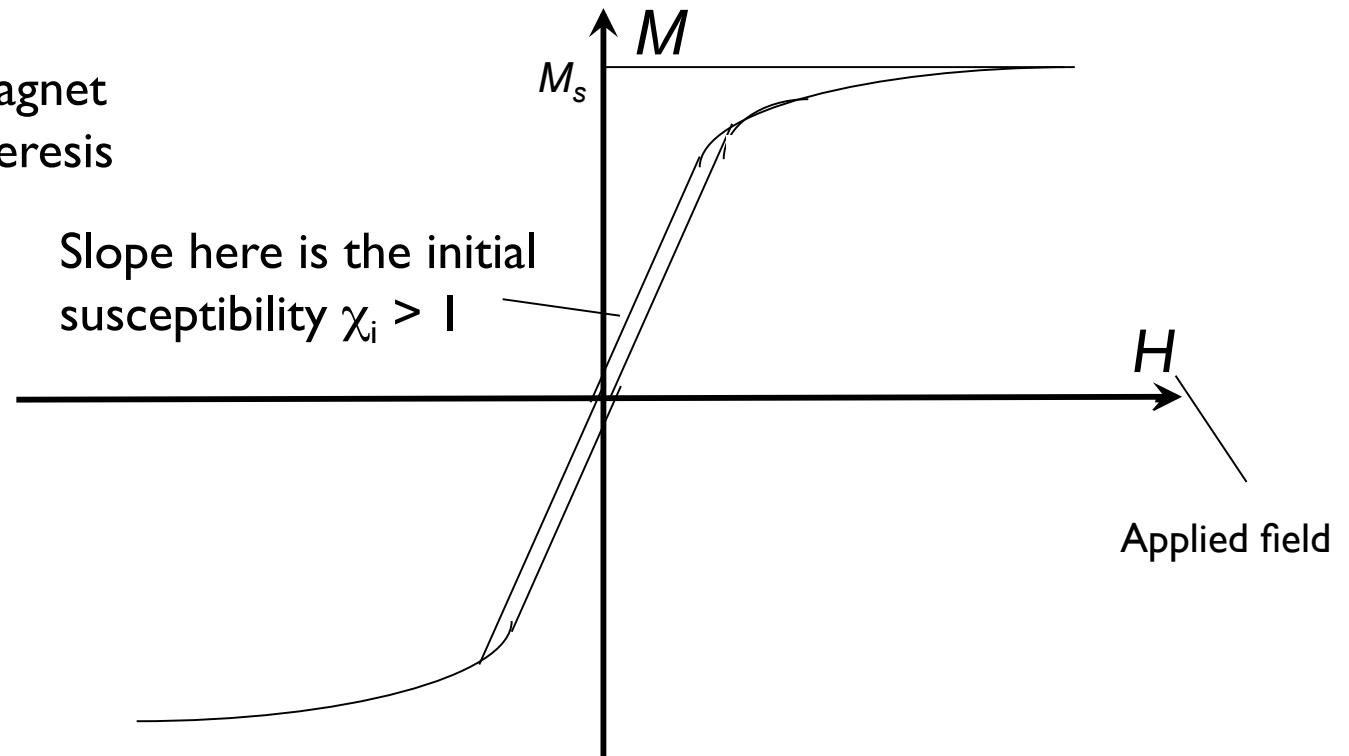
## 2.2 Magnetization curves - Hysteresis loop



The hysteresis loop shows the irreversible, nonlinear response of a ferromagnet to a magnetic field . It reflects the arrangement of the magnetization in ferromagnetic *domains*. A broad loop like this is typical of a *hard* or *permanent* magnet.

## Soft magnets

A soft or temporary magnet shows almost no hysteresis



Susceptibility is defined as  $\chi = M/H$

Iron, nickel and permalloy are soft ferromagnets. They have cubic crystal structures with no unique easy axis of magnetization.

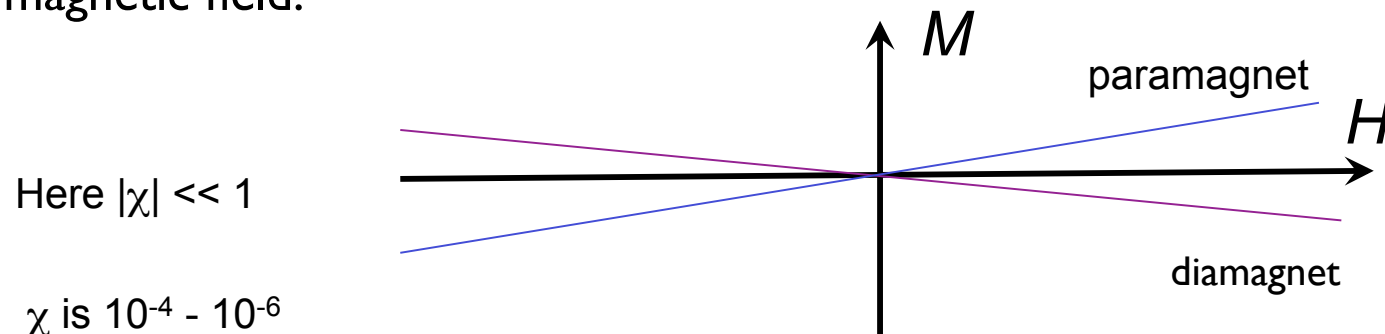
Spontaneous magnetization of a ferromagnet disappears above its Curie point,  $T_C$

	$M_s$ (MAm <sup>-1</sup> )	$T_C$ (°C)
Fe	1.71	771
Ni	0.49	355
Fe <sub>20</sub> Ni <sub>80</sub>	0.83	570

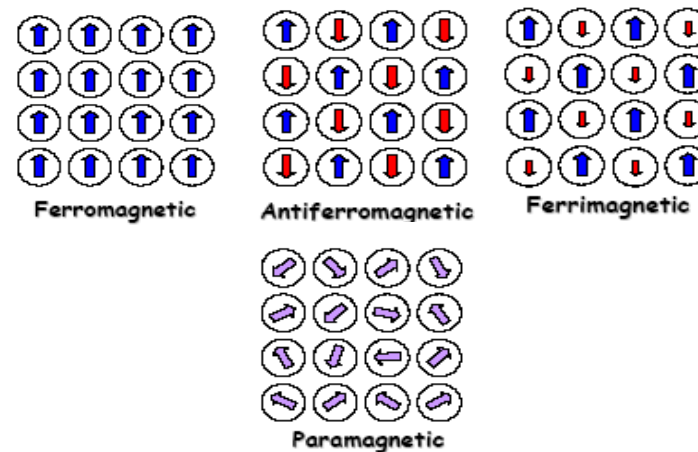
## Paramagnets and diamagnets; antiferromagnets.

Only a few elements and alloys are ferromagnetic. (See the magnetic periodic table).  
The atomic moments in a ferromagnet order spontaneously parallel to each other.

Most have no spontaneous magnetization, and they show only a very weak response to a magnetic field.



A few elements and many oxides are antiferromagnetic. The atomic moments order spontaneously antiparallel to each other.



Ordered  $T < T_c$

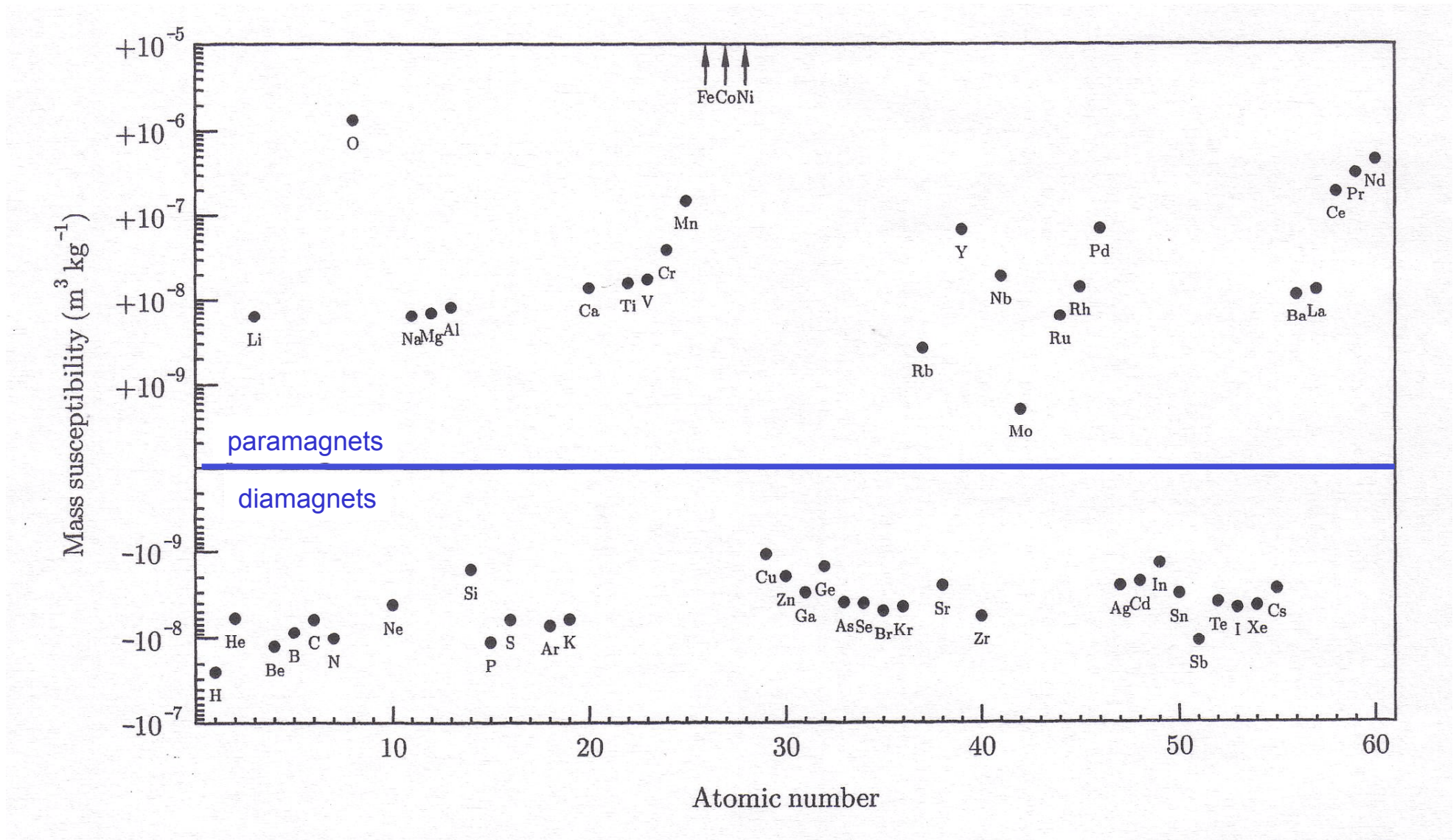
Disordered  $T > T_c$

# Magnetic Periodic Table

<h1>Magnetic Periodic Table</h1>																	
<div>Atomic Number →</div> <div>Atomic symbol →</div> <div>Atomic weight →</div> <div>Typical ionic charge →</div> <div>Antiferromagnetic <math>T_N(K)</math> →</div> <div>Ferromagnetic <math>T_C(K)</math> →</div>																	
1 <b>H</b> 1.00																	2 <b>He</b> 4.00
3 <b>Li</b> 6.94 1 + 2s <sup>0</sup>	4 <b>Be</b> 9.01 2 + 2s <sup>0</sup>											5 <b>B</b> 10.81	6 <b>C</b> 12.01	7 <b>N</b> 14.01	8 <b>O</b> 16.00 35	9 <b>F</b> 19.00	10 <b>Ne</b> 20.18
11 <b>Na</b> 22.99 1 + 3s <sup>0</sup>	12 <b>Mg</b> 24.21 2 + 3s <sup>0</sup>											13 <b>Al</b> 26.98 3 + 2p <sup>6</sup>	14 <b>Si</b> 28.09	15 <b>P</b> 30.97	16 <b>S</b> 32.07	17 <b>Cl</b> 35.45	18 <b>Ar</b> 39.95
19 <b>K</b> 38.21 1 + 4s <sup>0</sup>	20 <b>Ca</b> 40.08 2 + 4s <sup>0</sup>	21 <b>Sc</b> 44.96 3 + 3d <sup>0</sup>	22 <b>Ti</b> 47.88 4 + 3d <sup>0</sup>	23 <b>V</b> 50.94 3 + 3d <sup>2</sup>	24 <b>Cr</b> 52.00 3 + 3d <sup>3</sup> 312	25 <b>Mn</b> 55.85 2 + 3d <sup>5</sup> 96	26 <b>Fe</b> 55.85 3 + 3d <sup>6</sup> 1043	27 <b>Co</b> 58.93 2 + 3d <sup>7</sup> 1390	28 <b>Ni</b> 58.69 2 + 3d <sup>8</sup> 629	29 <b>Cu</b> 63.55 2 + 3d <sup>9</sup>	30 <b>Zn</b> 65.39 2 + 3d <sup>10</sup>	31 <b>Ga</b> 69.72 3 + 3d <sup>10</sup>	32 <b>Ge</b> 72.61	33 <b>As</b> 74.92	34 <b>Se</b> 78.96	35 <b>Br</b> 79.90	36 <b>Kr</b> 83.80
37 <b>Rb</b> 85.47 1 + 5s <sup>0</sup>	38 <b>Sr</b> 87.62 2 + 5s <sup>0</sup>	39 <b>Y</b> 88.91 2 + 4d <sup>0</sup>	40 <b>Zr</b> 91.22 4 + 4d <sup>0</sup>	41 <b>Nb</b> 92.91 5 + 4d <sup>0</sup>	42 <b>Mo</b> 95.94 5 + 4d <sup>1</sup>	43 <b>Tc</b> 97.9	44 <b>Ru</b> 101.1 3 + 4d <sup>5</sup>	45 <b>Rh</b> 102.4 3 + 4d <sup>6</sup>	46 <b>Pd</b> 106.4 2 + 4d <sup>8</sup>	47 <b>Ag</b> 107.9 1 + 4d <sup>10</sup>	48 <b>Cd</b> 112.4 2 + 4d <sup>10</sup>	49 <b>In</b> 114.8 3 + 4d <sup>10</sup>	50 <b>Sn</b> 118.7 4 + 4d <sup>10</sup>	51 <b>Sb</b> 121.8	52 <b>Te</b> 127.6	53 <b>I</b> 126.9	54 <b>Xe</b> 83.80
55 <b>Cs</b> 132.9 1 + 6s <sup>0</sup>	56 <b>Ba</b> 137.3 2 + 6s <sup>0</sup>	57 <b>La</b> 138.9 3 + 4f <sup>0</sup>	72 <b>Hf</b> 178.5 4 + 5d <sup>0</sup>	73 <b>Ta</b> 180.9 5 + 5d <sup>0</sup>	74 <b>W</b> 183.8 6 + 5d <sup>0</sup>	75 <b>Re</b> 186.2 4 + 5d <sup>5</sup>	76 <b>Os</b> 190.2 3 + 5d <sup>6</sup>	77 <b>Ir</b> 192.2 4 + 5d <sup>5</sup>	78 <b>Pt</b> 195.1 2 + 5d <sup>8</sup>	79 <b>Au</b> 197.0 1 + 5d <sup>10</sup>	80 <b>Hg</b> 200.6 2 + 5d <sup>10</sup>	81 <b>Tl</b> 204.4 3 + 5d <sup>10</sup>	82 <b>Pb</b> 207.2 4 + 5d <sup>10</sup>	83 <b>Bi</b> 209.0	84 <b>Po</b> 209	85 <b>At</b> 210	86 <b>Rn</b> 222
87 <b>Fr</b> 223	88 <b>Ra</b> 226.0 2 + 7s <sup>0</sup>	89 <b>Ac</b> 227.0 3 + 5f <sup>0</sup>															
			58 <b>Ce</b> 140.1 4 + 4f <sup>0</sup> 13	59 <b>Pr</b> 140.9 3 + 4f <sup>1</sup>	60 <b>Nd</b> 144.2 3 + 4f <sup>2</sup> 19	61 <b>Pm</b> 145	62 <b>Sm</b> 150.4 3 + 4f <sup>5</sup> 105	63 <b>Eu</b> 152.0 2 + 4f <sup>7</sup> 90	64 <b>Gd</b> 157.3 3 + 4f <sup>7</sup> 292	65 <b>Tb</b> 158.9 3 + 4f <sup>8</sup> 229 221	66 <b>Dy</b> 162.5 3 + 4f <sup>9</sup> 179 85	67 <b>Ho</b> 164.9 3 + 4f <sup>10</sup> 132 20	68 <b>Er</b> 167.3 3 + 4f <sup>11</sup> 85 20	69 <b>Tm</b> 168.9 3 + 4f <sup>12</sup> 56	70 <b>Yb</b> 173.0 3 + 4f <sup>13</sup>	71 <b>Lu</b> 175.0 3 + 4f <sup>14</sup>	
			90 <b>Th</b> 232.0 4 + 5f <sup>0</sup>	91 <b>Pa</b> 231.0 5 + 5f <sup>1</sup>	92 <b>U</b> 238.0 4 + 5f <sup>2</sup>	93 <b>Np</b> 238.0 5 + 5f <sup>2</sup>	94 <b>Pu</b> 244	95 <b>Am</b> 243	96 <b>Cm</b> 247	97 <b>Bk</b> 247	98 <b>Cf</b> 251	99 <b>Es</b> 252	100 <b>Fm</b> 257	101 <b>Md</b> 258	102 <b>No</b> 259	103 <b>Lr</b> 260	
<div><div><div></div>Nonmetal</div><div></div>Metal</div> <div><div></div>Radioactive</div> <div><div></div>Diamagnet</div> <div><div></div>Paramagnet</div> <div><b>BOLD</b> Magnetic atom</div> <div><div></div>Ferromagnet <math>T_C &gt; 290K</math></div> <div><div></div>Antiferromagnet with <math>T_N &gt; 290K</math></div> <div><div></div>Antiferromagnet/Ferromagnet with <math>T_N/T_C &lt; 290 K</math></div>																	



# Susceptibility of the elements



## 2.3 The magnetic fields fields **B** and **H**.

### - The **B**-field

**B** is the primary magnetic field. It satisfies Maxwell's equation

$$\nabla \cdot \mathbf{B} = 0$$

The vector operator  $\nabla$  means  $(\partial / \partial x, \partial / \partial y, \partial / \partial z)$ .  
' $\nabla \cdot$ ' is the divergence (*div*) of a vector. The scalar product  $\nabla \cdot \mathbf{B} = \partial B_x / \partial x + \partial B_y / \partial y + \partial B_z / \partial z$

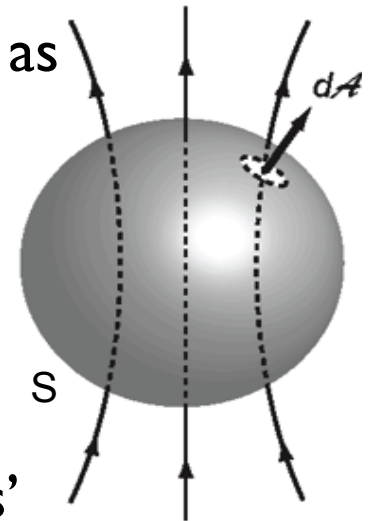
$\nabla \cdot \mathbf{B} = 0$  can be written in integral form over *any closed surface S* as

$$\oint_S \mathbf{B} \cdot d\mathbf{A} = 0 \quad (\text{Gauss's law}).$$

In other words the flux  $\Phi (= \mathbf{B} \cdot \mathbf{A})$  through any closed surface is zero. **B** is sometimes called magnetic flux density.

The lines of **B** form complete loops. There are no magnetic 'poles'

Units of **B** are Tesla (T)



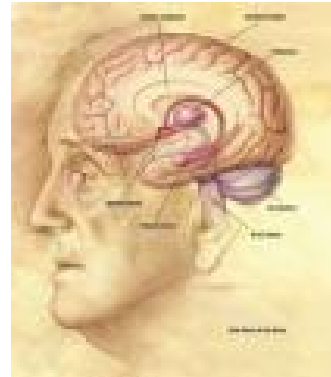
Typical values of  $B$  in free space (for  $H$  in  $A\ m^{-1}$  multiply by 800,000)



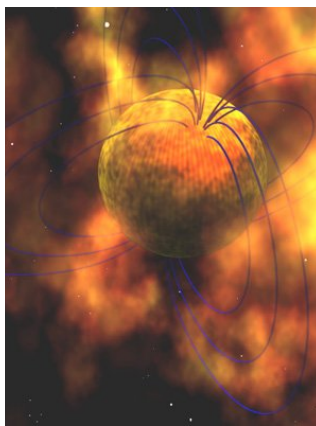
Earth  $50\ \mu T$



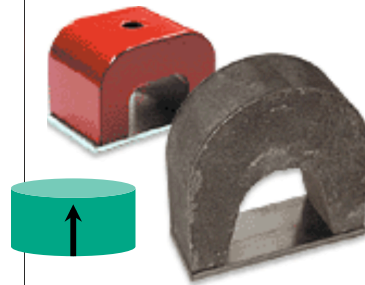
Helmholtz coils 10 mT



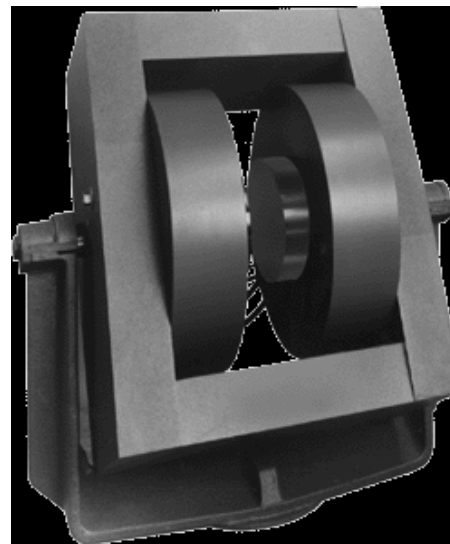
Human brain 1 fT



Magnetar  $10^{12}\ T$



Permanent magnets 0.5 T



Electromagnet 1 T



Superconducting magnet 10 T

## -The $\mathbf{H}$ -field

The other Maxwell equation for  $\mathbf{B}$  is  $(1/\mu_0)\nabla \times \mathbf{B} = \mathbf{j} + \epsilon_0\partial\mathbf{E}/\partial t$ . In a static situation

$$\nabla \times \mathbf{B} = \mu_0 \mathbf{j}$$

The equivalent integral formulation is Ampere's law  $\oint \mathbf{B} \cdot d\mathbf{l} = \mu_0 I$ . The differential form is the Biot-Savart law, which gives the field due to a current element  $I \delta\mathbf{l}$ ;

$$\delta\mathbf{B} = \mu_0 I \delta\mathbf{l} \times \mathbf{r} / 4\pi r^3$$

' $\nabla \times$ ' is the rotation (*curl*) of a vector.  $\nabla \times \mathbf{B}$  is

$$\mathbf{e}_x(\partial B_y/\partial z - \partial B_z/\partial y) - \mathbf{e}_y(\partial B_z/\partial x - \partial B_x/\partial z) + \mathbf{e}_z(\partial B_x/\partial y - \partial B_y/\partial x)$$

The current density  $\mathbf{j} = \mathbf{j}_c + \mathbf{j}_M$ , where  $\mathbf{j}_c$  is the conduction current density, and  $\mathbf{j}_M = \nabla \times \mathbf{M}$  is the current density associated with the magnetization.

The problem is that we can measure  $\mathbf{j}_c$  but we have no way to measure  $\mathbf{j}_M$

Since  $\nabla \times \mathbf{B} = \mu_0(\mathbf{j}_c + \mathbf{j}_M)$ . It follows that  $\nabla \times (\mathbf{B}/\mu_0 - \mathbf{M}) = \mathbf{j}_c$ .

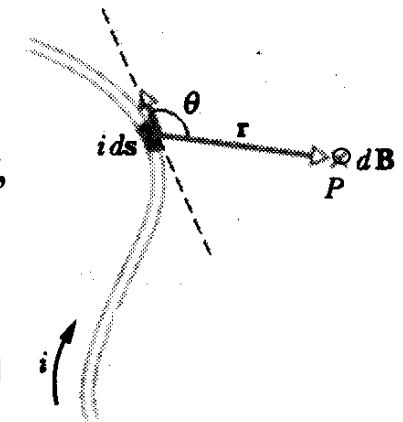
We just define

$$\mathbf{H} = (\mathbf{B}/\mu_0 - \mathbf{M})$$

or

$$\mathbf{B} = \mu_0(\mathbf{H} + \mathbf{M})$$

$\mathbf{H}$  has the same units as  $\mathbf{M}$   $\text{A m}^{-1}$



Now we can retain Ampere's law for the field  $\mathbf{H}$ , which does not depend on the unmeasurable currents  $\mathbf{j}_M$ .

In point form,

$$\nabla \times \mathbf{H} = \mathbf{j}_c$$

or in integral form

$$\oint \mathbf{H} \cdot d\mathbf{l} = I_c$$

The  $\mathbf{H}$ -field is not solenoidal. It will have sources (or sinks) wherever  $\nabla \times \mathbf{M} \neq 0$ , e.g. at the surface of a magnet. (These are the famous North and South 'poles').

In free space,  $\mathbf{M} = 0$  and the  $H$ -field is simply proportional to the  $B$ -field. There is no significant difference between them. Permeability is the ratio  $B/H$

In free space

$$\mathbf{B} = \mu_0 \mathbf{H}$$

$$1 \text{ T} \approx 800,000 \text{ A m}^{-1}$$

Note that the  $H$ -field is created not *only* by conduction currents. Any piece of magnetized material creates an  $H$ -field both in the space around it, and *within its own volume*.

Generally the field at a point is  $\mathbf{H} = \mathbf{H}_d + \mathbf{H}_0$ , where  $\mathbf{H}_0$  is the external field, and  $\mathbf{H}_d$  is the field created by the magnet itself, which is known as the *stray field* outside the magnet, and the *demagnetizing field* inside the magnet.



## Potentials for $\mathbf{B}$ and $\mathbf{H}$

It is convenient to derive a field from a potential, by taking a spatial derivative. For example  $\mathbf{E} = -\nabla\varphi_e(\mathbf{r})$  where  $\varphi_e(\mathbf{r})$  is the electric potential. Any constant  $\varphi_0$  can be added to  $\varphi_e(\mathbf{r})$ .

For  $\mathbf{B}$ , we know from Maxwell's equations that  $\nabla \cdot \mathbf{B} = 0$ . There is a vector identity  $\nabla \cdot \nabla \times \mathbf{A} = 0$ . Hence, we can derive  $\mathbf{B}(\mathbf{r})$  from a *vector potential*  $\mathbf{A}(\mathbf{r})$ ,

$$\mathbf{B}(\mathbf{r}) = \nabla \times \mathbf{A}(\mathbf{r})$$

The gradient of any scalar  $f$  can be added to  $\mathbf{A}$  (a *gauge transformation*) This is because  $\nabla \times \nabla f = 0$ .

Generally,  $\mathbf{H}(\mathbf{r})$  *cannot* be derived from a potential. It satisfies Maxwell's equation  $\nabla \times \mathbf{H} = \mathbf{j}_c + \partial \mathbf{D} / \partial t$ . In a static situation, when *no conduction currents* are present,  $\nabla \times \mathbf{H} = 0$ , and

$$\mathbf{H}(\mathbf{r}) = -\nabla\varphi_m(\mathbf{r})$$

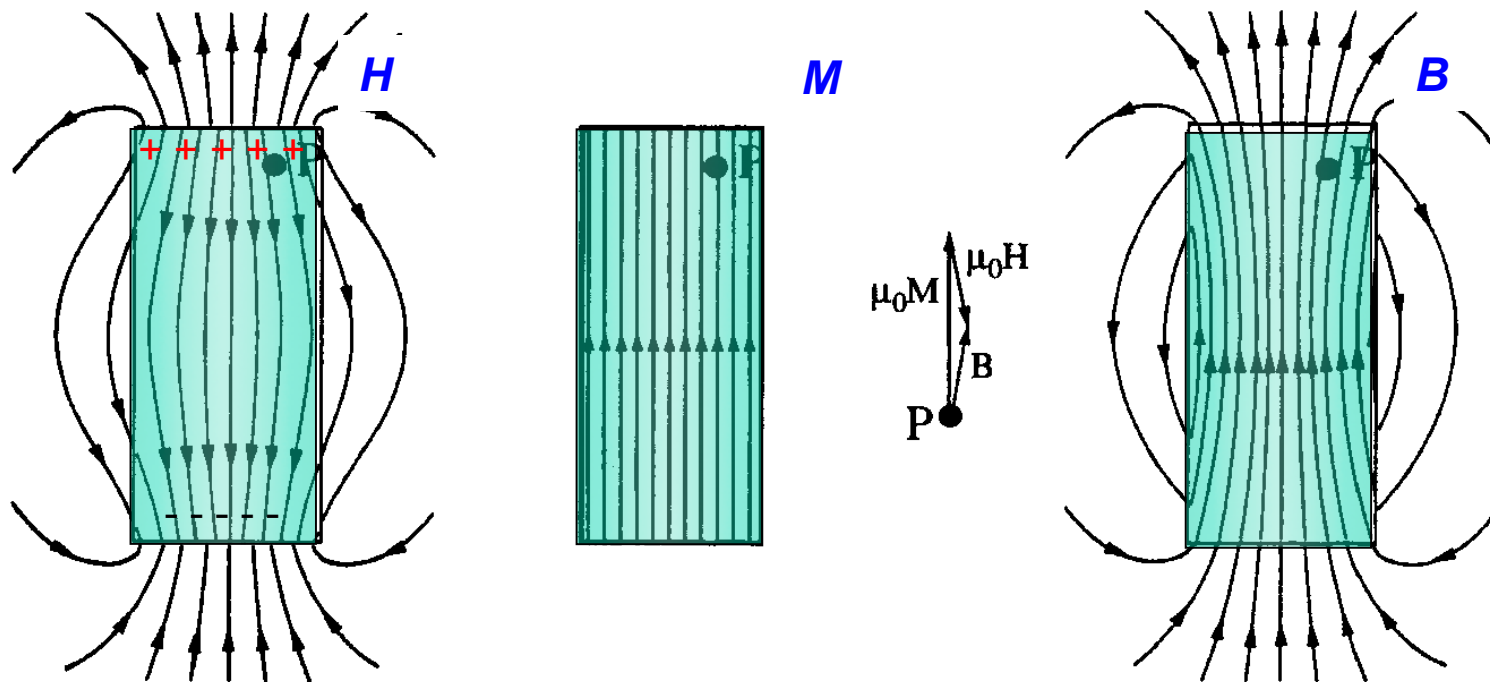
In these special conditions, it is possible to derive  $\mathbf{H}(\mathbf{r})$  from a magnetic scalar potential. We can imagine that  $\mathbf{H}$  is derived the distribution of magnetic ' $\pm$  charge' (N and S poles).

## $B$ , $H$ and $M$ in and around a permanent magnet.

The general relation between  $B$ ,  $H$  and  $M$  is

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

$$\text{i.e. } H = B/\mu_0 - M$$



We call the  $H$ -field due to a magnet; — *stray field* outside the magnet  
— *demagnetizing field*,  $H_d$ , inside the magnet

## Boundary conditions for $\mathbf{B}$ and $\mathbf{H}$

At any interface, it follows from Gauss' s law

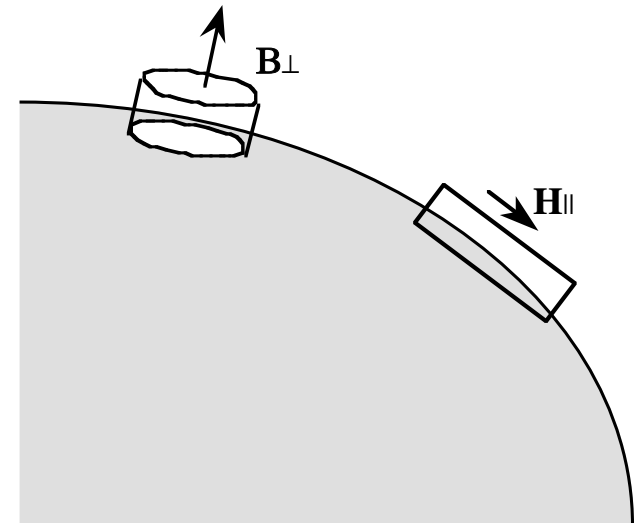
$$\int_S \mathbf{B} \cdot d\mathbf{A} = 0$$

that the *perpendicular component of  $\mathbf{B}$  is continuous*.

It follows from from Ampère' s law

$$\oint \mathbf{H} \cdot d\mathbf{l} = I_0 = 0$$

(there are no conduction currents on the surface)  
that the *parallel component of  $\mathbf{H}$  is continuous*.



## Demagnetizing field in a material - $H_d$

The demagnetizing field depends on the *shape* of the sample and the direction of magnetization.

For simple uniformly-magnetized shapes (ellipsoids of revolution) the demagnetizing field is related to the magnetization by a proportionality factor  $\mathcal{N}$  known as the *demagnetizing factor*. The value of  $\mathcal{N}$  can never exceed 1, nor can it be less than 0.

$$\mathbf{H}_d = - \mathcal{N} \mathbf{M}$$

More generally, this is a tensor relation.  $\mathcal{N}$  is then a 3 x 3 matrix, with trace 1. That is

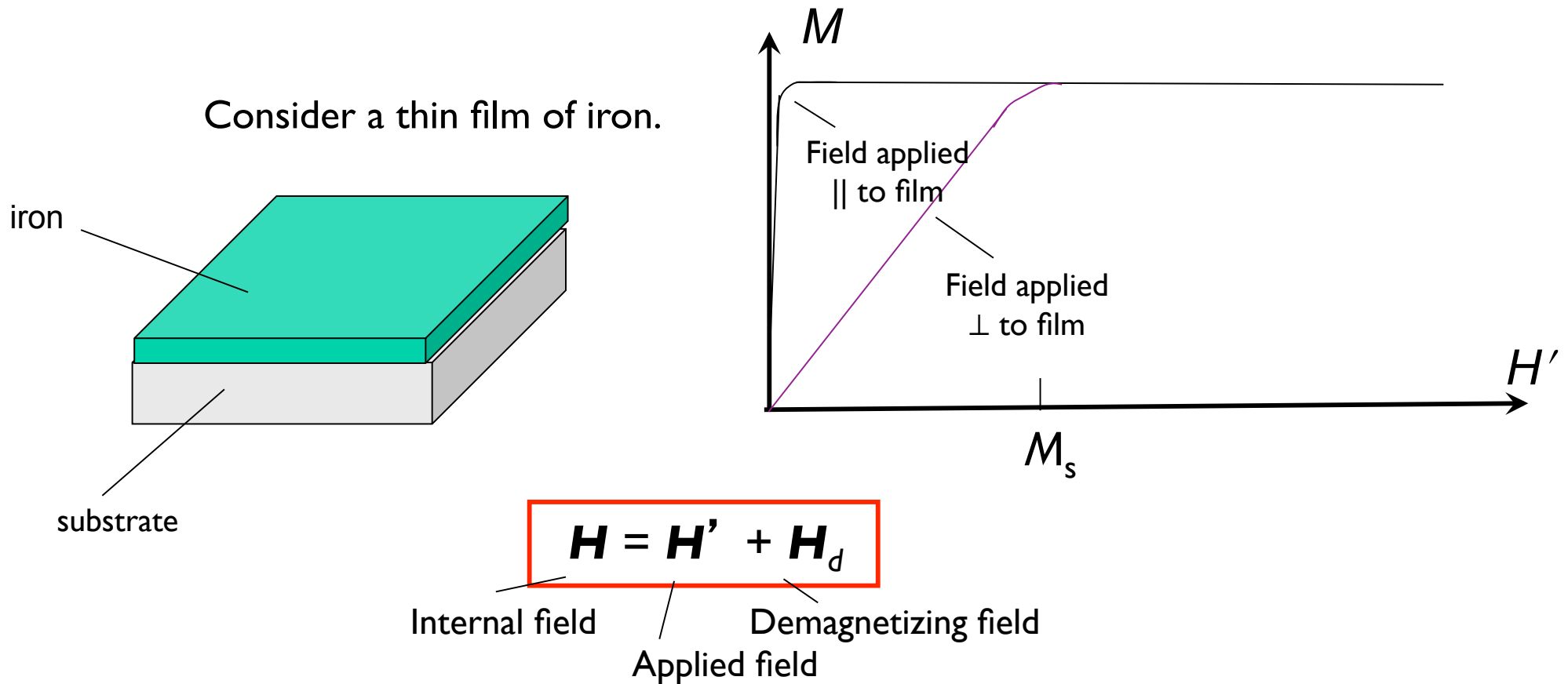
$$\mathcal{N}_x + \mathcal{N}_y + \mathcal{N}_z = 1$$

Note that the internal field  $H$  is always less than the applied field  $H'$  since

$$\mathbf{H} = \mathbf{H}' - \mathcal{N} \mathbf{M}$$

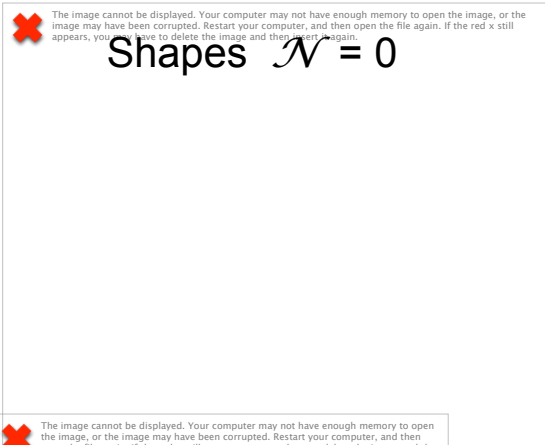
## 2.4 Magnetic fields - Internal and applied fields

These are *not* the same. If they were, any applied field would instantly saturate the magnetization.

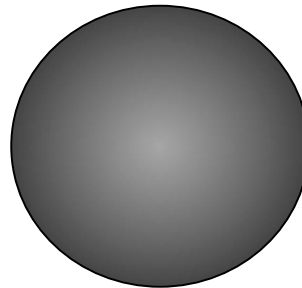




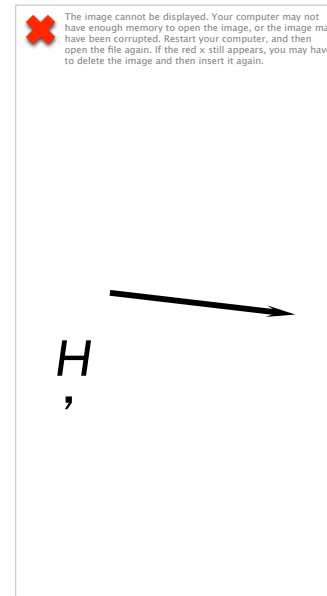
# Demagnetizing factor $\mathcal{N}$ for special shapes.



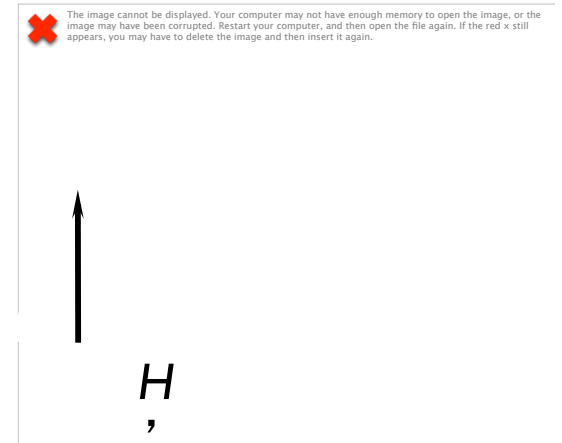
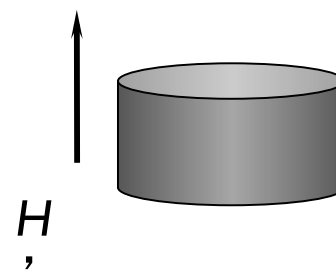
$$\mathcal{N} = 1/3$$



$$\mathcal{N} = 1/2$$



$$\mathcal{N} = 1$$



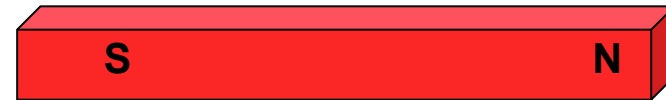
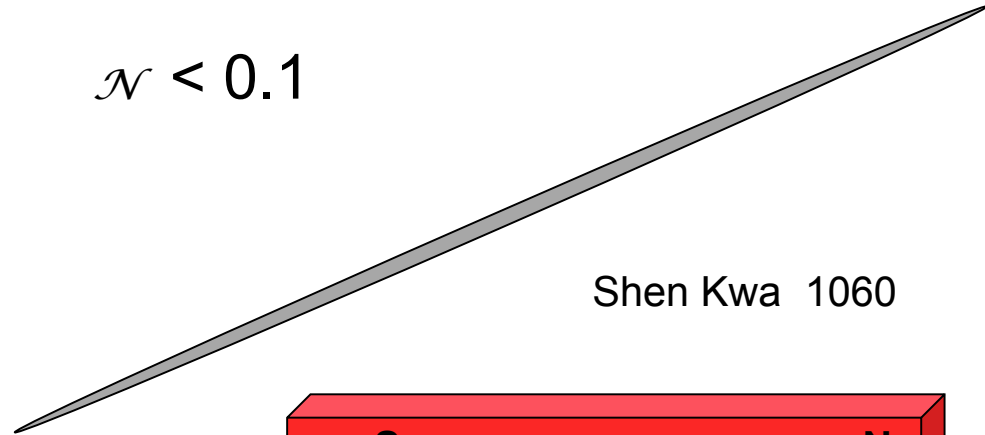
# The shape barrier

Daniel Bernouilli 1743



$$\mathcal{N} < 0.1$$

Shen Kwa 1060



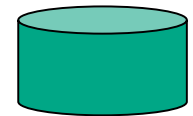
Gowind Knight 1760



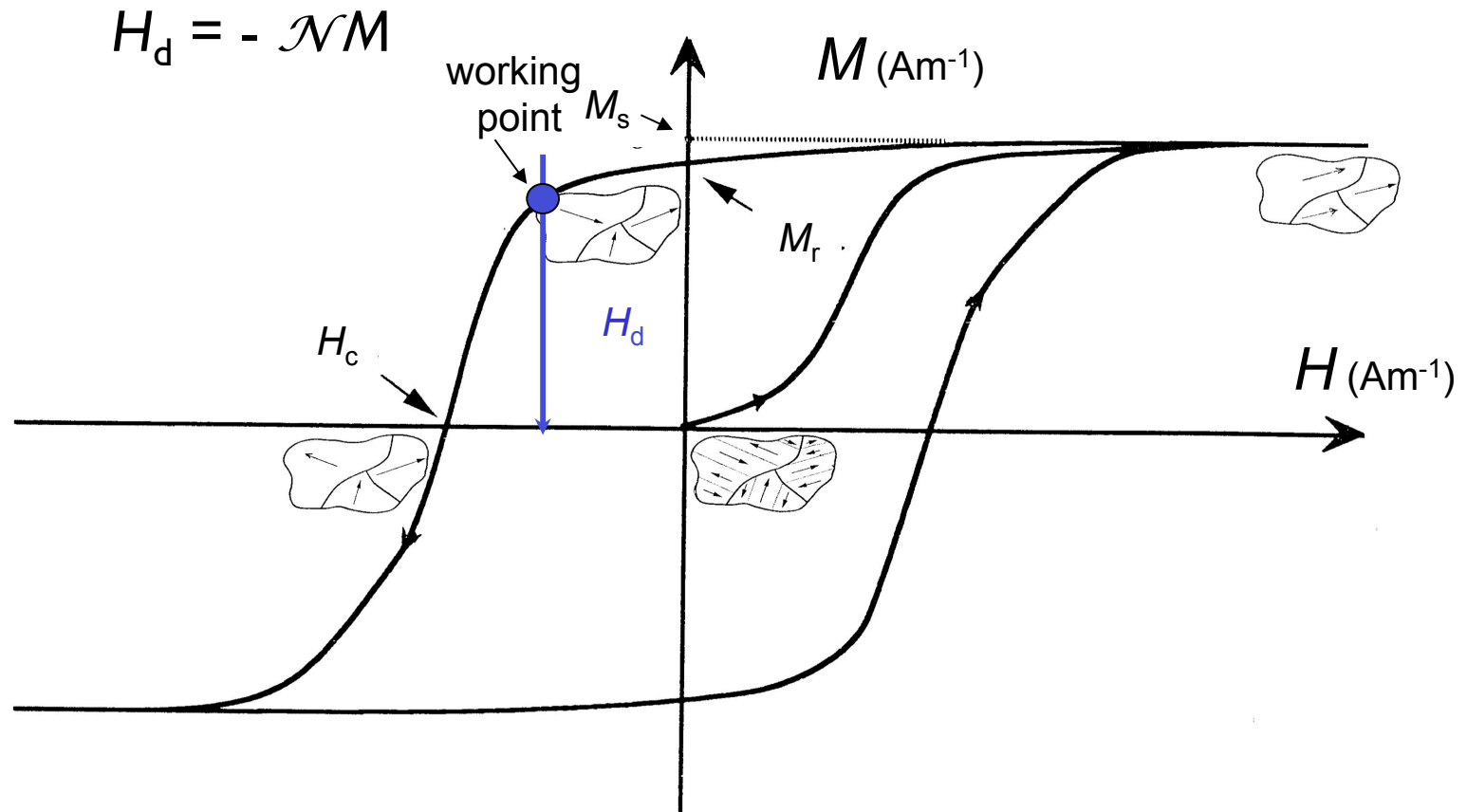
T. Mishima  
1931

$$\mathcal{N} = 0.5$$

New icon for permanent magnets!  $\Rightarrow$

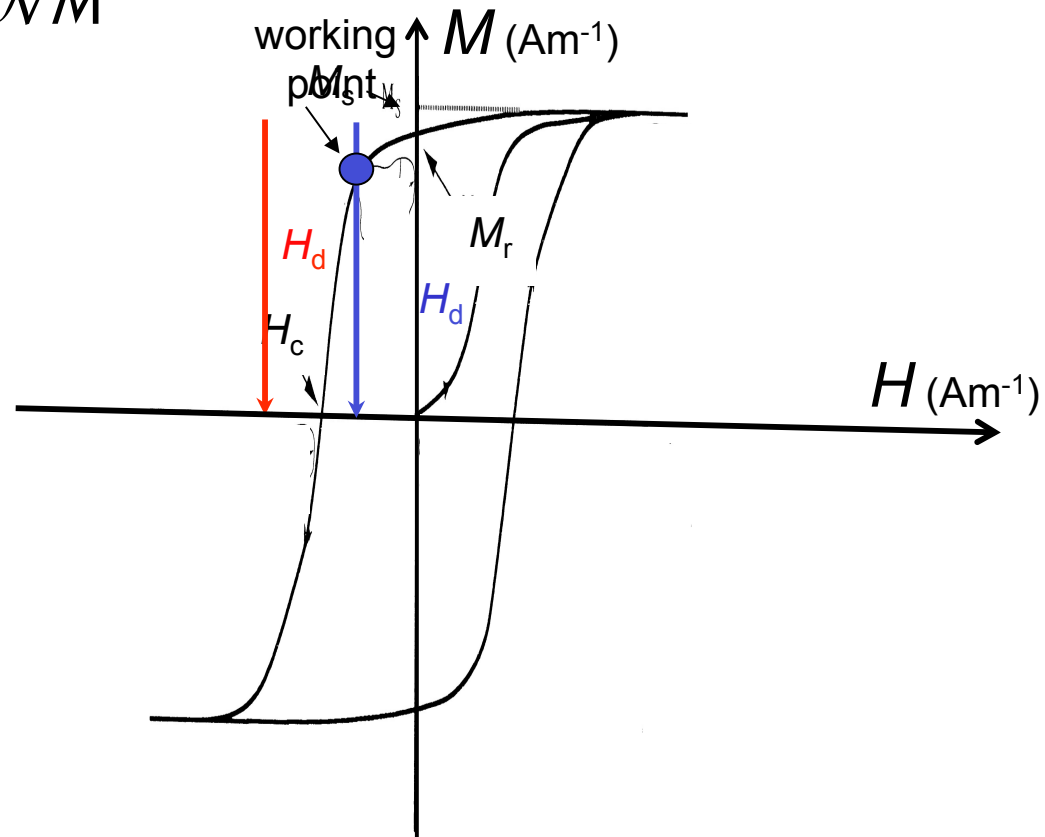


The shape barrier overcome !



The shape barrier overcome !

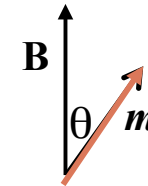
$$H_d = - \mathcal{N}M$$



## 2.5 Energy and force on a magnetic moment

- In free space an external field  $\mathbf{B}$  (or  $\mathbf{H}_0$ ), created by conduction currents or magnets or both interacts with a magnetic moment  $\mathbf{m}$  and modifies its energy:

$$E = -\mathbf{m} \cdot \mathbf{B} \quad (\text{i.e. } -m B \cos\theta)$$



- Differentiating gives the torque  $\Gamma = -\partial E / \partial \theta$

$$\Gamma = \mathbf{m} \times \mathbf{B} \quad (\text{i.e. } m B \sin\theta)$$

(the compass is an example)

Note the moment actually *precesses* around the field when  $\mathbf{m}$  is not parallel to  $\mathbf{B}$ .

The magnetic moment is due to electric currents, and the Lorentz force on a moving electron  $-e\mathbf{v} \times \mathbf{B}$  is perpendicular to its motion, and therefore the *total* energy does not change.

The magnetic moment is analogous to a spinning top, which precesses when acted on by a gravitational torque. The magnetic moment is proportional to an angular momentum

$$\mathbf{m} = \gamma \mathbf{l}$$

— Gyromagnetic ratio

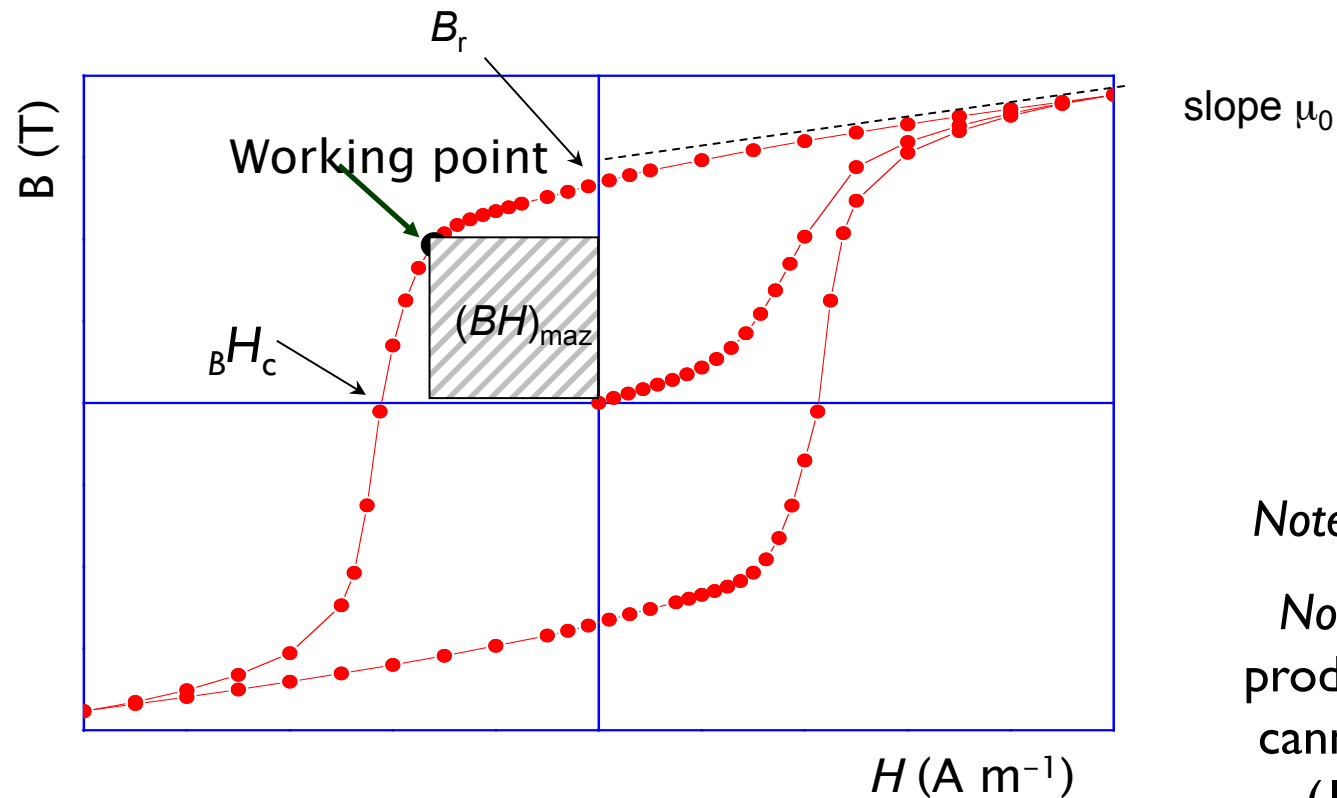
- The force on a magnetic moment  $\mathbf{f} = -\nabla E = \nabla(\mathbf{m} \cdot \mathbf{B})$  depends on the field gradient  
There is *no net force* in a uniform field.



## $B(H)$ hysteresis loop

Engineers usually show the  $B(H)$  hysteresis loop, rather than the  $M(H)$  loop.

They are related by  $B = \mu_0(H + M)$ . The high-field slope, when  $M$  is saturated, is  $\mu_0$



Note:  $B H_c \neq H_c$

Note: Energy product  $(BH)_{\max}$  cannot exceed  $(1/4\mu_0)B_r^2$ .

## Some expressions involving ***B***

$$\mathbf{F} = q(\mathbf{E} + \mathbf{v} \times \mathbf{B}) \quad \text{Force on a charged particle } q$$

$$\mathbf{F} = \mathbf{B} i \mathbf{l} \quad \text{Force on current-carrying wire}$$

$$\mathcal{E} = - d\Phi/dt \quad \text{Faraday's law of electromagnetic induction}$$

$$E = - \mathbf{m} \cdot \mathbf{B} \quad \text{Energy of a magnetic moment}$$

$$\mathbf{F} = \nabla \mathbf{m} \cdot \mathbf{B} \quad \text{Force on a magnetic moment}$$

$$\mathbf{\Gamma} = \mathbf{m} \times \mathbf{B} \quad \text{Torque on a magnetic moment}$$

**Note:** Whenever ***H*** interacts with matter,  $\mu_0$  comes in.

## A note on units:

Magnetism is an experimental science, and it is important to be able to calculate numerical values of the physical quantities involved. There is a strong case to use SI consistently

- SI units relate to the practical units of electricity measured on the multimeter and the oscilloscope
- It is possible to check the dimensions of any expression by inspection.
- They are almost universally used in teaching
- Units of  **$B$** ,  **$H$** ,  $\Phi$  or  $d\Phi/dt$  have been introduced.

BUT

Most literature still uses cgs units, You need to understand them too.

## SI / cgs conversions:

	SI units	cgs units
	$\mathbf{B} = \mu_0(\mathbf{H} + \mathbf{M})$	$\mathbf{B} = \mathbf{H} + 4\pi\mathbf{M}$
$m$	$\text{A m}^2$	emu
$\mathbf{M}$	$\text{A m}^{-1} \quad (10^{-3} \text{ emu cc}^{-1})$	emu cc $^{-1} \quad (1 \text{ kA m}^{-1})$
$\sigma$	$\text{A m}^2 \text{ kg}^{-1} \quad (1 \text{ emu g}^{-1})$	emu g $^{-1} \quad (1 \text{ A m}^2 \text{ kg}^{-1})$
$\mathbf{H}$	$\text{A m}^{-1} \quad (4\pi/1000 \approx 0.0125 \text{ Oe})$	Oersted $(1000/4\pi \approx 80 \text{ A m}^{-1})$
$\mathbf{B}$	Tesla $(10000 \text{ G})$	Gauss $(10^{-4} \text{ T})$
$\Phi$	Weber ( $\text{Tm}^2$ ) $(10^8 \text{ Mw})$	Maxwell ( $\text{G cm}^2$ ) $(10^{-8} \text{ Wb})$
$d\Phi/dt$	V $(10^8 \text{ Mw s}^{-1})$	Mw s $^{-1} \quad (10 \text{ nV})$
$\chi$	- $(4\pi \text{ cgs})$	- $(1/4\pi \text{ SI})$

Mechanical							
Quantity	Symbol	Unit	$m$	$l$	$t$	$i$	$\theta$
Area	$\mathcal{A}$	$\text{m}^2$	0	2	0	0	0
Volume	$V$	$\text{m}^3$	0	3	0	0	0
Velocity	$v$	$\text{m s}^{-1}$	0	1	-1	0	0
Acceleration	$a$	$\text{m s}^{-2}$	0	1	-2	0	0
Density	$d$	$\text{kg m}^{-3}$	1	-3	0	0	0
Energy	$\varepsilon$	J	1	2	-2	0	0
Momentum	$p$	$\text{kg m s}^{-1}$	1	1	-1	0	0
Angular momentum	$L$	$\text{kg m}^2 \text{s}^{-1}$	1	2	-1	0	0
Moment of inertia	$I$	$\text{kg m}^2$	1	2	0	0	0
Force	$f$	N	1	1	-2	0	0
Force density	$F$	$\text{N m}^{-3}$	1	-2	-2	0	0
Power	$P$	W	1	2	-3	0	0
Pressure	$P$	Pa	1	-1	-2	0	0
Stress	$\sigma$	$\text{N m}^{-2}$	1	-1	-2	0	0
Elastic modulus	$K$	$\text{N m}^{-2}$	1	-1	-2	0	0
Frequency	$f$	$\text{s}^{-1}$	0	0	-1	0	0
Diffusion coefficient	$D$	$\text{m}^2 \text{s}^{-1}$	0	2	-1	0	0
Viscosity (dynamic)	$\eta$	$\text{N s m}^{-2}$	1	-1	-1	0	0
Viscosity	$\nu$	$\text{m}^2 \text{s}^{-1}$	0	2	-1	0	0
Planck's constant	$\hbar$	J s	1	2	-1	0	0

Electrical							
Quantity	Symbol	Unit	$m$	$l$	$t$	$i$	$\theta$
Current	$I$	A	0	0	0	1	0
Current density	$j$	$\text{A m}^{-2}$	0	-2	0	1	0
Charge	$q$	C	0	0	1	1	0
Potential	$V$	V	1	2	-3	-1	0
Electromotive force	$\mathcal{E}$	V	1	2	-3	-1	0
Capacitance	$C$	F	-1	-2	4	2	0
Resistance	$R$	$\Omega$	1	2	-3	-2	0
Resistivity	$\varrho$	$\Omega \text{m}$	1	3	-3	-2	0
Conductivity	$\sigma$	$\text{S m}^{-1}$	-1	-3	3	2	0
Dipole moment	$p$	C m	0	1	1	1	0
Electric polarization	$P$	$\text{C m}^{-2}$	0	-2	1	1	0
Electric field	$E$	$\text{V m}^{-1}$	1	1	-3	-1	0
Electric displacement	$D$	$\text{C m}^{-2}$	0	-2	1	1	0
Electric flux	$\Psi$	C	0	0	1	1	0
Permittivity	$\varepsilon$	$\text{F m}^{-1}$	-1	-3	4	2	0
Thermopower	$S$	$\text{V K}^{-1}$	1	2	-3	-1	-1
Mobility	$\mu$	$\text{m}^2 \text{V}^{-1} \text{s}^{-1}$	-1	0	2	1	0

Magnetic							
Quantity	Symbol	Unit	$m$	$l$	$t$	$i$	$\theta$
Magnetic moment	$\mathbf{m}$	$\text{A m}^2$	0	2	0	1	0
Magnetization	$M$	$\text{A m}^{-1}$	0	-1	0	1	0
Specific moment	$\sigma$	$\text{A m}^2 \text{kg}^{-1}$	-1	2	0	1	0
Magnetic field strength	$H$	$\text{A m}^{-1}$	0	-1	0	1	0
Magnetic flux	$\Phi$	Wb	1	2	-2	-1	0
Magnetic flux density	$B$	T	1	0	-2	-1	0
Inductance	$L$	H	1	2	-2	-2	0
Susceptibility (M/H)	$\chi$		0	0	0	0	0
Permeability (B/H)	$\mu$	$\text{H m}^{-1}$	1	1	-2	-2	0
Magnetic polarization	$J$	T	1	0	-2	-1	0
Magnetomotive force	$\mathcal{F}$	A	0	0	0	1	0
Magnetic 'charge'	$q_m$	A m	0	1	0	1	0
Energy product	$(BH)$	$\text{J m}^{-3}$	1	-1	-2	0	0
Anisotropy energy	$K$	$\text{J m}^{-3}$	1	-1	-2	0	0
Exchange stiffness	$A$	$\text{J m}^{-1}$	1	1	-2	0	0
Hall coefficient	$R_H$	$\text{m}^3 \text{C}^{-1}$	0	3	-1	-1	0
Scalar potential	$\varphi$	A	0	0	0	1	0
Vector potential	$A$	T m	1	1	-2	-1	0
Permeance	$P_m$	$\text{T m}^2 \text{A}^{-1}$	1	2	-2	-2	0
Reluctance	$R_m$	$\text{A T}^{-1} \text{m}^{-2}$	-1	-2	2	2	0

Thermal							
Quantity	Symbol	Unit	$m$	$l$	$t$	$i$	$\theta$
Enthalpy	$H$	J	1	2	-2	0	0
Entropy	$S$	$\text{J K}^{-1}$	1	2	-2	0	-1
Specific heat	$C$	$\text{J K}^{-1} \text{kg}^{-1}$	0	2	-2	0	-1
Heat capacity	$c$	$\text{J K}^{-1}$	1	2	-2	0	-1
Thermal conductivity	$\kappa$	$\text{W m}^{-1} \text{K}^{-1}$	1	1	-3	0	-1
Sommerfeld coefficient	$\gamma$	$\text{J mol}^{-1} \text{K}^{-1}$	1	2	-2	0	-1
Boltzmann's constant	$k_B$	$\text{J K}^{-1}$	1	2	-2	0	-1

(1) Kinetic energy of a body:  $\varepsilon = \frac{1}{2}mv^2$

$$[\varepsilon] = [1, 2, -2, 0, 0]$$

$$[m] = [1, 0, 0, 0, 0]$$

$$[v^2] = \frac{2[0, -1, -1, 0, 0]}{[1, -2, -2, 0, 0]}$$

(2) Lorentz force on a moving charge;  $\mathbf{f} = q\mathbf{v} \times \mathbf{B}$

$$[f] = [1, 1, -2, 0, 0]$$

$$[q] = [0, 0, 1, 1, 0]$$

$$[v] = [0, 1, -1, 0, 0]$$

$$[B] = \frac{[1, 0, -2, -1, 0]}{[1, 1, -2, 0, 0]}$$

(3) Domain wall energy  $\gamma_w = \sqrt{AK}$  ( $\gamma_w$  is an energy per unit area)

$$[\gamma_w] = [\varepsilon A^{-1}]$$

$$= [1, 2, -2, 0, 0]$$

$$- [0, 2, 0, 0, 0]$$

$$= [1, 0, -2, 0, 0]$$

$$[\sqrt{AK}] = 1/2[AK]$$

$$[\sqrt{A}] = \frac{1}{2}[1, 1, -2, 0, 0]$$

$$[\sqrt{K}] = \frac{1}{2} \frac{[1, -1, -2, 0, 0]}{[1, 0, -2, 0, 0]}$$



- (4) Magnetohydrodynamic force on a moving conductor  $\mathbf{F} = \sigma \mathbf{v} \times \mathbf{B} \times \mathbf{B}$   
 ( $\mathbf{F}$  is a force per unit volume)

$$[\mathbf{F}] = [\mathbf{F} V^{-1}]$$

$$= [1, 1, -2, 0, 0]$$

$$-\frac{[0, 3, 0, 0, 0]}{[1, -2, -2, 0, 0]}$$

$$[\sigma] = [-1, -3, 3, 2, 0]$$

$$[\mathbf{v}] = [0, 1, -1, 0, 0]$$

$$[\mathbf{B}^2] = \frac{2[1, 0, -2, -1, 0]}{[1, -2, -2, 0, 0]}$$

- (5) Flux density in a solid  $\mathbf{B} = \mu_0(\mathbf{H} + \mathbf{M})$  (note that quantities added or subtracted in a bracket must have the same dimensions)

$$[\mathbf{B}] = [1, 0, -2, -1, 0]$$

$$[\mu_0] = [1, 1, -2, -2, 0]$$

$$[\mathbf{M}], [\mathbf{H}] = \frac{[0, -1, 0, 1, 0]}{[1, 0, -2, -1, 0]}$$

- (6) Maxwell's equation  $\nabla \times \mathbf{H} = \mathbf{j} + d\mathbf{D}/dt$ .

$$[\nabla \times \mathbf{H}] = [H r^{-1}]$$

$$= [0, -1, 0, 1, 0]$$

$$-[0, 1, 0, 0, 0]$$

$$= [0, -2, 0, 1, 0]$$

$$[\mathbf{j}] = [0, -2, 0, 1, 0]$$

$$[d\mathbf{D}/dt] = [D t^{-1}]$$

$$= [0, -2, 1, 1, 0]$$

$$-[0, 0, 1, 0, 0]$$

$$= [0, -2, 0, 1, 0]$$

- (7) Ohm's Law  $V = IR$

$$= [1, 2, -3, -1, 0]$$

$$[0, 0, 0, 1, 0]$$

$$+ [1, 2, -3, -2, 0]$$

$$= [1, 2, -3, -1, 0]$$

- (8) Faraday's Law  $\mathcal{E} = -\partial\Phi/\partial t$

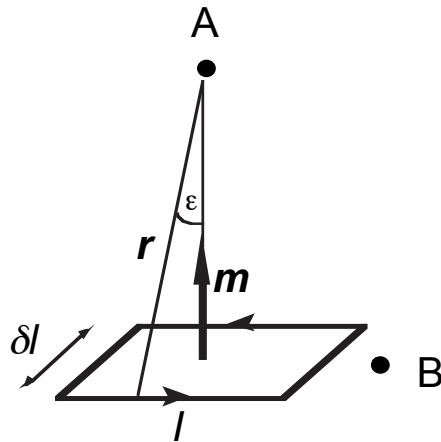
$$= [1, 2, -3, -1, 0]$$

$$[1, 2, -2, -1, 0]$$

$$-[0, 0, 1, 0, 0]$$

$$= [1, 2, -3, -1, 0]$$

## Calculation of the field of a dipole (current loop)



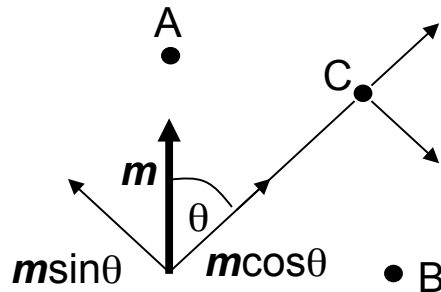
$$B_A = 4\delta B \sin \epsilon \quad \sin \epsilon = \delta l / 2r, \quad m = I(\delta l)^2 \quad B_A = 2 \frac{\mu_0}{4\pi} \frac{\mathbf{m}}{r^3}.$$

$$B_B = \frac{\mu_0}{4\pi} I \delta l \left\{ \frac{1}{(r - \delta l/2)^2} - \frac{1}{(r + \delta l/2)^2} - \frac{2 \sin \epsilon}{r^2} \right\}$$

$$\approx \frac{\mu_0}{4\pi} \frac{I \delta l}{r^2} \left\{ \left(1 + \frac{\delta l}{r}\right) - \left(1 - \frac{\delta l}{r}\right) - \frac{\delta l}{r} \right\}$$

$$B_A = 2 \frac{\mu_0}{4\pi} \frac{\mathbf{m}}{r^3}.$$

$$B_B = \frac{\mu_0}{4\pi} \frac{\mathbf{m}}{r^3}$$



So at a general point C, in polar coordinates:

$$B_r = 2 \left( \frac{\mu_0 \mathbf{m}}{4\pi r^3} \right) \cos \theta; \quad B_\theta = \left( \frac{\mu_0 \mathbf{m}}{4\pi r^3} \right) \sin \theta; \quad B_\phi = 0$$

Hence :  $\mathbf{B}(\mathbf{r}, \theta) = (\mu_0 m / 4\pi r^3) [2 \cos \theta \mathbf{e}_r + \sin \theta \mathbf{e}_\theta]$

$$\mathbf{B} = \frac{\mu_0}{4\pi} \left[ 3 \frac{(\mathbf{m} \cdot \mathbf{r}) \mathbf{r}}{r^5} - \frac{\mathbf{m}}{r^3} \right]$$

### 3. Magnetism of the electron

The origin of magnetism in solids is the *quantized angular momentum of the negatively-charged electrons*.

There are *two* distinct sources;

- orbital motion
- spin.

## Einstein-de Haas experiment.

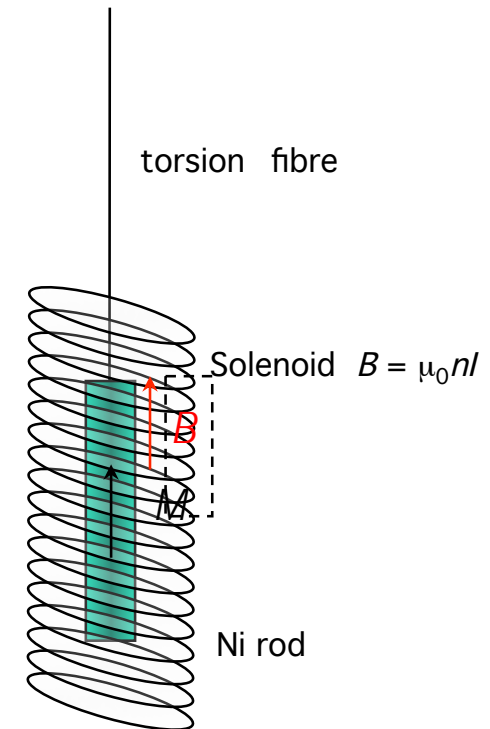
This demonstrates the reality of the relation between magnetization and angular momentum.

A nickel rod is suspended on a torsion fibre. The field in the solenoid is reversed, changing the direction of magnetization of the nickel. It rotates, to conserve angular momentum as the angular momenta of the electrons are reversed.

In Ni the moment is essentially due to the spin of the electrons. An electron has a spin moment of a Bohr magneton

However,  $m$  for Ni is only  $0.6 \mu_B/\text{atom}$ . There is less than one electron with an unpaired spin, although the number of electrons per atom in nickel is  $Z = 28$

Nickel is a metal, where the valence electrons are localized, but have no net moment. The conduction electrons are delocalized, and spin polarized.



# Magnetic Periodic Table

<h1>Magnetic Periodic Table</h1>																																																																																																																																																																																	
<div><div>Atomic Number →</div><div>Atomic symbol →</div><div>Atomic weight →</div><div>Typical ionic charge →</div><div>Antiferromagnetic T<sub>N</sub>(K) →</div><div>Ferromagnetic T<sub>C</sub>(K) →</div></div>																																																																																																																																																																																	
<table><tr><td colspan="2">1 <b>H</b> 1.00</td><td colspan="14"></td><td colspan="2">2 He 4.00</td></tr><tr><td>3 <b>Li</b> 6.94 1 + 2s<sup>0</sup></td><td>4 Be 9.01 2 + 2s<sup>0</sup></td><td colspan="10"></td><td>5 B 10.81</td><td>6 C 12.01</td><td>7 N 14.01</td><td>8 <b>O</b> 16.00 35</td><td>9 F 19.00</td><td>10 Ne 20.18</td></tr><tr><td>11 <b>Na</b> 22.99 1 + 3s<sup>0</sup></td><td>12 <b>Mg</b> 24.21 2 + 3s<sup>0</sup></td><td colspan="10"></td><td>13 <b>Al</b> 26.98 3 + 2p<sup>6</sup></td><td>14 Si 28.09</td><td>15 P 30.97</td><td>16 S 32.07</td><td>17 Cl 35.45</td><td>18 Ar 39.95</td></tr><tr><td>19 <b>K</b> 38.21 1 + 4s<sup>0</sup></td><td>20 <b>Ca</b> 40.08 2 + 4s<sup>0</sup></td><td>21 <b>Sc</b> 44.96 3 + 3d<sup>0</sup></td><td>22 <b>Ti</b> 47.88 4 + 3d<sup>0</sup></td><td>23 <b>V</b> 50.94 3 + 3d<sup>2</sup></td><td>24 <b>Cr</b> 52.00 3 + 3d<sup>3</sup> 312</td><td>25 <b>Mn</b> 55.85 2 + 3d<sup>5</sup> 96</td><td>26 <b>Fe</b> 55.85 3 + 3d<sup>6</sup> 1043</td><td>27 <b>Co</b> 58.93 2 + 3d<sup>7</sup> 1390</td><td>28 <b>Ni</b> 58.69 2 + 3d<sup>8</sup> 629</td><td>29 <b>Cu</b> 63.55 2 + 3d<sup>9</sup></td><td>30 <b>Zn</b> 65.39 2 + 3d<sup>10</sup></td><td>31 <b>Ga</b> 69.72 3 + 3d<sup>10</sup></td><td>32 <b>Ge</b> 72.61</td><td>33 <b>As</b> 74.92</td><td>34 <b>Se</b> 78.96</td><td>35 <b>Br</b> 79.90</td><td>36 <b>Kr</b> 83.80</td></tr><tr><td>37 <b>Rb</b> 85.47 1 + 5s<sup>0</sup></td><td>38 <b>Sr</b> 87.62 2 + 5s<sup>0</sup></td><td>39 <b>Y</b> 88.91 2 + 4d<sup>0</sup></td><td>40 <b>Zr</b> 91.22 4 + 4d<sup>0</sup></td><td>41 <b>Nb</b> 92.91 5 + 4d<sup>0</sup></td><td>42 <b>Mo</b> 95.94 5 + 4d<sup>1</sup></td><td>43 <b>Tc</b> 97.9</td><td>44 <b>Ru</b> 101.1 3 + 4d<sup>6</sup></td><td>45 <b>Rh</b> 102.4 3 + 4d<sup>6</sup></td><td>46 <b>Pd</b> 106.4 2 + 4d<sup>8</sup></td><td>47 <b>Ag</b> 107.9 1 + 4d<sup>10</sup></td><td>48 <b>Cd</b> 112.4 2 + 4d<sup>10</sup></td><td>49 <b>In</b> 114.8 3 + 4d<sup>10</sup></td><td>50 <b>Sn</b> 118.7 4 + 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5f<sup>0</sup></td><td colspan="15"></td></tr><tr><td colspan="3"></td><td>58 <b>Ce</b> 140.1 4 + 4f<sup>0</sup> 13</td><td>59 <b>Pr</b> 140.9 3 + 4f<sup>1</sup></td><td>60 <b>Nd</b> 144.2 3 + 4f<sup>2</sup> 19</td><td>61 <b>Pm</b> 145</td><td>62 <b>Sm</b> 150.4 3 + 4f<sup>5</sup> 105</td><td>63 <b>Eu</b> 152.0 2 + 4f<sup>7</sup> 90</td><td>64 <b>Gd</b> 157.3 3 + 4f<sup>7</sup> 292</td><td>65 <b>Tb</b> 158.9 3 + 4f<sup>8</sup> 229 221</td><td>66 <b>Dy</b> 162.5 3 + 4f<sup>9</sup> 179 85</td><td>67 <b>Ho</b> 164.9 3 + 4f<sup>10</sup> 132 20</td><td>68 <b>Er</b> 167.3 3 + 4f<sup>11</sup> 85 20</td><td>69 <b>Tm</b> 168.9 3 + 4f<sup>12</sup> 56</td><td>70 <b>Yb</b> 173.0 3 + 4f<sup>13</sup></td><td>71 <b>Lu</b> 175.0 3 + 4f<sup>14</sup></td></tr><tr><td colspan="3"></td><td>90 <b>Th</b> 232.0 4 + 5f<sup>0</sup></td><td>91 <b>Pa</b> 231.0 5 + 5f<sup>1</sup></td><td>92 <b>U</b> 238.0 4 + 5f<sup>2</sup></td><td>93 <b>Np</b> 238.0 5 + 5f<sup>2</sup></td><td>94 <b>Pu</b> 244</td><td>95 <b>Am</b> 243</td><td>96 <b>Cm</b> 247</td><td>97 <b>Bk</b> 247</td><td>98 <b>Cf</b> 251</td><td>99 <b>Es</b> 252</td><td>100 <b>Fm</b> 257</td><td>101 <b>Md</b> 258</td><td>102 <b>No</b> 259</td><td>103 <b>Lr</b> 260</td></tr></table>																		1 <b>H</b> 1.00																2 He 4.00		3 <b>Li</b> 6.94 1 + 2s <sup>0</sup>	4 Be 9.01 2 + 2s <sup>0</sup>											5 B 10.81	6 C 12.01	7 N 14.01	8 <b>O</b> 16.00 35	9 F 19.00	10 Ne 20.18	11 <b>Na</b> 22.99 1 + 3s <sup>0</sup>	12 <b>Mg</b> 24.21 2 + 3s <sup>0</sup>											13 <b>Al</b> 26.98 3 + 2p <sup>6</sup>	14 Si 28.09	15 P 30.97	16 S 32.07	17 Cl 35.45	18 Ar 39.95	19 <b>K</b> 38.21 1 + 4s <sup>0</sup>	20 <b>Ca</b> 40.08 2 + 4s <sup>0</sup>	21 <b>Sc</b> 44.96 3 + 3d <sup>0</sup>	22 <b>Ti</b> 47.88 4 + 3d <sup>0</sup>	23 <b>V</b> 50.94 3 + 3d <sup>2</sup>	24 <b>Cr</b> 52.00 3 + 3d <sup>3</sup> 312	25 <b>Mn</b> 55.85 2 + 3d <sup>5</sup> 96	26 <b>Fe</b> 55.85 3 + 3d <sup>6</sup> 1043	27 <b>Co</b> 58.93 2 + 3d <sup>7</sup> 1390	28 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3 <b>Li</b> 6.94 1 + 2s <sup>0</sup>	4 Be 9.01 2 + 2s <sup>0</sup>											5 B 10.81	6 C 12.01	7 N 14.01	8 <b>O</b> 16.00 35	9 F 19.00	10 Ne 20.18																																																																																																																																																																
11 <b>Na</b> 22.99 1 + 3s <sup>0</sup>	12 <b>Mg</b> 24.21 2 + 3s <sup>0</sup>											13 <b>Al</b> 26.98 3 + 2p <sup>6</sup>	14 Si 28.09	15 P 30.97	16 S 32.07	17 Cl 35.45	18 Ar 39.95																																																																																																																																																																
19 <b>K</b> 38.21 1 + 4s <sup>0</sup>	20 <b>Ca</b> 40.08 2 + 4s <sup>0</sup>	21 <b>Sc</b> 44.96 3 + 3d <sup>0</sup>	22 <b>Ti</b> 47.88 4 + 3d <sup>0</sup>	23 <b>V</b> 50.94 3 + 3d <sup>2</sup>	24 <b>Cr</b> 52.00 3 + 3d <sup>3</sup> 312	25 <b>Mn</b> 55.85 2 + 3d <sup>5</sup> 96	26 <b>Fe</b> 55.85 3 + 3d <sup>6</sup> 1043	27 <b>Co</b> 58.93 2 + 3d <sup>7</sup> 1390	28 <b>Ni</b> 58.69 2 + 3d <sup>8</sup> 629	29 <b>Cu</b> 63.55 2 + 3d <sup>9</sup>	30 <b>Zn</b> 65.39 2 + 3d <sup>10</sup>	31 <b>Ga</b> 69.72 3 + 3d <sup>10</sup>	32 <b>Ge</b> 72.61	33 <b>As</b> 74.92	34 <b>Se</b> 78.96	35 <b>Br</b> 79.90	36 <b>Kr</b> 83.80																																																																																																																																																																
37 <b>Rb</b> 85.47 1 + 5s <sup>0</sup>	38 <b>Sr</b> 87.62 2 + 5s <sup>0</sup>	39 <b>Y</b> 88.91 2 + 4d <sup>0</sup>	40 <b>Zr</b> 91.22 4 + 4d <sup>0</sup>	41 <b>Nb</b> 92.91 5 + 4d <sup>0</sup>	42 <b>Mo</b> 95.94 5 + 4d <sup>1</sup>	43 <b>Tc</b> 97.9	44 <b>Ru</b> 101.1 3 + 4d <sup>6</sup>	45 <b>Rh</b> 102.4 3 + 4d <sup>6</sup>	46 <b>Pd</b> 106.4 2 + 4d <sup>8</sup>	47 <b>Ag</b> 107.9 1 + 4d <sup>10</sup>	48 <b>Cd</b> 112.4 2 + 4d <sup>10</sup>	49 <b>In</b> 114.8 3 + 4d <sup>10</sup>	50 <b>Sn</b> 118.7 4 + 4d <sup>10</sup>	51 <b>Sb</b> 121.8	52 <b>Te</b> 127.6	53 <b>I</b> 126.9	54 <b>Xe</b> 83.80																																																																																																																																																																
55 <b>Cs</b> 132.9 1 + 6s <sup>0</sup>	56 <b>Ba</b> 137.3 2 + 6s <sup>0</sup>	57 <b>La</b> 138.9 3 + 4f <sup>0</sup>	72 <b>Hf</b> 178.5 4 + 5d <sup>0</sup>	73 <b>Ta</b> 180.9 5 + 5d <sup>0</sup>	74 <b>W</b> 183.8 6 + 5d <sup>0</sup>	75 <b>Re</b> 186.2 4 + 5d <sup>5</sup>	76 <b>Os</b> 190.2 3 + 5d <sup>6</sup>	77 <b>Ir</b> 192.2 4 + 5d <sup>5</sup>	78 <b>Pt</b> 195.1 2 + 5d <sup>8</sup>	79 <b>Au</b> 197.0 1 + 5d <sup>10</sup>	80 <b>Hg</b> 200.6 2 + 5d <sup>10</sup>	81 <b>Tl</b> 204.4 3 + 5d <sup>10</sup>	82 <b>Pb</b> 207.2 4 + 5d <sup>10</sup>	83 <b>Bi</b> 209.0	84 <b>Po</b> 209	85 <b>At</b> 210	86 <b>Rn</b> 222																																																																																																																																																																
87 <b>Fr</b> 223	88 <b>Ra</b> 226.0 2 + 7s <sup>0</sup>	89 <b>Ac</b> 227.0 3 + 5f <sup>0</sup>																																																																																																																																																																															
			58 <b>Ce</b> 140.1 4 + 4f <sup>0</sup> 13	59 <b>Pr</b> 140.9 3 + 4f <sup>1</sup>	60 <b>Nd</b> 144.2 3 + 4f <sup>2</sup> 19	61 <b>Pm</b> 145	62 <b>Sm</b> 150.4 3 + 4f <sup>5</sup> 105	63 <b>Eu</b> 152.0 2 + 4f <sup>7</sup> 90	64 <b>Gd</b> 157.3 3 + 4f <sup>7</sup> 292	65 <b>Tb</b> 158.9 3 + 4f <sup>8</sup> 229 221	66 <b>Dy</b> 162.5 3 + 4f <sup>9</sup> 179 85	67 <b>Ho</b> 164.9 3 + 4f <sup>10</sup> 132 20	68 <b>Er</b> 167.3 3 + 4f <sup>11</sup> 85 20	69 <b>Tm</b> 168.9 3 + 4f <sup>12</sup> 56	70 <b>Yb</b> 173.0 3 + 4f <sup>13</sup>	71 <b>Lu</b> 175.0 3 + 4f <sup>14</sup>																																																																																																																																																																	
			90 <b>Th</b> 232.0 4 + 5f <sup>0</sup>	91 <b>Pa</b> 231.0 5 + 5f <sup>1</sup>	92 <b>U</b> 238.0 4 + 5f <sup>2</sup>	93 <b>Np</b> 238.0 5 + 5f <sup>2</sup>	94 <b>Pu</b> 244	95 <b>Am</b> 243	96 <b>Cm</b> 247	97 <b>Bk</b> 247	98 <b>Cf</b> 251	99 <b>Es</b> 252	100 <b>Fm</b> 257	101 <b>Md</b> 258	102 <b>No</b> 259	103 <b>Lr</b> 260																																																																																																																																																																	
<div><div><div></div>Nonmetal</div><div></div>Metal</div> <div><div></div>Radioactive</div> <div><div></div>Diamagnet</div> <div><div></div>Paramagnet</div> <div><b>BOLD</b> Magnetic atom</div> <div><div></div>Ferromagnet T<sub>C</sub> &gt; 290K</div> <div><div></div>Antiferromagnet with T<sub>N</sub> &gt; 290K</div> <div><div></div>Antiferromagnet/Ferromagnet with T<sub>N</sub>/T<sub>C</sub> &lt; 290 K</div>																																																																																																																																																																																	

# Magnetism of the electron

- **orbital motion**; Bohr's quantum theory.
- **spin**; An intrinsic property of the electron; Dirac's theory

Spin itself and spin-orbit coupling of these two types of magnetic moments are relativistic effects.

The description of magnetism in solids is fundamentally different depending on whether the electrons are *localized* on the ion cores, or *delocalized* in energy bands.

We focus mainly on localized magnetism in this course, where an integral number of electrons are localized on each atom



### 3.1 Spin and orbital moments of the electron

The magnetic properties of solids derive essentially from the magnetism of their electrons. (Nuclei also possess angular momentum, but their magnetic moments, but they are  $\approx 1000$  times smaller).

An electron possesses

mass

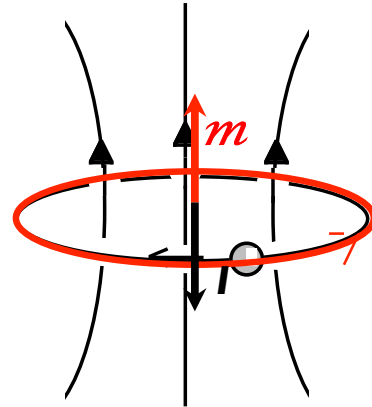
$$m_e = 9.109 \cdot 10^{-31} \text{ kg}$$

charge

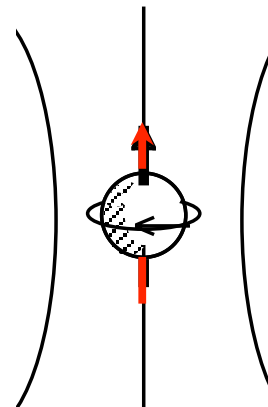
$$-e = -1.602 \cdot 10^{-19} \text{ C}$$

angular momentum (*spin*)

$$\hbar/2 = 0.527 \cdot 10^{-34} \text{ J s}$$



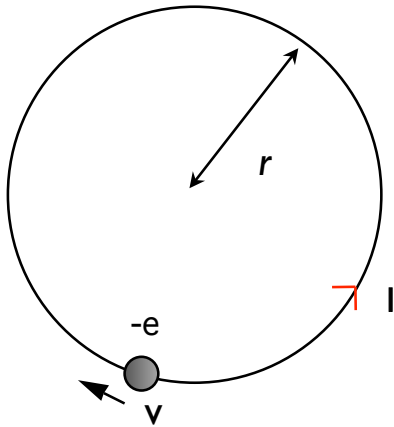
Orbital moment



Spin

On an atomic scale, magnetism is always associated with *angular momentum*. Electronic charge is -ve, hence the angular momentum and magnetic moment are oppositely directed.

### 3.1.1 Orbital moment



An electron in a circular orbit, radius  $r$ , is equivalent to a current loop

The circulating current is  $I$ ;  $I = -ev/2\pi r$

The moment is  $m = IA$ ;

$$m = (-ev/2\pi r) \pi r^2 = -evr/2 \quad (1)$$

In Bohr's quantum theory, orbital angular momentum  $\mathbf{l}$  is quantized in units of  $\hbar$ ;

$h$  is Planck's constant,  $6.62 \times 10^{-34} \text{ J s}$ ;

$$\hbar = h/2\pi = 1.055 \times 10^{-34} \text{ J s}.$$

The orbital angular momentum is  $\mathbf{l} = \mathbf{r} \wedge m_e \mathbf{v}$ ; Units are  $\text{J s}$

It is actually the  $z$ -component of  $\mathbf{l}$  that is quantized in units of  $\hbar$ , taking a value  $l_z = m_l \hbar$  where  $m_l$  is a quantum number, an *integer*  $0, \pm 1, \pm 2 \dots$  with no units.

Eliminating  $vr$  in the expression (1) for  $m$  gives

$$m = -m_l(e\hbar/2m_e) = m_l\mu_B$$

The quantity  $(e\hbar/2m_e)$  is the Bohr magneton ( $\mu_B$ ), the basic unit of atomic magnetism;

$$\mu_B = 9.274 \times 10^{-24} \text{ A m}^2$$

### 3.1.2 Spin moment

The electron has a mysterious built-in spin angular momentum. Spin is a consequence of relativistic quantum mechanics. The spin quantum number is  $s = 1/2$ .

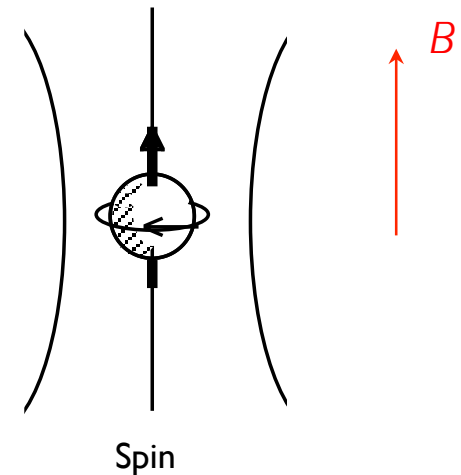
The spin angular momentum is  $\mathbf{s}$ . The z-component is quantized in units of  $\frac{1}{2}\hbar$ , taking only two values  $m_s = \pm 1/2 \hbar$

Nevertheless, the magnetic moment associated with electron spin is also  $1\mu_B$ . (not  $\frac{1}{2}\mu_B$ )

$$m = -gm_s(e\hbar/2m_e) \text{ where } g \approx 2. \text{ (after higher order corrections, 2.0023)}$$

The two states,  $\downarrow$  'spin down' and  $\uparrow$  'spin up' with  $m_s = \pm 1/2$  have moments  $\mp 1\mu_B$  measured along the axis of quantization (z) which is usually defined by some external magnetic field.

[ likewise, if the orbital quantum number was  $l = 1$ ,  $m_l = -1, 0, 1$  ]



The *gyromagnetic ratio*  $\gamma$ , is defined as the ratio of magnetic moment to angular momentum

\* For orbital angular momentum  $m = \gamma I$ , hence

$$\gamma = -(e/2m_e)$$

The *g-factor* is defined as the ratio of  $m$  (in units of  $\mu_B$ ) to  $I$  (in units of  $\hbar$ )

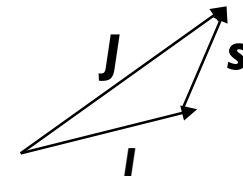
$$g = 1 \text{ for orbital motion}$$

\* For spin angular momentum  $\gamma = -(e/m_e)$

$$g = 2 \text{ for spin} \quad (\text{after higher order corrections, } 2.0023)$$

Spin angular momentum is *twice* as effective as orbital angular momentum in creating a magnetic moment.

Generally an atomic electron possesses both spin and orbital angular. They produce a total angular momentum  $\mathbf{j}$ ,  $\mathbf{j} = \mathbf{l} + \mathbf{s}$ ;  $m = -g_j(e/2m_e)\mathbf{j}$



## 3.2 Electrons in a field

$$\mathbf{m} = \gamma \mathbf{I}$$

$$\boldsymbol{\Gamma} = \mathbf{m} \times \mathbf{B}$$

$$\boldsymbol{\Gamma} = d\mathbf{I}/dt \text{ (Newton's law)}$$

$$d\mathbf{m}/dt = \gamma \mathbf{m} \times \mathbf{B}$$

$$= \gamma \begin{vmatrix} \mathbf{e}_x & \mathbf{e}_y & \mathbf{e}_z \\ m_x & m_y & m_z \\ 0 & 0 & B_z \end{vmatrix}$$

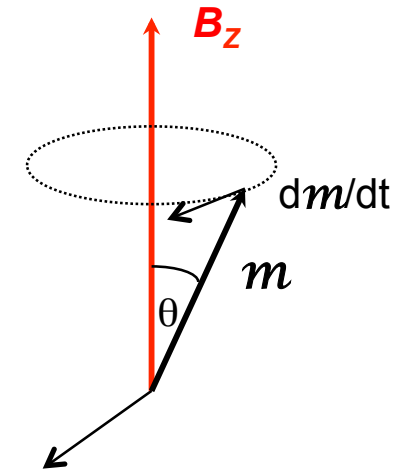
$$dm_x/dt = \gamma m_y B_z \quad dm_y/dt = -\gamma m_x B_z \quad dm_z/dt = 0$$

Solution is  $\mathbf{m}(t) = \mathbf{m} ( \sin\theta \cos\omega_L t, \sin\theta \sin\omega_L t, \cos\theta )$  where  $\omega_L = \gamma B_z$

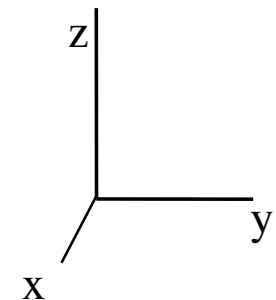
Magnetic moment precesses at the Larmor precession frequency  $f_L = \gamma B/2\pi$



## Larmor precession



$$\boldsymbol{\Gamma} = \mathbf{m} \times \mathbf{B}$$



28 GHz T<sup>-1</sup> for spin

# Magnetism of free atoms

Atomic Number → **66** Dy ← Atomic symbol  
Atomic weight ← 162.5  
Typical ionic change → 3 + 4f<sup>9</sup>  
Antiferromagnetic T<sub>N</sub>(K) → 179 85 ← Ferromagnetic T<sub>C</sub>(K)

1 <b>H</b> 1.00																	2 <b>He</b> 4.00	
3 <b>Li</b> 6.94 1 + 2s <sup>0</sup>	4 <b>Be</b> 9.01 2 + 2s <sup>0</sup>																	10 <b>Ne</b> 20.18
11 <b>Na</b> 22.99 1 + 3s <sup>0</sup>	12 <b>Mg</b> 24.21 2 + 3s <sup>0</sup>																	18 <b>Ar</b> 39.95
19 <b>K</b> 38.21 1 + 4s <sup>0</sup>	20 <b>Ca</b> 40.08 2 + 4s <sup>0</sup>	21 <b>Sc</b> 44.96 3 + 3d <sup>0</sup>	22 <b>Ti</b> 47.88 4 + 3d <sup>0</sup>	23 <b>V</b> 50.94 3 + 3d <sup>2</sup>	24 <b>Cr</b> 52.00 3 + 3d <sup>3</sup> 312	25 <b>Mn</b> 55.85 2 + 3d <sup>5</sup> 96	26 <b>Fe</b> 55.85 3 + 3d <sup>5</sup> 1043	27 <b>Co</b> 58.93 2 + 3d <sup>7</sup> 1390	28 <b>Ni</b> 58.69 2 + 3d <sup>8</sup> 629	29 <b>Cu</b> 63.55 2 + 3d <sup>9</sup>	30 <b>Zn</b> 65.39 2 + 3d <sup>10</sup>	31 <b>Ga</b> 69.72 3 + 3d <sup>10</sup>	32 <b>Ge</b> 72.61	33 <b>As</b> 74.92	34 <b>Se</b> 78.96	35 <b>Br</b> 79.90	36 <b>Kr</b> 83.80	
37 <b>Rb</b> 85.47 1 + 5s <sup>0</sup>	38 <b>Sr</b> 87.62 2 + 5s <sup>0</sup>	39 <b>Y</b> 88.91 2 + 4d <sup>0</sup>	40 <b>Zr</b> 91.22 4 + 4d <sup>0</sup>	41 <b>Nb</b> 92.91 5 + 4d <sup>0</sup>	42 <b>Mo</b> 95.94 5 + 4d <sup>1</sup>	43 <b>Tc</b> 97.9	44 <b>Ru</b> 101.1 3 + 4d <sup>5</sup>	45 <b>Rh</b> 102.4 3 + 4d <sup>6</sup>	46 <b>Pd</b> 106.4 2 + 4d <sup>8</sup>	47 <b>Ag</b> 107.9 1 + 4d <sup>10</sup>	48 <b>Cd</b> 112.4 2 + 4d <sup>10</sup>	49 <b>In</b> 114.8 3 + 4d <sup>10</sup>	50 <b>Sn</b> 118.7 4 + 4d <sup>10</sup>	51 <b>Sb</b> 121.8	52 <b>Te</b> 127.6	53 <b>I</b> 126.9	54 <b>Xe</b> 83.80	
55 <b>Cs</b> 132.9 1 + 6s <sup>0</sup>	56 <b>Ba</b> 137.3 2 + 6s <sup>0</sup>	57 <b>La</b> 138.9 3 + 4f <sup>0</sup>	58 <b>Ce</b> 140.1 4 + 4f <sup>0</sup> 13	59 <b>Pr</b> 140.9 3 + 4f <sup>1</sup>	60 <b>Nd</b> 144.2 3 + 4f <sup>2</sup> 19	61 <b>Pm</b> 145	62 <b>Sm</b> 150.4 3 + 4f <sup>3</sup> 105	63 <b>Eu</b> 152.0 2 + 4f <sup>6</sup> 90	64 <b>Gd</b> 157.3 3 + 4f <sup>7</sup> 292	65 <b>Tb</b> 158.9 3 + 4f <sup>8</sup> 229 221	66 <b>Dy</b> 162.5 3 + 4f <sup>9</sup> 179 85	67 <b>Ho</b> 164.9 3 + 4f <sup>10</sup> 132 20	68 <b>Er</b> 167.3 3 + 4f <sup>11</sup> 85 20	69 <b>Tm</b> 168.9 3 + 4f <sup>12</sup> 56	70 <b>Yb</b> 173.0 3 + 4f <sup>13</sup>	71 <b>Lu</b> 175.0 3 + 4f <sup>14</sup>		
87 <b>Fr</b> 223	88 <b>Ra</b> 226.0 2 + 7s <sup>0</sup>	89 <b>Ac</b> 227.0 3 + 5f <sup>0</sup>	90 <b>Th</b> 232.0 4 + 5f <sup>0</sup>	91 <b>Pa</b> 231.0 5 + 5f <sup>0</sup>	92 <b>U</b> 238.0 4 + 5f <sup>2</sup>	93 <b>Np</b> 238.0 5 + 5f <sup>2</sup>	94 <b>Pu</b> 244	95 <b>Am</b> 243	96 <b>Cm</b> 247	97 <b>Bk</b> 247	98 <b>Cf</b> 251	99 <b>Es</b> 252	100 <b>Fm</b> 257	101 <b>Md</b> 258	102 <b>No</b> 259	103 <b>Lr</b> 260		

Legend:

- Nonmetal
- Metal
- Radioactive
- Diamagnet
- Paramagnet
- Magnetic atom
- Ferromagnet T<sub>C</sub> > 290K
- Antiferromagnet with T<sub>N</sub> > 290K
- Antiferromagnet/Ferromagnet with T<sub>N</sub>/T<sub>C</sub> < 290 K

100



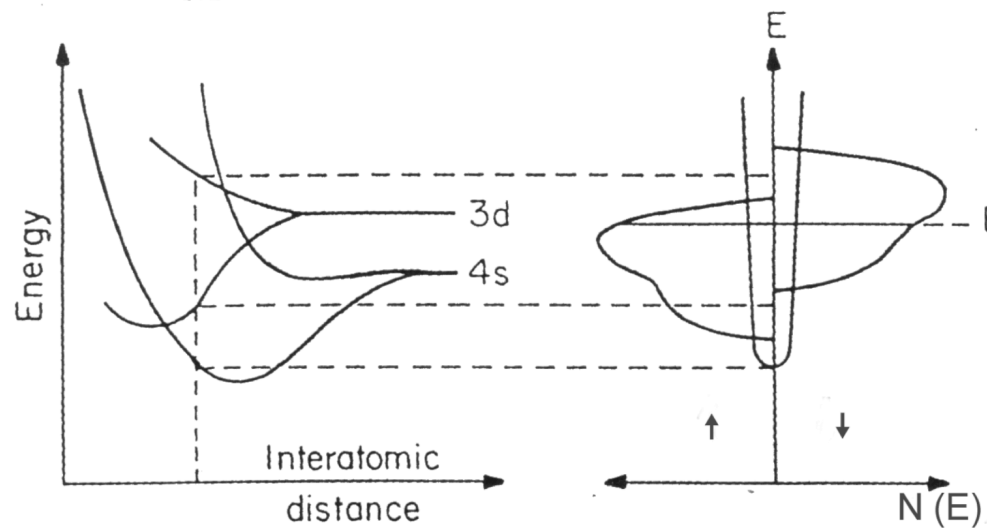
### 3.3 Magnetism of electrons in free atoms and solids.

Magnetism in *free atoms* is reduced by shell filling.

Electrons in filled shells have paired spins with  $\uparrow$  and  $\downarrow$  and no net moment. Only unpaired electrons in unfilled (usually outermost) shells have a moment.

Magnetism in *solids* tends to be destroyed by chemical interactions of the outer electrons:

- electron transfer to form filled shells in ionic compounds e.g.  $\text{Na}^+\text{Cl}^-$  both ions are  $2p^6$
- covalent bond formation in semiconductors
- band formation in metals



Formation of *d* and *s*-bands in a metal. The broad *s*-bands have no moment. The *d*-bands may have one if they are sufficiently narrow.

Nickel has a configuration  $3d^{9.4}4s^{0.6}$ . There are 0.6 unpaired 3d electrons,  $m = 0.6 \mu_B$

Existence of magnetism in a solid depends critically on crystal structure and composition.

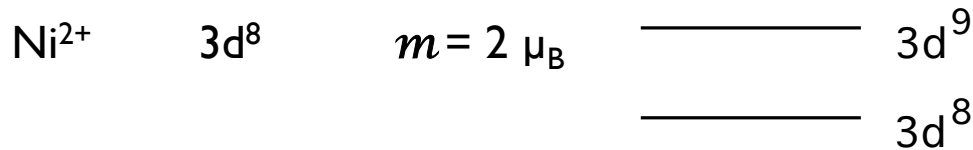
Atomic moments of iron in different compounds in Bohr magnetons/Fe.

$\gamma\text{-Fe}_2\text{O}_3$	$\alpha\text{-Fe}$	$\text{YFe}_2$	$\gamma\text{-Fe}$	$\text{YFe}_2\text{Si}_2$
ferrimagnet	ferromagnet	ferromagnet	antiferromagnet	Pauli paramagnet
5.0	2.2	1.45	unstable	0

### 3.4 Localized and delocalized electrons

#### LOCALIZED MAGNETISM

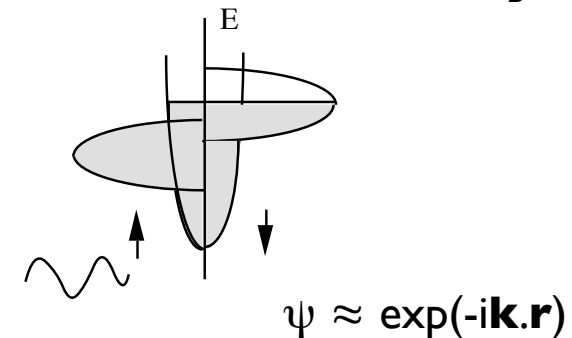
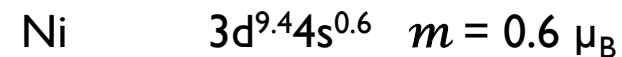
Integral number of 3d or 4f electrons  
on the ion core; Integral number of unpaired spins;  
Discrete energy levels.



Boltzmann statistics

#### DELOCALIZED MAGNETISM

Nonintegral number of unpaired spins  
per atom.  
Spin-polarized energy bands with strong  
correlations.



Fermi-Dirac statistics

4f metals	<i>localized electrons</i>
4f compounds	<i>localized electrons</i>
3d compounds	<i>localized/delocalized electrons</i>
3d metals	<i>delocalized electrons.</i>

Above the ferromagnetic Curie temperature, the moments do not disappear, they just become disordered in a paramagnetic state when  $T > T_C$ .

## 3.5 Theory of electronic magnetism

Maxwell's equations relate magnetic and electric fields to their sources. The other fundamental relation of electrodynamics is the expression for the force on a moving particle with charge  $q$ ,

$$\mathbf{F} = q(\mathbf{E} + \mathbf{v} \times \mathbf{B})$$

The two terms are respectively the Coulomb and Lorentz forces. The latter gives the torque equation  $\mathbf{\Gamma} = \mathbf{m} \times \mathbf{B}$ . The corresponding Hamiltonian for the particle in a vector potential  $\mathbf{A}$  representing the magnetic field  $\mathbf{B}$  ( $\mathbf{B} = \nabla \times \mathbf{A}$ ) and a scalar potential  $\phi_e$  representing the electric field  $\mathbf{E}$  ( $\mathbf{E} = -\nabla\phi_e$ ) is

$$\mathcal{H} = (1/2m)(\mathbf{p} - q\mathbf{A})^2 + q\phi_e$$

### 3.5.1 Orbital moment

The Hamiltonian of an electron with electrostatic potential energy  $V(\mathbf{r}) = -e\phi_e$  is

$$\mathcal{H} = (1/2m)(\mathbf{p} + e\mathbf{A})^2 + V(\mathbf{r})$$

Now  $(\mathbf{p} + e\mathbf{A})^2 = \mathbf{p}^2 + e^2\mathbf{A}^2 + 2e\mathbf{A} \cdot \mathbf{p}$  since  $\mathbf{A}$  and  $\mathbf{p}$  commute when  $\nabla \cdot \mathbf{A} = 0$ . So

$$\mathcal{H} = [\mathbf{p}^2/2m + V(\mathbf{r})] + (e/m)\mathbf{A} \cdot \mathbf{p} + (e^2/2m)\mathbf{A}^2$$

$$\mathcal{H} = \mathcal{H}_0 + \mathcal{H}_1 + \mathcal{H}_2$$

where  $\mathcal{H}_0$  is the unperturbed Hamiltonian,  $\mathcal{H}_1$  gives the paramagnetic response of the orbital moment and  $\mathcal{H}_2$  describes the small diamagnetic response. Consider a uniform field  $\mathbf{B}$  along  $\mathbf{z}$ . Then the vector potential in component form is  $\mathbf{A} = (1/2)(-yB, xB, 0)$ ,

so  $\mathbf{B} = \nabla \times \mathbf{A} = \mathbf{e}_z(\partial A_y/\partial x - \partial A_x/\partial y) = \mathbf{e}_z B$ . More generally

$$\mathbf{A} = (1/2)\mathbf{B} \times \mathbf{r}$$

Now  $(e/m)\mathbf{A} \cdot \mathbf{p} = (e/2m)\mathbf{B} \times \mathbf{r} \cdot \mathbf{p} = (e/2m)\mathbf{B} \cdot \mathbf{r} \times \mathbf{p} = (e/2m)\mathbf{B} \cdot \mathbf{l}$  since  $\mathbf{l} = \mathbf{r} \times \mathbf{p}$ . The second term in the Hamiltonian is then the Zeeman interaction for the orbital moment

$$\mathcal{H}_1 = (\mu_B/\hbar)\mathbf{B} \cdot \mathbf{l}$$

The third term is  $(e^2/8m)(\mathbf{B} \times \mathbf{r})^2 = (e^2/8m^2)B^2(x^2+y^2)$ . If the orbital is spherically symmetric,  $\langle x^2 \rangle = \langle y^2 \rangle = \langle r^2 \rangle/3$ . The corresponding energy  $E = (e^2 B^2/12m) \langle r^2 \rangle$ . Since  $M = -\partial E/\partial B$  and susceptibility  $\chi = \mu_0 N M/B$ , It follows that the orbital diamagnetic susceptibility is  $\chi = \mu_0 N e^2 \langle r^2 \rangle/6m$ .

### 3.5.2 Spin moment

The time-dependent Schrödinger equation

$$-(\hbar^2/2m)\nabla^2\psi + V\psi = i\hbar\partial\psi/\partial t$$

is not relativistically invariant because the operators  $\partial/\partial t$  and  $\partial/\partial x$  do not appear to the same power. We need to use a 4-vector  $X = (ct, x, y, z)$  with derivatives  $\partial/\partial X$ .

Dirac discovered the relativistic quantum mechanical theory of the electron, which involves the Pauli spin operators  $\sigma_i$ , with coupled equations for electrons and positrons. The nonrelativistic limit of the theory, including the interaction with a magnetic field  $\mathbf{B}$  represented by a vector potential  $\mathbf{A}$  can be written as

$$\mathcal{H} = [(1/2m)(\mathbf{p} + e\mathbf{A})^2 + V(\mathbf{r})] - p^4/8m^3c^2 + (e/m)\mathbf{B} \cdot \mathbf{s} + (1/2m^2c^2r)(dV/dr) - (1/4m^2c^2)(dV/dr) \partial/\partial r$$

- The second term is a higher-order correction to the kinetic energy
- The third term is the interaction of the electron spin with the magnetic field, so that the complete expression for the Zeeman interaction of the electron is

$$\mathcal{H}_Z = (\mu_B/\hbar)\mathbf{B} \cdot (\mathbf{l} + 2\mathbf{s})$$

The factor 2 is not quite exact. The expression is  $2(1 + \alpha/2\pi - \dots) \approx 2.0023$ , where  $\alpha = e^2/4\pi\epsilon_0\hbar c \approx 1/137$  is the fine-structure constant.

- The fourth term is the spin-orbit interaction., which for a central potential  $V(r) = -Ze^2/4\pi\epsilon_0 r$  with  $Ze$  as the nuclear charge becomes  $-Ze^2\mu_0\mathbf{l}\cdot\mathbf{s}/8\pi m^2 r^3$  since  $\mu_0\epsilon_0 = 1/c^2$ . In an atom  $\langle 1/r^3 \rangle \approx (0.1 \text{ nm})^{-3}$  so the magnitude of the spin-orbit coupling  $\lambda$  is 2.5 K for hydrogen ( $Z = 1$ ), 60 K for 3d elements ( $Z \approx 25$ ), and 160 K for actinides ( $Z \approx 65$ ).

In a noncentral potential, the spin-orbit interaction is  $(\mathbf{s} \times \nabla V) \cdot \mathbf{p}$

- The final term just shifts the levels when  $l = 0$

### 3.5.3 Magnetism and relativity

The classification of interactions according to their relativistic character is based on the kinetic energy

$$E = mc^2\sqrt{1 + (v^2/c^2)}$$

The order of magnitude of the velocity of electrons in solids is  $\alpha c$ . Expanding the equation in powers of  $c$

$$E = mc^2 + (1/2)\alpha^2 mc^2 - (1/8)\alpha^4 mc^2$$

Here the rest mass of the electron,  $mc^2 = 511 \text{ keV}$ ; the second and third terms, which represent the order of magnitude of electrostatic and magnetostatic energies are respectively 13.6 eV and 0.18 meV. Magnetic dipolar interactions are therefore of order 2 K. (1 eV = 11605 K)



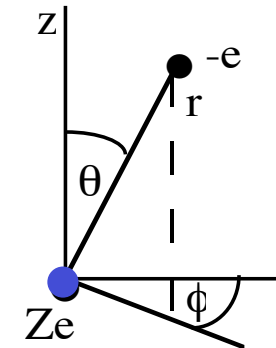
## 4. Magnetism of localized electrons on the atom

The quantum mechanics of an electron in a central potential leads to single-electron states classified in terms of the quantum numbers  $n, l, m_l, s$  and  $m_s$ , which have different orbital and spin angular momenta. In a multi-electron atom, the angular momenta are coupled to give a series of energy levels; which are split by a magnetic or an electric field. The lowest energy level is the one of interest for magnetism.

## 4.1 The single-electron hydrogenic atom; angular momentum.

The Hamiltonian  $\mathcal{H}_0$  for an electron in a central potential due to a nucleus of charge  $Ze$  at the origin and an electron at  $(r, \theta, \phi)$

$$\mathcal{H}_0 = -(\hbar^2/2m)\nabla^2 - Ze^2/4\pi\epsilon_0 r$$



[KE is  $p^2/2m$ ; the momentum operator in quantum mechanics  $\mathbf{p} = -i\hbar\nabla$ ]

In polar coordinates:  $x = r \sin\theta \cos\phi$ ,  $y = r \sin\theta \sin\phi$ ,  $z = r \cos\theta$

$$\nabla^2 = \partial^2 / \partial r^2 + (2/r) \partial / \partial r + 1/r^2 \{ \partial^2 / \partial \theta^2 + \cot\theta \partial / \partial \theta + (1/\sin^2\theta) \partial^2 / \partial \phi^2 \}$$

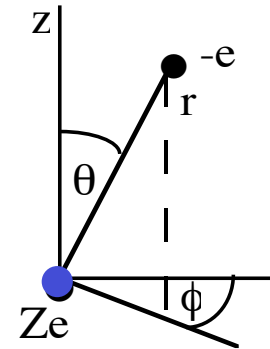
$$\begin{aligned} \mathbf{l} = \mathbf{r} \wedge \mathbf{p} &= -i\hbar[(y \partial / \partial z - z \partial / \partial y)\mathbf{e}_x - (x \partial / \partial z - z \partial / \partial x)\mathbf{e}_y + (x \partial / \partial y - y \partial / \partial x)\mathbf{e}_z] \\ &= i\hbar[\sin\phi \partial / \partial \theta + \cot\theta \cos\phi \partial / \partial \phi]\mathbf{e}_x + (-\cos\phi \partial / \partial \theta + \cot\theta \sin\phi \partial / \partial \phi)\mathbf{e}_y \\ &\quad - (\partial / \partial \phi)\mathbf{e}_z \end{aligned}$$

$$l^2 = l_x^2 + l_y^2 + l_z^2 = \{ \partial^2 / \partial \theta^2 + \cot\theta \partial / \partial \theta + (1/\sin^2\theta) \partial^2 / \partial \phi^2 \} - \text{the term in parentheses in } \nabla^2$$

Schrödinger's equation for an electron in a central potential due to a nucleus of charge  $Ze$  at the origin and an electron at  $(r, \theta, \phi)$

$$\mathcal{H}_0 \psi_i = E_i \psi_i$$

$$[-(\hbar^2/2m)\nabla^2 - Ze^2/4\pi\epsilon_0 r] \psi_i = E_i \psi_i$$



Solutions for  $E_i$  are the eigenvalues (energy levels) of the atom.

The corresponding wavefunctions  $\psi_i$  are the eigenfunctions (orbitals) of the atom

The meaning of the wave function  $\psi$  is that the probability of finding the electron in a small volume  $dV$  at  $\mathbf{r}$  is  $\psi^*(\mathbf{r})\psi(\mathbf{r})dV$ . It is usually a complex quantity;  $\psi^*$  is the complex conjugate of  $\psi$ .  $\psi$  contains all observable knowledge about the electron.

The basic property of angular momentum is that  $[L_x, L_y] = i\hbar L_z$  etc. where  $[L_x, L_y] = L_x L_y - L_y L_x$ .  $[\mathbf{X}, \mathbf{Y}]$  is the **commutator**. If it is zero, the operators commute and the quantities they represent can be *measured simultaneously*.

No two components of angular momentum commute, but for any *one* of them  $[L^2, L_i] = 0$

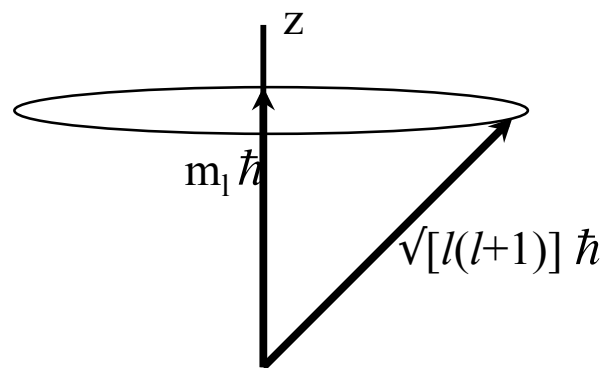
## Vector model

$I^2$  the square of the orbital angular momentum of an electron in a central potential has eigenvalues  $l(l+1)\hbar^2$ .

The orbital angular momentum has magnitude  $\sqrt{l(l+1)}\hbar$

$I_z$  Its projection along  $\mathbf{z}$  is  $m_l\hbar$ , which can have any value from  $-\hbar$  to  $+\hbar$ . ( $2l+1$  different possible values).

We can model the total angular momentum as a vector which precesses around  $\mathbf{z}$ .



Another way to represent the operators in quantum mechanics is as matrices.

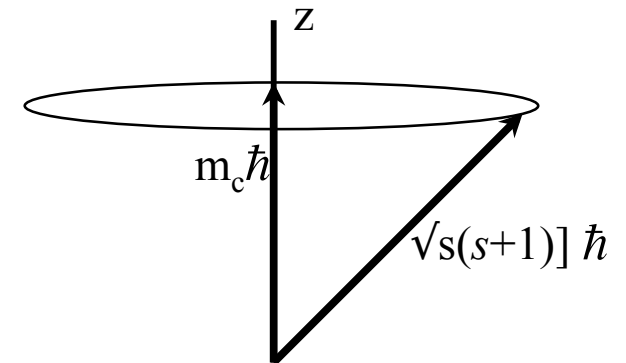
If a matrix is *diagonal*, the eigenvalues are the the diagonal elements.

The procedure for solving a problem in quantum mechanics is therefore to write down the Hamiltonian as a matrix operator, and diagonalize it.  $E_i$  are the eigenvalues.

For the components of the spin angular momentum, the *Pauli spin matrices* are

$$\mathbf{s}_x = \begin{bmatrix} 0 & 1 \\ 1 & 0 \end{bmatrix} \hbar/2 \quad \mathbf{s}_y = \begin{bmatrix} 0 & -i \\ i & 0 \end{bmatrix} \hbar/2 \quad \mathbf{s}_z = \begin{bmatrix} 1 & 0 \\ 0 & -1 \end{bmatrix} \hbar/2$$

$$\mathbf{s}^2 = \mathbf{s}_x^2 + \mathbf{s}_y^2 + \mathbf{s}_z^2 = \begin{bmatrix} 1 & 0 \\ 0 & 1 \end{bmatrix} 3\hbar^2/4$$



Eigenfunctions of the Schrödinger equation for an electron in a central potential are

$$\psi_{n,l,m_l}(r) = R_{n,l} Y_{l,m_l}(\theta, \phi)$$

radial part      angular part

- ♦ The angular part  $Y_{l,m_l}(\theta, \phi)$  are *spherical harmonics* that depend on two integers  $l, m_l$ , where  $n > l \geq 0$  and  $|m_l| \leq l$ .

The spherical harmonics are each a product of terms  $\Theta(\theta)$  and  $\Phi(\phi)$ ;  $Y_{l,m_l}(\theta, \phi) = \Theta(\theta)\Phi(\phi)$

$$\Phi(\phi) = \exp(im_l\phi) \quad \text{where } m_l = 0, \pm 1, \pm 2, \dots$$

The z-component of orbital angular momentum, represented by the operator  $I_z = -i\hbar(\partial / \partial \phi)$ , has eigenvalues  $\langle \Phi | I_z | \Phi \rangle = m_l \hbar$ .

$\Theta(\theta) = P_l^{m_l}(\cos\theta)$ , are the associated Legendre polynomials with  $l \geq |m_l|$ , so  $m_l = 0, \pm 1, \pm 2, \dots, \pm l$ .

## Spherical harmonics.

Z

**s**  $Y_0^0 = \sqrt{1/4\pi}$

**p**  $Y_1^0 = \sqrt{3/4\pi} \cos \theta \quad Y_1^{\pm 1} = \pm \sqrt{3/8\pi} \sin \theta e^{\pm i\phi}$

**d**  $Y_2^0 = \sqrt{5/16\pi}(3\cos^2\theta - 1) \quad Y_2^{\pm 1} = \pm \sqrt{15/8\pi} \sin\theta \cos\theta e^{\pm i\phi} \quad Y_2^{\pm 2} = \sqrt{15/32\pi} \sin^2\theta e^{\pm 2i\phi}$

**f**  $Y_3^0 = \sqrt{7/16\pi}(5\cos^3\theta - 3\cos\theta) \quad Y_3^{\pm 1} = \pm \sqrt{21/64\pi}(5\cos^2\theta - 1)\sin\theta e^{\pm i\phi}$   
 $Y_3^{\pm 2} = \sqrt{105/32\pi} \sin^2\theta \cos\theta e^{\pm 2i\phi} \quad Y_3^{\pm 3} = \pm \sqrt{35/64\pi} \sin^3\theta e^{\pm 3i\phi}$

♦ The radial part  $R(r)$  depends on  $l$ , also on  $n$ , the total quantum number;  $n > l$ ; hence  $l = 0, 1, \dots, (n-1)$ .

$$R(r) = V_n^l(Zr/na_0)\exp[-(Zr/na_0)]$$

$V_l^0 = 1$ . Here  $a_0 = 4\pi\epsilon_0\hbar^2/me^2 = 52.9$  pm is the first *Bohr radius*, the basic length scale in atomic physics.  
 The energy levels of the one-electron atom are

$$E = -Zme^4/8h^2\epsilon_0^2n^2 = -ZR/n^2$$

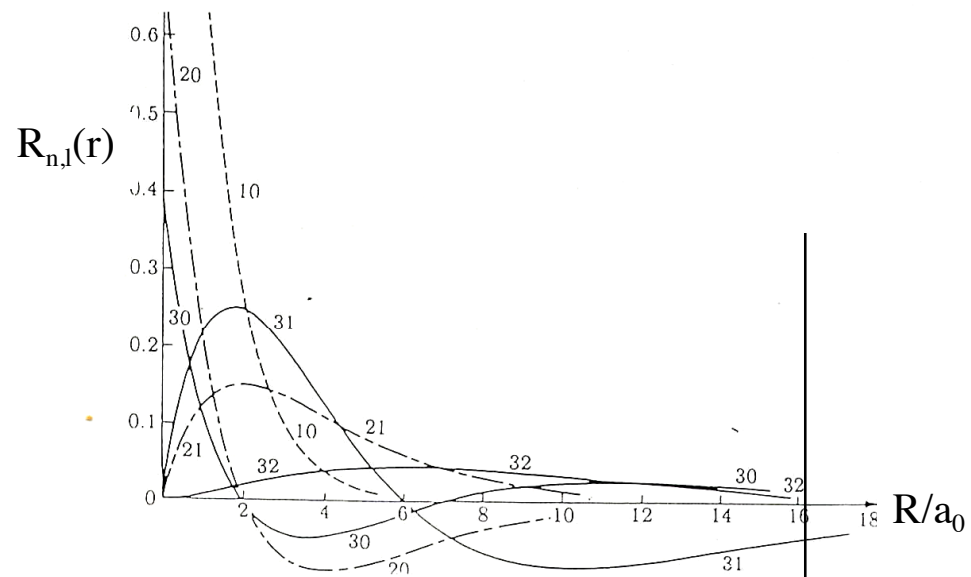
The quantity  $R = me^4/8h^2\epsilon_0 = 13.6$  eV is the Rydberg, the basic energy unit in atomic physics.  
 For the central Coulomb potential  $\phi_e$ , the potential energy  $V(r)$  depends only on  $r$ , not on  $\theta$  or  $\phi$ .  
 $E$  depends only on  $n$ .



The three quantum numbers  $n$ ,  $l$ ,  $m_l$  denote an *orbital*, a spatial distribution of electronic charge. Orbitals are denoted  $n_x$ ,  $x = s, p, d, f$  for  $l = 0, 1, 2, 3$ . Each orbital can accommodate up to two electrons with spin  $m_s = \pm 1/2$ . The hydrogenic orbitals are listed in the table

	<b>n</b>	<b>l</b>	<b><math>m_l</math></b>	<b><math>m_s</math></b>	<b>No of states</b>
<b>1s</b>	<b>1</b>	<b>0</b>	<b>0</b>	<b><math>\pm 1/2</math></b>	<b>2</b>
<b>2s</b>	<b>2</b>	<b>0</b>	<b>0</b>	<b><math>\pm 1/2</math></b>	<b>2</b>
<b>2p</b>	<b>2</b>	<b>1</b>	<b>0, <math>\pm 1</math></b>	<b><math>\pm 1/2</math></b>	<b>6</b>
<b>3s</b>	<b>3</b>	<b>0</b>	<b>0</b>	<b><math>\pm 1/2</math></b>	<b>2</b>
<b>3p</b>	<b>3</b>	<b>1</b>	<b>0, <math>\pm 1</math></b>	<b><math>\pm 1/2</math></b>	<b>6</b>
<b>3d</b>	<b>3</b>	<b>2</b>	<b>0, <math>\pm 1, \pm 2</math></b>	<b><math>\pm 1/2</math></b>	<b>10</b>
<b>4s</b>	<b>4</b>	<b>0</b>	<b>0</b>	<b><math>\pm 1/2</math></b>	<b>2</b>
<b>4p</b>	<b>4</b>	<b>1</b>	<b>0, <math>\pm 1</math></b>	<b><math>\pm 1/2</math></b>	<b>6</b>
<b>4d</b>	<b>4</b>	<b>2</b>	<b>0, <math>\pm 1, \pm 2</math></b>	<b><math>\pm 1/2</math></b>	<b>10</b>
<b>4f</b>	<b>4</b>	<b>3</b>	<b>0, <math>\pm 1, \pm 2, \pm 3</math></b>	<b><math>\pm 1/2</math></b>	<b>14</b>

- The Pauli principle states that no two electrons can have the same four quantum numbers. Each orbital can be occupied by at most two electrons with opposite spin.



$$Y_{l,m_l}(\theta, \phi)$$



$$m_l = 0$$

*s orbital*

$$l = 0$$



$$m_l = 0$$



$$m_l = \pm 1$$

*p orbitals*

$$l = 1$$



$$m_l = 0$$



$$m_l = \pm 1$$

*d orbitals*

$$l = 2$$



$$m_l = \pm 2$$

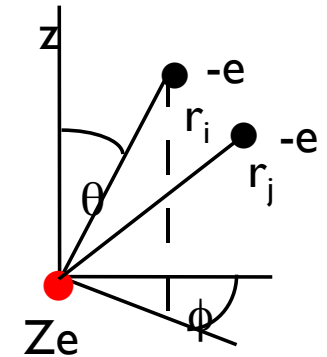
## 4.2 The many-electron atom

The hydrogenic atom was composed of a nucleus of charge  $Ze$  at the origin and a single electron at  $r, \theta, \phi$ . When there are several electrons, they interact via inter-electronic Coulomb interactions. Terms like  $e^2/4\pi\epsilon_0|r_i - r_j|$  have to be added to the Hamiltonian. A many-body problem!

$$\mathcal{H} = \sum_i (p_i^2/2m) + \sum_i (Ze^2/4\pi\epsilon_0 r_i) + (1/2) \sum_{i \neq j} (e^2/4\pi\epsilon_0 |r_i - r_j|)$$

An approximate way to treat the interactions is to suppose that each electron sees a different spherical charge distribution represented by a different central potential  $V_i(r)$  for each electron

$$\mathcal{H}_i = p_i^2/2m + V_i(r)$$



The potential with many electrons is not a simple Coulomb potential well; the degeneracy of electrons with different  $l$  is raised. The 4s shell, for example, is then lower in energy than the 3d shell, which defines the shape of the periodic table.

The quantities  $V_i(r)$  must be determined self-consistently (the Hartree-Fock approximation)

The eigenstates of the many-electron atom or ion have the following properties:

$$\begin{aligned} [\mathcal{H}, \mathbf{S}^2] &= 0, & [\mathcal{H}, S_z] &= 0 & \text{where } S &= \sum_i s_i \text{ a sum of the spin moments} \\ [\mathcal{H}, \mathbf{L}^2] &= 0, & [\mathcal{H}, L_z] &= 0 & \text{where } L &= \sum_i l_i \text{ a sum of the orbital moments} \end{aligned}$$

# Magnetic Periodic Table

Atomic Number → **66 Dy** ← Atomic symbol  
 Typical ionic change → **3 + 4<sup>f</sup>** ← Atomic weight  
 Antiferromagnetic T<sub>N</sub>(K) → **179 85** ← Ferromagnetic T<sub>C</sub>(K)

<b>1 H</b> 1.00																	<b>2 He</b> 4.00				
<b>3 Li</b> 6.94 1 + 2s <sup>0</sup>	<b>4 Be</b> 9.01 2 + 2s <sup>0</sup>															<b>5 B</b> 10.81	<b>6 C</b> 12.01	<b>7 N</b> 14.01	<b>8 O</b> 16.00 35	<b>9 F</b> 19.00	<b>10 Ne</b> 20.18
<b>11 Na</b> 22.99 1 + 3s <sup>0</sup>	<b>12 Mg</b> 24.21 2 + 3s <sup>0</sup>															<b>13 Al</b> 26.98 3 + 2p <sup>6</sup>	<b>14 Si</b> 28.09	<b>15 P</b> 30.97	<b>16 S</b> 32.07	<b>17 Cl</b> 35.45	<b>18 Ar</b> 39.95
<b>19 K</b> 38.21 1 + 4s <sup>0</sup>	<b>20 Ca</b> 40.08 2 + 4s <sup>0</sup>	<b>21 Sc</b> 44.96 3 + 3d <sup>0</sup>	<b>22 Ti</b> 47.88 4 + 3d <sup>0</sup>	<b>23 V</b> 50.94 3 + 3d <sup>2</sup>	<b>24 Cr</b> 52.00 3 + 3d <sup>3</sup> 312	<b>25 Mn</b> 55.85 2 + 3d <sup>5</sup> 96	<b>26 Fe</b> 55.85 3 + 3d <sup>6</sup> 1043	<b>27 Co</b> 58.93 2 + 3d <sup>7</sup> 1390	<b>28 Ni</b> 58.69 2 + 3d <sup>8</sup> 629	<b>29 Cu</b> 63.55 2 + 3d <sup>9</sup>	<b>30 Zn</b> 65.39 2 + 3d <sup>10</sup>	<b>31 Ga</b> 69.72 3 + 3d <sup>10</sup>	<b>32 Ge</b> 72.61	<b>33 As</b> 74.92	<b>34 Se</b> 78.96	<b>35 Br</b> 79.90	<b>36 Kr</b> 83.80				
<b>37 Rb</b> 85.47 1 + 5s <sup>0</sup>	<b>38 Sr</b> 87.62 2 + 5s <sup>0</sup>	<b>39 Y</b> 88.91 2 + 4d <sup>0</sup>	<b>40 Zr</b> 91.22 4 + 4d <sup>0</sup>	<b>41 Nb</b> 92.91 5 + 4d <sup>0</sup>	<b>42 Mo</b> 95.94 5 + 4d <sup>1</sup>	<b>43 Tc</b> 97.9	<b>44 Ru</b> 101.1 3 + 4d <sup>5</sup>	<b>45 Rh</b> 102.4 3 + 4d <sup>6</sup>	<b>46 Pd</b> 106.4 2 + 4d <sup>8</sup>	<b>47 Ag</b> 107.9 1 + 4d <sup>10</sup>	<b>48 Cd</b> 112.4 2 + 4d <sup>10</sup>	<b>49 In</b> 114.8 3 + 4d <sup>10</sup>	<b>50 Sn</b> 118.7 4 + 4d <sup>10</sup>	<b>51 Sb</b> 121.8	<b>52 Te</b> 127.6	<b>53 I</b> 126.9	<b>54 Xe</b> 83.80				
<b>55 Cs</b> 132.9 1 + 6s <sup>0</sup>	<b>56 Ba</b> 137.3 2 + 6s <sup>0</sup>	<b>57 La</b> 138.9 3 + 4f <sup>0</sup>	<b>72 Hf</b> 178.5 4 + 5d <sup>0</sup>	<b>73 Ta</b> 180.9 5 + 5d <sup>0</sup>	<b>74 W</b> 183.8 6 + 5d <sup>0</sup>	<b>75 Re</b> 186.2 4 + 5d <sup>3</sup>	<b>76 Os</b> 190.2 3 + 5d <sup>6</sup>	<b>77 Ir</b> 192.2 4 + 5d <sup>6</sup>	<b>78 Pt</b> 195.1 2 + 5d <sup>8</sup>	<b>79 Au</b> 197.0 1 + 5d <sup>10</sup>	<b>80 Hg</b> 200.6 2 + 5d <sup>10</sup>	<b>81 Tl</b> 204.4 3 + 5d <sup>10</sup>	<b>82 Pb</b> 207.2 4 + 5d <sup>10</sup>	<b>83 Bi</b> 209.0	<b>84 Po</b> 209	<b>85 At</b> 210	<b>86 Rn</b> 222				
<b>87 Fr</b> 223	<b>88 Ra</b> 226.0 2 + 7s <sup>0</sup>	<b>89 Ac</b> 227.0 3 + 5f <sup>0</sup>																			
			<b>58 Ce</b> 140.1 4 + 4f <sup>0</sup> 13	<b>59 Pr</b> 140.9 3 + 4f <sup>2</sup>	<b>60 Nd</b> 144.2 3 + 4f <sup>3</sup> 19	<b>61 Pm</b> 145	<b>62 Sm</b> 150.4 3 + 4f <sup>5</sup> 105	<b>63 Eu</b> 152.0 2 + 4f <sup>7</sup> 90	<b>64 Gd</b> 157.3 3 + 4f <sup>7</sup> 292	<b>65 Tb</b> 158.9 3 + 4f <sup>8</sup> 229 221	<b>66 Dy</b> 162.5 3 + 4f <sup>9</sup> 179 85	<b>67 Ho</b> 164.9 3 + 4f <sup>10</sup> 132 20	<b>68 Er</b> 167.3 3 + 4f <sup>11</sup> 85 20	<b>69 Tm</b> 168.9 3 + 4f <sup>12</sup> 56	<b>70 Yb</b> 173.0 3 + 4f <sup>13</sup>	<b>71 Lu</b> 175.0 3 + 4f <sup>14</sup>					
			<b>90 Th</b> 232.0 4 + 5f <sup>0</sup>	<b>91 Pa</b> 231.0 5 + 5f <sup>0</sup>	<b>92 U</b> 238.0 4 + 5f <sup>2</sup>	<b>93 Np</b> 238.0 5 + 5f <sup>2</sup>	<b>94 Pu</b> 244	<b>95 Am</b> 243	<b>96 Cm</b> 247	<b>97 Bk</b> 247	<b>98 Cf</b> 251	<b>99 Es</b> 252	<b>100 Fm</b> 257	<b>101 Md</b> 258	<b>102 No</b> 259	<b>103 Lr</b> 260					

Nonmetal

Metal

Radioactive

Diamagnet

Paramagnet

**BOLD** Magnetic atom

Ferromagnet T<sub>C</sub> > 290K

Antiferromagnet with T<sub>N</sub> > 290K

Antiferromagnet/Ferromagnet with T<sub>N</sub>/T<sub>C</sub> < 290 K

Each eigenstate of  $\mathcal{H}$  for the many-electron atom can be labelled by the quantum numbers corresponding to the eigenstates of  $\mathbf{L}^2, \mathbf{L}_z, \mathbf{S}^2, \mathbf{S}_z$  i.e.  $L, M_L, S, M_S$

Eigenfunctions

$$\psi^\alpha_{LSM_L M_S}$$

Eigenvalues

$$E^\alpha_{LSM_L M_S}$$

$$\begin{aligned} \mathcal{H} |\psi^\alpha_{LSM_L M_S}\rangle &= E^\alpha_{LSM_L M_S} |\psi^\alpha_{LSM_L M_S}\rangle \\ \mathbf{L}^2 |\psi^\alpha_{LSM_L M_S}\rangle &= L(L+1) \hbar |\psi^\alpha_{LSM_L M_S}\rangle & \mathbf{L}_z |\psi^\alpha_{LSM_L M_S}\rangle &= M_L \hbar |\psi^\alpha_{LSM_L M_S}\rangle \\ \mathbf{S}^2 |\psi^\alpha_{LSM_L M_S}\rangle &= S(S+1) \hbar |\psi^\alpha_{LSM_L M_S}\rangle & \mathbf{S}_z |\psi^\alpha_{LSM_L M_S}\rangle &= M_S \hbar |\psi^\alpha_{LSM_L M_S}\rangle \end{aligned}$$

The eigenstates for different  $M_L$  or  $M_S$  values are degenerate in the absence of a field, but the states for different  $L, S$  are separated.

Hence each  $(L, S)$  state is  $(2L+1)(2S+1)$  times degenerate.

An  $(L, S)$  state is known as an atomic *term*

spin degeneracy

Notation

$2S+1$   $L$

letter to denote orbital moment  
S, P, D .....

*Example:*  $^3D$  means  $S = 1, L = 2$ , total degeneracy  $3 \times 5 = 15$

The energy splitting of the terms is of order 1 eV. In spectroscopy the energy unit  $\text{cm}^{-1}$  is often used: Useful energy conversions are  $1 \text{ eV} \equiv 11605 \text{ K}$  and  $1 \text{ cm}^{-1} \equiv 1.44 \text{ K}$

## 4.3 Addition of angular momenta

Consider two angular momenta  $\mathbf{j}_1$  and  $\mathbf{j}_2$  with eigenstates  $|j_1, m_1\rangle$  and  $|j_2, m_2\rangle$

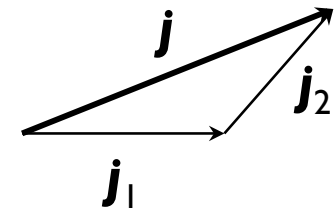
$$\text{i.e. } \mathbf{j}_1^2 |j_1, m_1\rangle = j_1(j_1+1) \hbar^2 |j_1, m_1\rangle \quad \mathbf{j}_{1z} |j_1, m_1\rangle = m_1 \hbar |j_1, m_1\rangle$$

$$\mathbf{j}_2^2 |j_2, m_2\rangle = j_2(j_2+1) \hbar^2 |j_2, m_2\rangle \quad \mathbf{j}_{2z} |j_2, m_2\rangle = m_2 \hbar |j_2, m_2\rangle$$

The eigenstates of  $(\mathbf{j}_1 + \mathbf{j}_2)$  are  $|j_1, m_1\rangle |j_2, m_2\rangle$  denoted as  $|j_1, j_2, m_1, m_2\rangle$

Now  $-j_1 \leq m_1 \leq j_1$  and  $-j_2 \leq m_2 \leq j_2$  so the space spanned by the states  $|j_1, j_2, m_1, m_2\rangle$  has dimension  $(2j_1 + 1)(2j_2 + 1)$  and

the eigenstates of  $\mathbf{j}^2$  and  $\mathbf{j}_z$  are  $|j_1, j_2, j, m\rangle$  with  $|j_1 - j_2| \leq j \leq |j_1 + j_2|$



When several electrons are present on the same atom, at most two of them having opposite spin can occupy the same orbital (Pauli principle).

Their spin and orbital angular momenta add to give resultant quantum numbers


$$S = \sum s_i, \quad L = \sum l_i. \quad \text{Subject to constraint of Pauli principle}$$

**Example:** Consider a 6-electron atom (carbon). Configuration  $1s^2 2s^2 2p^2$

The two s-shells are filled, and they have no net angular momentum. The  $p$ -electrons have  $l = 1$ ,  $L = l_1 + l_2$  Hence  $|l_1 - l_2| \leq L \leq |l_1 + l_2|$ ;  $0 \leq L \leq 2$ ,  $L = 0, 1, 2$

Also  $s = 1/2$ ,  $S = s_1 + s_2$  Hence  $|s_1 - s_2| \leq S \leq |s_1 + s_2|$ ;  $0 \leq S \leq 1$ ,  $S = 0, 1$

Not all combinations are possible ! There are 15 allowed states, belonging to three terms.

							
						$M_L$	$M_S$
				↑↓		2	0
				↑↑		1	1
				↑↓		1	0
				↑↓		1	0
				↑↑		1	-1
				↑↑		0	1
				↑↓		0	0
				↑↓		0	0
				↑↓		0	0
				↑↓		0	-1
				↑↓		0	-1
				↑↓		-1	0
				↑↓		-1	0
				↑↓		-1	1
				↑↓		-2	0
Term	L	S	( $M_L, M_S$ )				
$1S$	0	0	(0,0)				
$3P$	1	1	(1,1)(1,0)(1,-1)(0,1)(0,0)(0,-1)(-1,1)(-1,0)(-1,-1)				
$1D$	2	0	(2,0)(1,0)(0,0)(-1,0)(-2,0)				



$M_s \backslash M_l$	-2	-1	0	1	2
-1	-	1	1	1	-
0	1	2	3	2	1
1	-	1	1	1	-

	1	1	1	
	1	1	1	
	1	1	1	

$^3P$

+

1	1	1	1	1

$^1D$

+

		1		

$^1S$

Another way of stating the Pauli principle is that the total wavefunction must be *antisymmetric when two electrons are interchanged*.

The spin of the two *p*-electrons can be  $S = 0$  (spin singlet) or  $S = 1$  (spin triplet)

$$S = 0, M_s = 0 \quad \psi_{\text{spin}} = [|\uparrow\downarrow\rangle - |\downarrow\uparrow\rangle]/\sqrt{2} \quad \text{antisymmetric}$$

$$\begin{aligned} S = 1, M_s = 1 & \quad \psi_{\text{spin}} = |\uparrow\uparrow\rangle \\ M_s = 0 & \quad \psi_{\text{spin}} = [|\uparrow\downarrow\rangle + |\downarrow\uparrow\rangle]/\sqrt{2} \quad \text{symmetric} \\ M_s = 1 & \quad \psi_{\text{spin}} = |\downarrow\downarrow\rangle \end{aligned}$$

SPIN     Antisymmetric when  $S=0$   
            Symmetric when  $S=1$

ORBIT    Antisymmetric when  $L = 1, 3$   
            Symmetric when  $L = 0, 2, 4$

The total wavefunction must be antisymmetric,

$$\begin{array}{ll} L=0, S=0 (^1S) & \text{--- } L=0, S=1 (^3S) \text{ ---} \\ \text{--- } L=1, S=0 (^1P) & L=1, S=1 (^3P) \\ L=2, S=0 (^1D) & \text{--- } L=2, S=1 (^3D) \text{ ---} \end{array}$$

### 4.3.1 Spin-orbit coupling

Spin-orbit coupling is a relativistic effect, represented by an extra term in the Hamiltonian

$$\mathcal{H} = \mathcal{H}_0 + \mathcal{H}_{so}$$

It can be regarded as the interaction between the spin moment of the electron and the magnetic field created by the relative orbital motion of the nucleus.

$$\mathcal{H}_{so} = -\mathbf{m} \cdot \mathbf{B}_{orb} = 2(\mu_B/\hbar) \mathbf{s} \cdot \mathbf{B}_{orb}$$

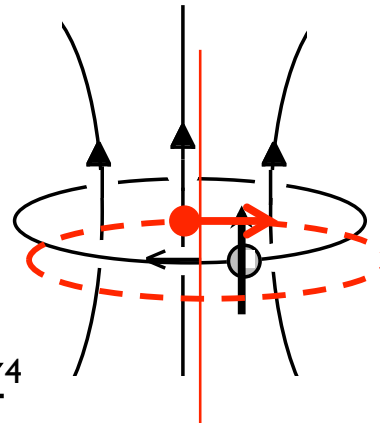
The field due to a current loop is

$$B = \mu_0 I / 2r \text{ where } I = Ze v / 2\pi r$$

$$B_{orb} = \mu_0 Z e v / 4\pi r^2$$

The interaction varies approximately as  $Z^4$

It is usually written in terms of the orbital moment as



$$\mathcal{H}_{so} = -\lambda \mathbf{l} \cdot \mathbf{s} \quad \text{where the spin-orbit coupling constant has units of } J/\hbar^2$$

In the presence of the spin-orbit interaction,  $m_l$  and  $m_s$  are no longer good quantum numbers, though spherical symmetry is retained so  $l$  and  $s$  are still good.

$\mathbf{l}$  and  $\mathbf{s}$  couple to form the total angular momentum  $\mathbf{j}$ .  $J = l \pm s = l \pm 1/2$

In multi-electron atoms the spin-orbit interaction is

$$\mathcal{H}_{so} = -\Lambda \mathbf{L} \cdot \mathbf{S}$$

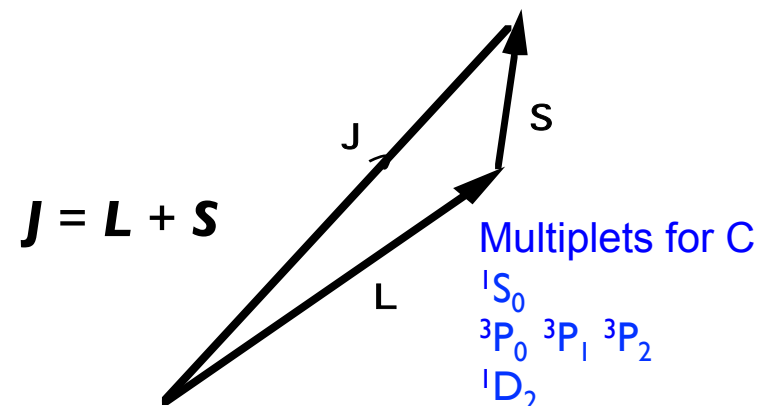
We can therefore have a multiplet of states with different  $J$  values issuing from a given  $(L, S)$  term.

$$L - S \leq J \leq L + S$$

General notation for multiplets is  $^{2S+1}L_J$

$\Lambda$  is  $> 0$  for the first half of the 3d or 4f series and  $< 0$  for the second half. It becomes large in heavy elements.  $\Lambda$  is related to the one-electron spin-orbit coupling constant  $\lambda$  by  $\Lambda = \pm \lambda / 2S$  for the first and second halves of the series.

The identity  $\mathbf{J}^2 = \mathbf{L}^2 + \mathbf{S}^2 + 2 \mathbf{L} \cdot \mathbf{S}$  is used to evaluate  $\mathcal{H}_{so}$ . The eigenvalues of  $\mathbf{J}^2$  are  $J(J + 1)\hbar^2$  etc, hence  $\mathbf{L} \cdot \mathbf{S}$  can be calculated



Addition of  $\mathbf{L}$  and  $\mathbf{S}$  in the vector model

Spin-orbit coupling constants in  
the 3d and 4f series  
In Kelvin

	ion	$\Lambda$
3d <sup>1</sup>	Ti <sup>3+</sup>	124
3d <sup>2</sup>	Ti <sup>2+</sup>	88
3d <sup>3</sup>	V <sup>2+</sup>	82
3d <sup>4</sup>	Cr <sup>2+</sup>	85
3d <sup>6</sup>	Fe <sup>2+</sup>	-164
3d <sup>7</sup>	Co <sup>2+</sup>	-272
3d <sup>8</sup>	Ni <sup>2+</sup>	-493

4f <sup>1</sup>	Ce <sup>3+</sup>	920
4f <sup>2</sup>	Pr <sup>3+</sup>	540
4f <sup>3</sup>	Nd <sup>3+</sup>	430
4f <sup>5</sup>	Sm <sup>3+</sup>	350
4f <sup>8</sup>	Tb <sup>3+</sup>	-410
4f <sup>9</sup>	Dy <sup>3+</sup>	-550
4f <sup>10</sup>	Ho <sup>3+</sup>	-780
4f <sup>11</sup>	Er <sup>3+</sup>	-1170
4f <sup>12</sup>	Tm <sup>3+</sup>	-1900
4f <sup>13</sup>	Yb <sup>3+</sup>	-4140

### 4.3.2 Atomic multiplets, Hund's rules, examples

For a given electronic configuration, we have a series of terms, split by energies of order 1 eV and each is split by a lesser amount into a series of J multiplets by spin-orbit coupling. So how do we find the lowest-energy state of the atom? This is normally the only state that is populated at room-temperature

Use **Hund's rules**: These are an empirical prescription deduced from study of optical spectra which give the lowest energy state.

- i) First maximize S for the configuration
- ii) Then maximize L consistent with that S
- iii) Finally couple L and S;  $J = L - S$  if shell is < half-full;  $J = L + S$  if shell is > half-full.

In the example of the six-electron carbon atom;  $1s^2 2s^2 2p^2$ ,

- i)  $S = 1$
- ii)  $L = 1$
- iii)  $J = 0$  since the shell is less than half-full

The ground state of carbon is  $^3P_0$ , which is nonmagnetic ! ( $J = 0$ ).

# Magnetism of free atoms

Atomic Number → **66** **Dy** ← Atomic symbol  
Atomic weight ← 162.5  
Typical ionic change → 3 + 4f<sup>9</sup>  
Antiferromagnetic T<sub>N</sub>(K) → 179 85 ← Ferromagnetic T<sub>C</sub>(K)

1 <b>H</b> 1.00																	2 <b>He</b> 4.00	
3 <b>Li</b> 6.94 1 + 2s <sup>0</sup>	4 <b>Be</b> 9.01 2 + 2s <sup>0</sup>																	10 <b>Ne</b> 20.18
11 <b>Na</b> 22.99 1 + 3s <sup>0</sup>	12 <b>Mg</b> 24.21 2 + 3s <sup>0</sup>																	18 <b>Ar</b> 39.95
19 <b>K</b> 38.21 1 + 4s <sup>0</sup>	20 <b>Ca</b> 40.08 2 + 4s <sup>0</sup>	21 <b>Sc</b> 44.96 3 + 3d <sup>0</sup>	22 <b>Ti</b> 47.88 4 + 3d <sup>0</sup>	23 <b>V</b> 50.94 3 + 3d <sup>2</sup>	24 <b>Cr</b> 52.00 3 + 3d <sup>3</sup> 312	25 <b>Mn</b> 55.85 2 + 3d <sup>5</sup> 96	26 <b>Fe</b> 55.85 3 + 3d <sup>5</sup> 1043	27 <b>Co</b> 58.93 2 + 3d <sup>7</sup> 1390	28 <b>Ni</b> 58.69 2 + 3d <sup>8</sup> 629	29 <b>Cu</b> 63.55 2 + 3d <sup>9</sup>	30 <b>Zn</b> 65.39 2 + 3d <sup>10</sup>	31 <b>Ga</b> 69.72 3 + 3d <sup>10</sup>	32 <b>Ge</b> 72.61	33 <b>As</b> 74.92	34 <b>Se</b> 78.96	35 <b>Br</b> 79.90	36 <b>Kr</b> 83.80	
37 <b>Rb</b> 85.47 1 + 5s <sup>0</sup>	38 <b>Sr</b> 87.62 2 + 5s <sup>0</sup>	39 <b>Y</b> 88.91 2 + 4d <sup>0</sup>	40 <b>Zr</b> 91.22 4 + 4d <sup>0</sup>	41 <b>Nb</b> 92.91 5 + 4d <sup>0</sup>	42 <b>Mo</b> 95.94 5 + 4d <sup>1</sup>	43 <b>Tc</b> 97.9	44 <b>Ru</b> 101.1 3 + 4d <sup>5</sup>	45 <b>Rh</b> 102.4 3 + 4d <sup>6</sup>	46 <b>Pd</b> 106.4 2 + 4d <sup>8</sup>	47 <b>Ag</b> 107.9 1 + 4d <sup>10</sup>	48 <b>Cd</b> 112.4 2 + 4d <sup>10</sup>	49 <b>In</b> 114.8 3 + 4d <sup>10</sup>	50 <b>Sn</b> 118.7 4 + 4d <sup>10</sup>	51 <b>Sb</b> 121.8	52 <b>Te</b> 127.6	53 <b>I</b> 126.9	54 <b>Xe</b> 83.80	
55 <b>Cs</b> 132.9 1 + 6s <sup>0</sup>	56 <b>Ba</b> 137.3 2 + 6s <sup>0</sup>	57 <b>La</b> 138.9 3 + 4f <sup>0</sup>	58 <b>Ce</b> 140.1 4 + 4f <sup>0</sup> 13	59 <b>Pr</b> 140.9 3 + 4f <sup>1</sup>	60 <b>Nd</b> 144.2 3 + 4f <sup>2</sup> 19	61 <b>Pm</b> 145	62 <b>Sm</b> 150.4 3 + 4f <sup>3</sup> 105	63 <b>Eu</b> 152.0 2 + 4f <sup>6</sup> 90	64 <b>Gd</b> 157.3 3 + 4f <sup>7</sup> 292	65 <b>Tb</b> 158.9 3 + 4f <sup>8</sup> 229 221	66 <b>Dy</b> 162.5 3 + 4f <sup>9</sup> 179 85	67 <b>Ho</b> 164.9 3 + 4f <sup>10</sup> 132 20	68 <b>Er</b> 167.3 3 + 4f <sup>11</sup> 85 20	69 <b>Tm</b> 168.9 3 + 4f <sup>12</sup> 56	70 <b>Yb</b> 173.0 3 + 4f <sup>13</sup>	71 <b>Lu</b> 175.0 3 + 4f <sup>14</sup>		
87 <b>Fr</b> 223	88 <b>Ra</b> 226.0 2 + 7s <sup>0</sup>	89 <b>Ac</b> 227.0 3 + 5f <sup>0</sup>	90 <b>Th</b> 232.0 4 + 5f <sup>0</sup>	91 <b>Pa</b> 231.0 5 + 5f <sup>0</sup>	92 <b>U</b> 238.0 4 + 5f <sup>2</sup>	93 <b>Np</b> 238.0 5 + 5f <sup>2</sup>	94 <b>Pu</b> 244	95 <b>Am</b> 243	96 <b>Cm</b> 247	97 <b>Bk</b> 247	98 <b>Cf</b> 251	99 <b>Es</b> 252	100 <b>Fm</b> 257	101 <b>Md</b> 258	102 <b>No</b> 259	103 <b>Lr</b> 260		

Legend:

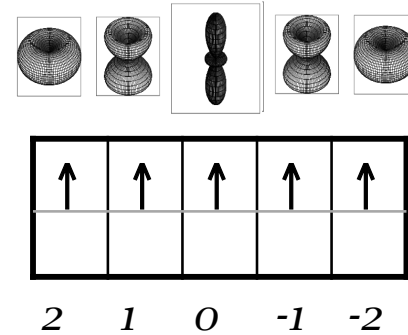
- Nonmetal
- Metal
- Radioactive
- Diamagnet
- Paramagnet
- Magnetic atom
- Ferromagnet T<sub>C</sub> > 290K
- Antiferromagnet with T<sub>N</sub> > 290K
- Antiferromagnet/Ferromagnet with T<sub>N</sub>/T<sub>C</sub> < 290 K

79 out of the 103 first elements are magnetic as free atoms Moments  $\ll Z\mu_B$

### 4.3.3 Examples



$S = 5/2 \quad L = 0 \quad J = 5/2$

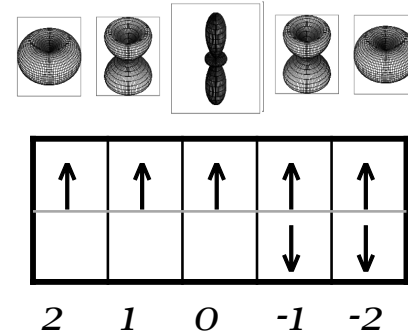
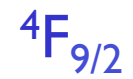


Note; Maximizing  $S$  is equivalent to maximizing  $M_s = \sum m_{s_i}$ , since  $M_s \leq S$





$$S = 3/2 \quad L = 3 \quad J = 9/2$$

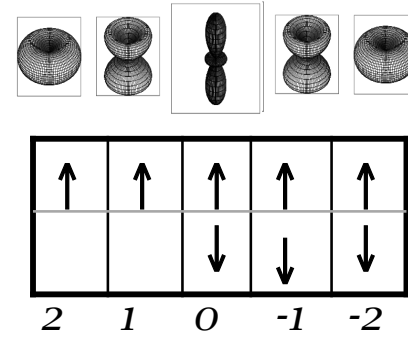


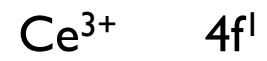
Note; Maximizing  $L$  is equivalent to maximizing  $M_L = \sum m_{li}$ , since  $M_L \leq L$

$\text{Ni}^{2+}$        $3d^8$

$S = 1$        $L = 3$        $J = 4$

${}^3F_4$

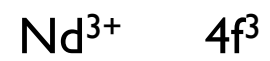




$S = 1/2 \quad L = 3 \quad J = 5/2$



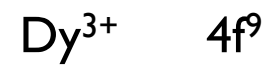
↑						
3	2	1	0	-1	-2	-3



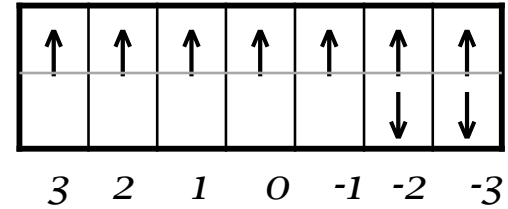
$$S = 3/2 \quad L = 6 \quad J = 9/2$$



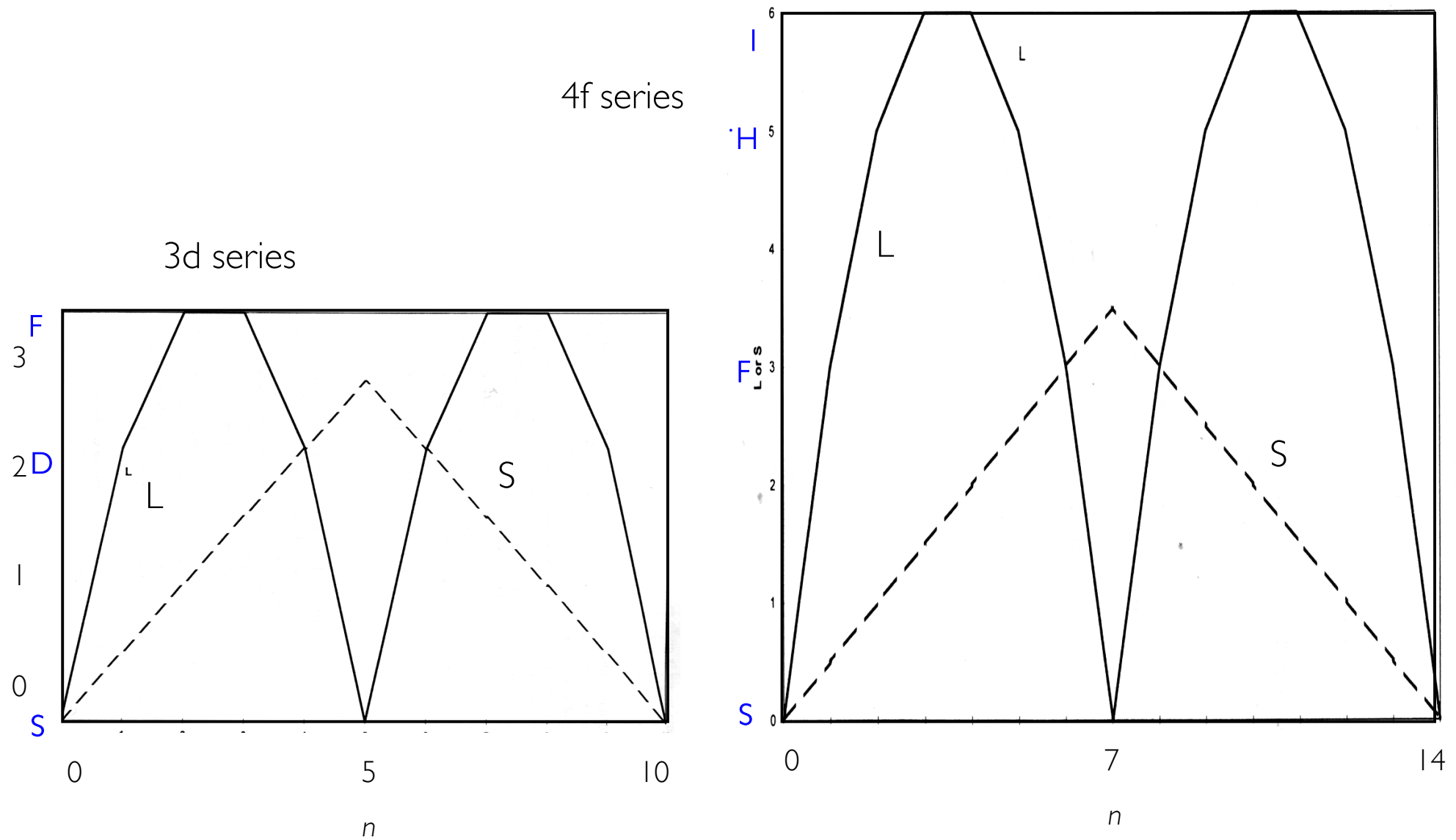
↑	↑	↑				
3	2	1	0	-1	-2	-3



$S = 5/2 \quad L = 5 \quad J = 15/2$



## Variation of L and S for the 3d and 4f series of atoms



## 4.4 Zeeman Splitting

The magnetic moment of an ion is represented by the expression  $\mathbf{m} = -(\mathbf{L} + 2\mathbf{S})\mu_B/\hbar$

The Zeeman Hamiltonian for the magnetic moment in a field  $\mathbf{B}$  applied along  $\mathbf{e}_z$  is  $\mathcal{H}_{\text{Zeeman}} = -\mathbf{m} \cdot \mathbf{B}$

$$\mathcal{H}_{\text{Zeeman}} = (\mu_B/\hbar)(\mathbf{L}_z + 2\mathbf{S}_z)B$$

For a particular J-multiplet the matrix elements of  $\mathbf{L} + 2\mathbf{S}$  are proportional to those of  $\mathbf{J}$  (Wigner Eckart theorem)

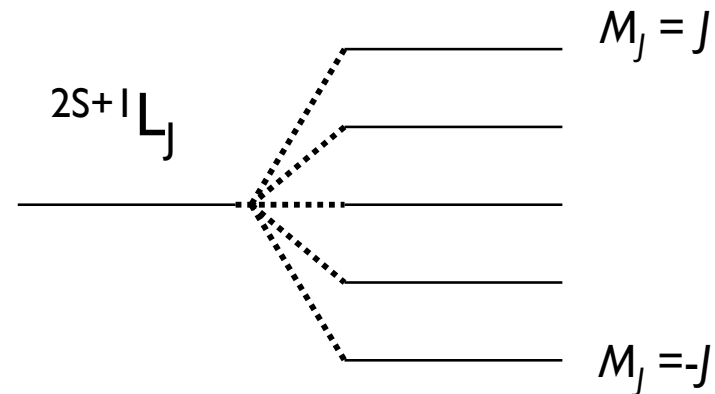
$$\langle \text{LSJM}_J | \mathbf{L} + 2\mathbf{S} | \text{LSJM}_J \rangle = g_J \langle \text{LSJM}_J | \mathbf{J} | \text{LSJM}_J \rangle \quad g_J \text{ is the Landé g-factor}$$

$$(\mathbf{L} + 2\mathbf{S}) = g_J \mathbf{J}$$

$$m_z = g_J J_z \mu_B/\hbar$$

$$\mathcal{H}_{\text{Zeeman}} = g_J J_z B (\mu_B/\hbar)$$

$$\mathcal{H}_{\text{Zeeman}} \psi_{\text{LSJM}} = g_J \mu_B M_J B \psi_{\text{LSJM}}$$





### 4.4.1 Landé g-factor

The vector model of the atom, including magnetic moments. First project  $\mathbf{m}$  onto  $\mathbf{J}$ .  $\mathbf{J}$  then precesses around  $\mathbf{z}$ .

The g-factor for the atom or ion is the ratio of the component of magnetic moment along  $\mathbf{J}$  in units of  $\mu_B$  to the magnitude of the angular momentum in units of  $\hbar$ .

$g_J \mathbf{J} = (\mathbf{L} + 2\mathbf{S})$  Take scalar product with  $\mathbf{J}$

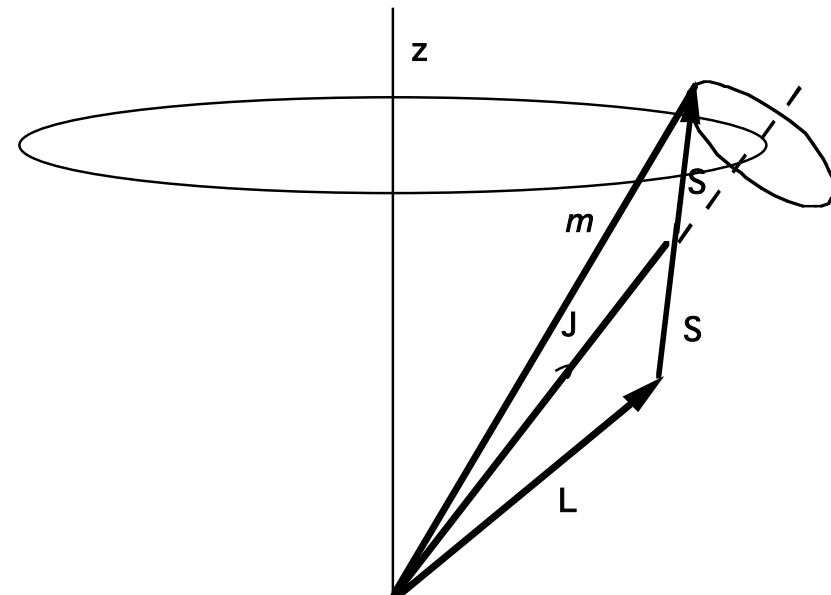
$$g_J = -(\mathbf{m} \cdot \mathbf{J} / \mu_B) / (J^2 / \hbar) = -\mathbf{m} \cdot \mathbf{J} (\hbar / \mu_B) / [J(J+1)]$$

$$\begin{aligned} \text{but } \mathbf{m} \cdot \mathbf{J} &= -(\mu_B / \hbar) \{ (\mathbf{L} + 2\mathbf{S}) \cdot (\mathbf{L} + \mathbf{S}) \} \\ &= -(\mu_B / \hbar) \{ (\mathbf{L}^2 + 3\mathbf{L} \cdot \mathbf{S} + 2\mathbf{S}^2) \} \\ &= -(\mu_B / \hbar) \{ (\mathbf{L}^2 + 2\mathbf{S}^2 + (3/2)(\mathbf{J}^2 - \mathbf{L}^2 - \mathbf{S}^2)) \} \quad \text{since } \mathbf{J}^2 = \mathbf{L}^2 + \mathbf{S}^2 + 2\mathbf{L} \cdot \mathbf{S} \\ &= -(\mu_B / \hbar) \{ ((3/2)\mathbf{J}^2 - (1/2)\mathbf{L}^2 + (1/2)\mathbf{S}^2) \} \\ &= -(\mu_B / \hbar) \{ ((3/2)J(J+1) - (1/2)L(L+1) + (1/2)S(S+1)) \} \end{aligned}$$

hence

$$g = 3/2 + \{S(S+1) - L(L+1)\} / 2J(J+1)$$

$$\mathbf{m} = -(\mathbf{L} + 2\mathbf{S})\mu_B / \hbar$$



$$J^2 = J(J+1)\hbar^2; \quad J_z = M_J \hbar$$

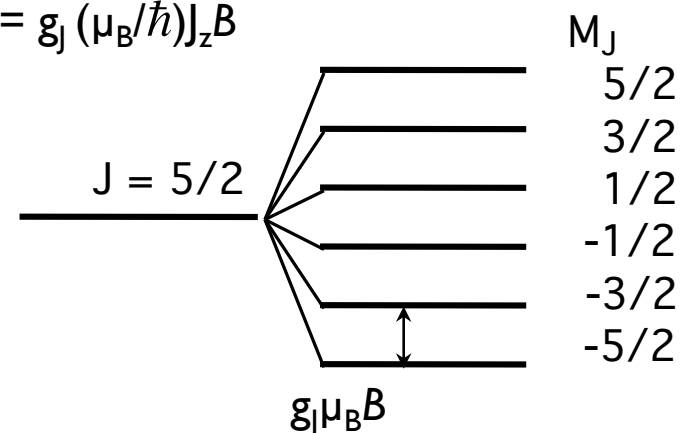
$$\text{Check; } g_S = 2, g_L = 1$$

Also, from the vector diagram it follows that  $m_z/J_z = \mathbf{m} \cdot \mathbf{J} / J^2 = -g_j(\mu_B/\hbar)$ .

The magnetic Zeeman energy is  $E_Z = -m_z B$ . This is  $-(m_z/J_z)(J_z B) = g_j(\mu_B/\hbar)J_z B$

Hence

$$E_Z = g_j \mu_B M_j B$$



The effect of applying a magnetic field on an ion with  $J = 5/2$

Note the magnitudes of the energies involved: If  $g = 2$ ,  $\mu_B = 9.27 \cdot 10^{-24} \text{ J T}^{-1}$ . The splitting of any two adjacent energy levels is  $g\mu_B B$ . For  $B = 1 \text{ T}$ , this is only  $\approx 2 \cdot 10^{-23} \text{ J}$ , equivalent to  $1.4 \text{ K}$ .  $[k_B = 1.38 \cdot 10^{-23} \text{ J K}^{-1}]$

The basis of *electron spin resonance* is to apply a magnetic field to split the energy levels, and then apply radiation of frequency  $\nu$  so that  $E = h\nu$  is sufficient to induce transitions between the Zeeman levels. Since  $h = 6.63 \cdot 10^{-34} \text{ J s}^{-1}$ ,  $\nu \approx 28 \text{ GHz}$  for resonance in  $1 \text{ T}$ . This is in the microwave range.

It is possible to deduce the total moment from the susceptibility, which should give  $m_{\text{eff}} = g\sqrt{J(J+1)}\mu_B$ . for free ions The maximum value of  $m_z$  is deduced from the saturation magnetization.

Generally  $m_{\text{eff}} > m_z$

For  $4f$  ions in solids  $J$  is the good quantum number, but for  $3d$  ions  $S$  is the good quantum number

## Summary: Example of $\text{Co}^{2+}$



↑	↑	↑	↑	↑
			↓	↓

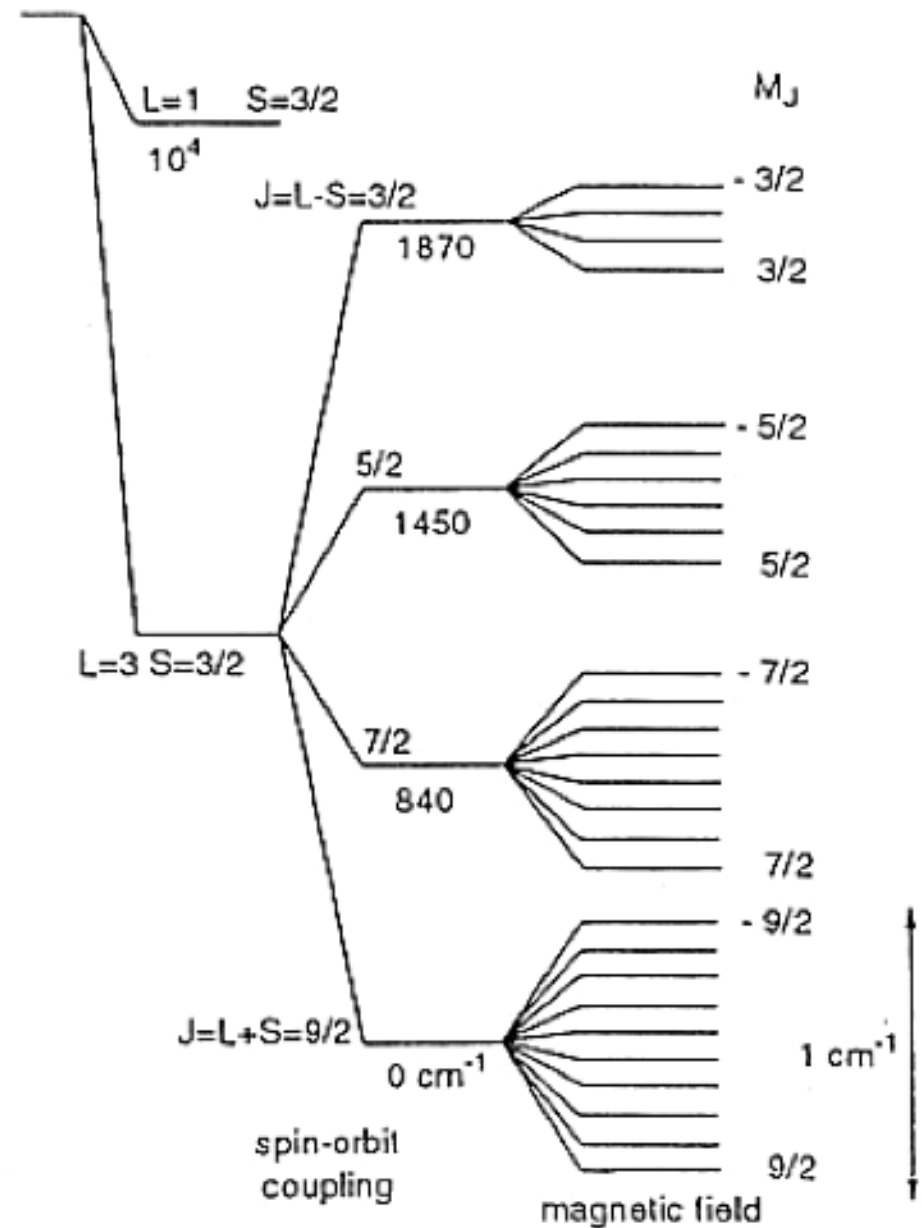
2    1    0    -1    -2

$$S = 3/2; L = 3$$

Ground Term  $^4F$

Ground Multiplet  $^4F_{9/2}$

Energy levels of  $\text{Co}^{2+}$  ion,  $3d^7$ . Note that the Zeeman splitting in an applied field of 0.1 T is not to scale.



## 4.5 Ions in Solids

Summarizing, for free ions;

- ◆ Filled electronic shells are not magnetic (the spins are paired;  $m_s = \pm 1/2$ )
- ◆ Only partly-filled shells may possess a magnetic moment
- ◆ The magnetic moment is given by  $\mathbf{m} = g_j \mu_B \mathbf{J}$ , where  $\hbar \mathbf{J}$  represents the total angular momentum. For a given configuration the values of  $J$  and  $g_j$  in the ground state are given by **Hund's rules**



When the ion is embedded in a solid, the **crystal field** interaction is important. This is the electrostatic Coulomb interaction of an ion with its surroundings.

The third point is modified:

- ◆ Orbital angular momentum for  $3d$  ions is **quenched**. The spin only moment is  $\mathbf{m} \approx g \mu_B \mathbf{S}$ , with  $g = 2$ .
- ◆ Magnetocrystalline anisotropy appears, making certain crystallographic axes easy directions of magnetization.

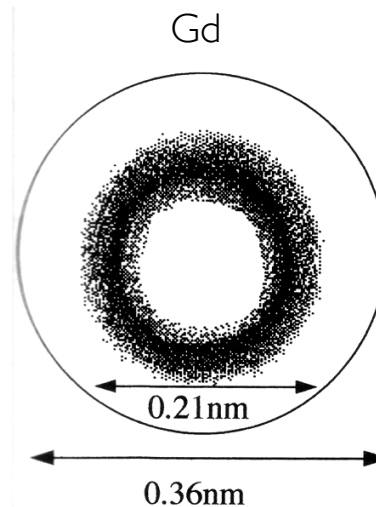
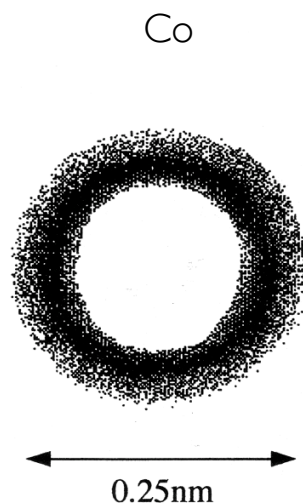
The Hamiltonian is now

$$\mathcal{H} = \mathcal{H}_0 + \mathcal{H}_{so} + \mathcal{H}_{cf} + \mathcal{H}_Z$$

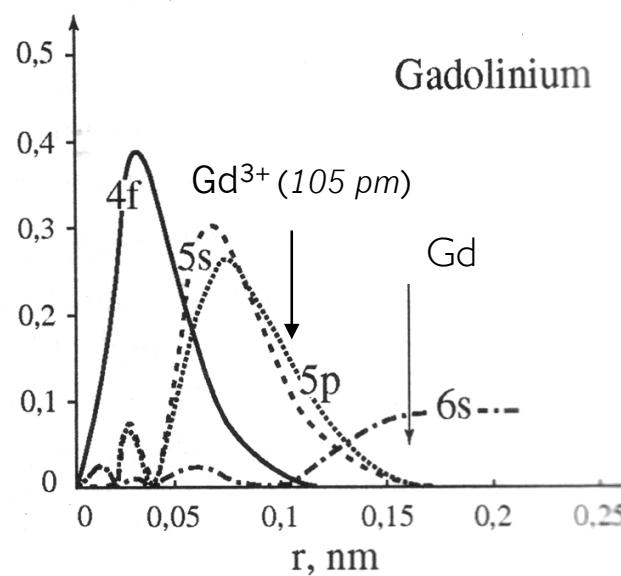
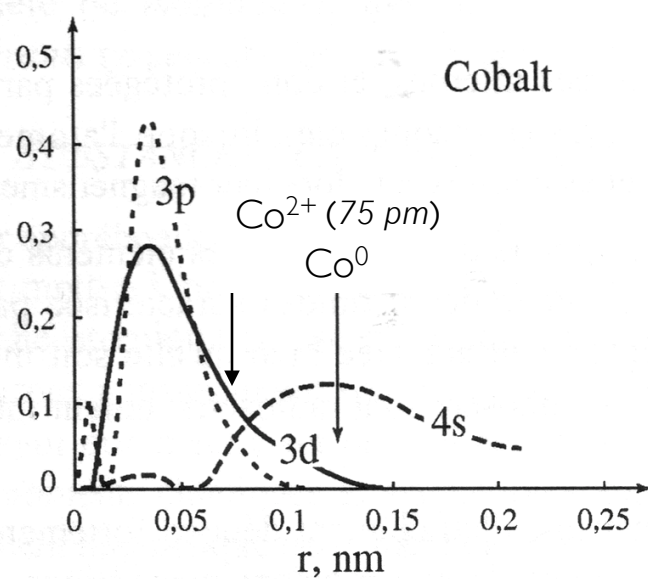
Typical magnitudes of energy terms (in K)

	$\mathcal{H}_0$	$\mathcal{H}_{so}$	$\mathcal{H}_{cf}$	$\mathcal{H}_Z$ in 1 T
<b>3d</b>	<b>1 - 5 10<sup>4</sup></b>	<b>10<sup>2</sup> -10<sup>3</sup></b>	<b>10<sup>4</sup></b>	<b>1</b>
<b>4f</b>	<b>1 - 6 10<sup>5</sup></b>	<b>1 - 5 10<sup>3</sup></b>	<b>≈3 10<sup>2</sup></b>	<b>1</b>

$\mathcal{H}_{so}$  must be considered before  $\mathcal{H}_{cf}$  for 4f ions, and the converse for 3d ions. Hence J is a good quantum number for 4f ions, but S is a good quantum number for 3d ions. The 4f electrons are generally localized, and 3d electrons are localized in oxides and other ionic compounds.

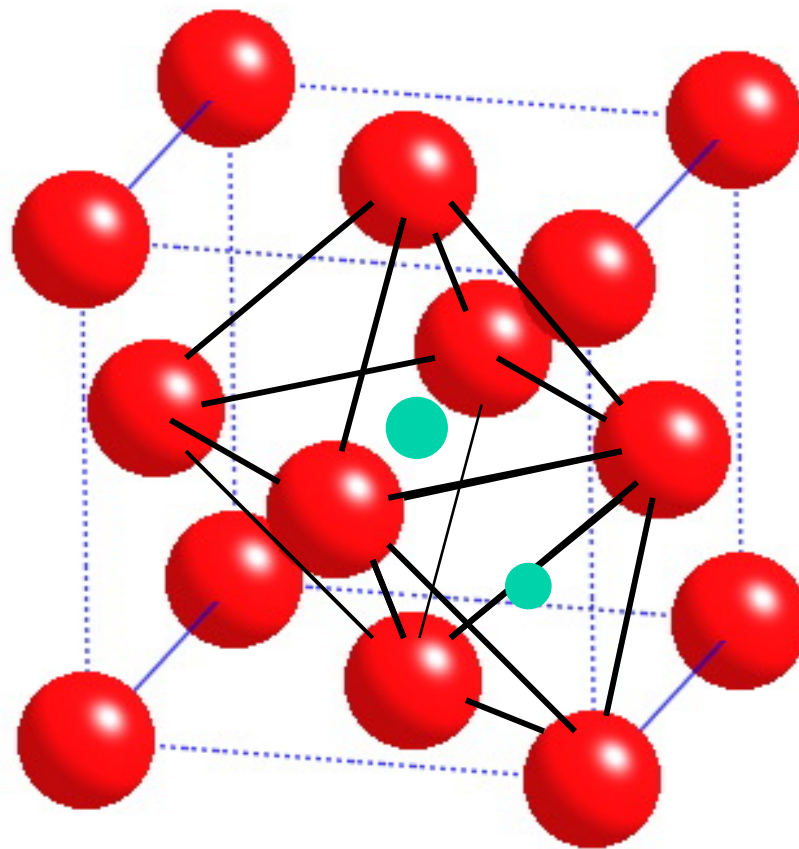


As metallic atoms or ions the transition metals occupy one third of the volume of the rare earths.



## Oxides

Oxides are usually insulating. Structures are based on dense-packed  $\text{O}^{2-}$  arrays, with cations in interstitial sites.

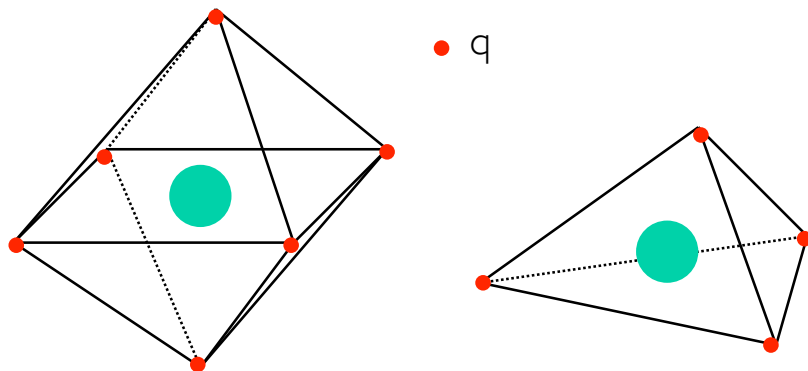


Octahedral and tetrahedral sites are common in transition metal oxides and other compounds.

Both have *cubic* symmetry if undistorted

$$R_{\text{oct}} = (2^{1/2} - 1)r_{\text{O}} = 58 \text{ pm}$$

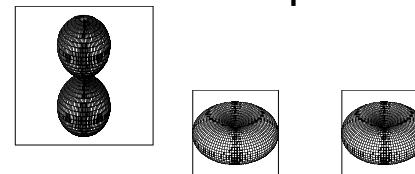
$$R_{\text{tet}} = ((3/2)^{1/2} - 1)r_{\text{O}} = 32 \text{ pm}$$



*Octahedral and tetrahedral sites.*

To demonstrate quenching of orbital angular momentum, consider the 2p states  $\psi^0$ ,  $\psi^1$ ,  $\psi^{-1}$  corresponding to  $l = 1$ ,  $m_l = 0, \pm 1$ .

$$\begin{aligned}\psi^0 &= R(r) \cos \theta \\ \psi^{\pm 1} &= R(r) \sin \theta \exp \{ \pm i\phi \}\end{aligned}$$



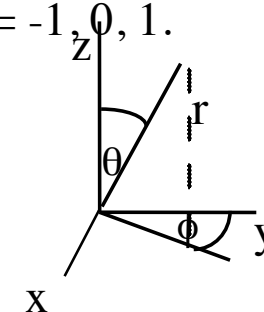
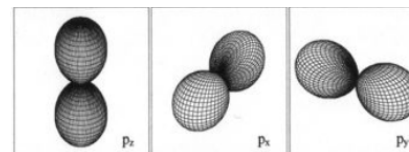
The functions are eigenstates in the central potential  $V(r)$  but they are not eigenstates of  $H_{cf}$ . Suppose the oxygens can be represented by point charges  $q$  at their centres, then for the octahedron,

$$\mathcal{H}_{cf} = V_{cf} = D(x^4 + y^4 + z^4 - 3y^2z^2 - 3z^2x^2 - 3x^2y^2)$$

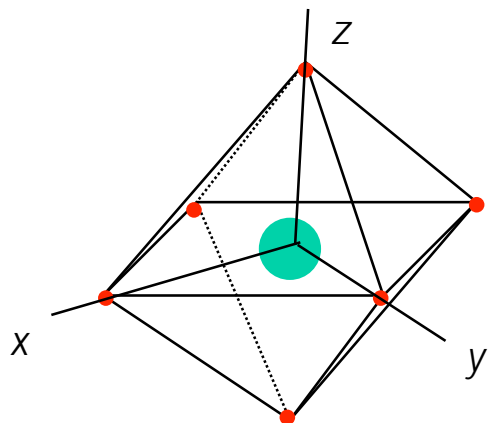
where  $D \approx eq/4\pi\epsilon_0 a^6$ . But  $\psi^{\pm 1}$  are *not* eigenfunctions of  $V_{cf}$ , e.g.  $\int \psi_i^* V_{cf} \psi_j dV \neq \delta_{ij}$ , where  $i, j = -1, 0, 1$ .

We seek linear combinations that are eigenfunctions, namely

$$\begin{aligned}\psi^0 &= R(r) \cos \theta &= zR(r) &= p_z \\ (1/\sqrt{2})(\psi^1 + \psi^{-1}) &= R'(r) \sin \theta \cos \phi &= yR(r) &= p_y \\ (1/\sqrt{2})(\psi^1 - \psi^{-1}) &= R'(r) \sin \theta \sin \phi &= xR(r) &= p_x\end{aligned}$$







• q

The  $2p$  eigenfunctions are degenerate in an undistorted cubic environment

$$\begin{aligned}
 \psi^0 &= R(r) \cos \theta &= zR(r) &= p_z \\
 (1/\sqrt{2})(\psi^1 + \psi^{-1}) &= R'(r) \sin \theta \cos \phi &= yR(r) &= p_x \\
 (1/\sqrt{2})(\psi^1 - \psi^{-1}) &= R'(r) \sin \theta \sin \phi &= xR(r) &= p_y
 \end{aligned}$$

=====  
 $p_x \ p_y \ p_z$

Note that the  $z$ -component of angular momentum;  $\mathbf{L}_z = i\hbar/\partial\phi$  is *zero* for these wavefunctions. Hence the orbital angular momentum is quenched.

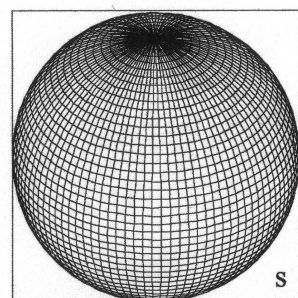
The same is true of the  $3d$  eigenfunctions, which are

$$\begin{aligned}
 d_{xy} &= (1/\sqrt{2})(\psi^2 - \psi^{-2}) = R'(r) \sin^2 \theta \sin 2\phi \approx xyR(r) & & d_{x^2-y^2}, d_z^2 \\
 d_{yz} &= (1/\sqrt{2})(\psi^1 - \psi^{-1}) = R'(r) \sin \theta \cos \theta \sin \phi \approx yzR(r) & t_{2g} \text{ orbitals} & \\
 d_{zx} &= (1/\sqrt{2})(\psi^1 + \psi^{-1}) = R'(r) \sin \theta \cos \theta \cos \phi \approx zxR(r) & & \\
 d_{x^2-y^2} &= (1/\sqrt{2})(\psi^2 + \psi^{-2}) = R'(r) \sin^2 \theta \cos 2\phi \approx (x^2 - y^2)R(r) & e_g \text{ orbitals} & \\
 d_{3z^2-r^2} &= \psi^0 = R'(r)(3\cos^2 \theta - 1) \approx (3z^2 - r^2)R(r) & & d_{xy} \ d_{yz} \ d_{zx}
 \end{aligned}$$

The  $3d$  eigenfunctions split into a set of three and a set of two in an undistorted cubic environment

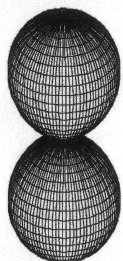
*Notation*;  $a$  or  $b$  denote a nondegenerate single-electron orbital,  $e$  a twofold degenerate orbital and  $t$  a threefold degenerate orbital. Capital letters refer to multi-electron states.  $a, A$  are nondegenerate and symmetric with respect to the principal axis of symmetry (the sign of the wavefunction is unchanged),  $b, B$  are antisymmetric with respect to the principal axis (the sign of the wavefunction changes). Subscripts  $g$  and  $u$  indicate whether the wavefunction is symmetric or

## Orbitals in the crystal field

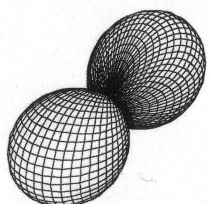


s

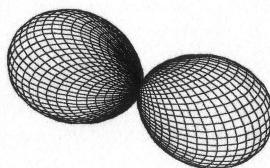
$n = 1$   
 $l = 0$  *s orbital*



$p_z$

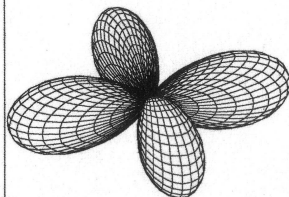


$p_x$

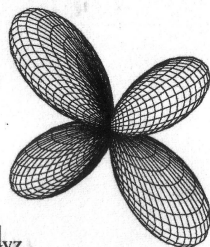


$p_y$

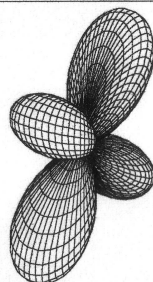
$n = 2$   
 $l = 1$  *p orbitals*



$d_{xy}$

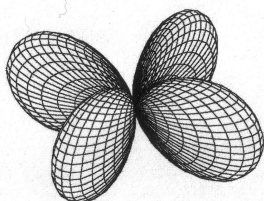


$d_{yz}$



$d_{zx}$

$n = 3$   
 $l = 2$  *d orbitals*



$d_{x^2-y^2}$

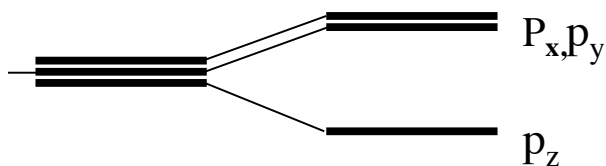


$d_{z^2}$

$t_{2g}$

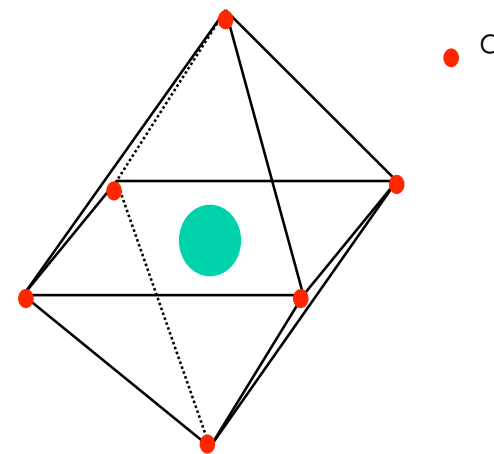
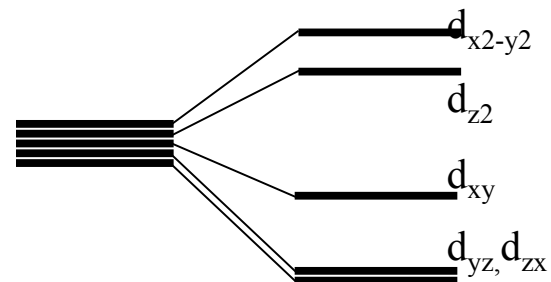
$e_g$

If the site is distorted, the degeneracy of the one-electron energy levels is raised. For example, a tetragonal extension of the octahedron along the z-axis will lower  $p_z$  and raise  $p_x$  and  $p_y$ . The effect on the d-states is shown below. The degeneracy of the d-levels in different symmetry is shown in the table.



The effect of a tetragonal distortion of octahedral symmetry on the one-electron energy levels.

The splitting of the l-electron levels in different symmetry



	1	Cubic	Tetragonal	Trigonal	Rhombohedral
$s$	1	1	1	1	1
$p$	2	3	1,2	1,2	1,1,1
$d$	3	2,3	1,1,1,2	1,2,2	1,1,1,1,1
$f$	4	1,3,3	1,1,1,2,2	1,1,1,2,2	1,1,1,1,1,1,1

• A system with a single electron (or hole) in a degenerate level will tend to distort spontaneously. The effect is particularly strong  $d^4$  and  $d^9$  ions in octahedral symmetry ( $Mn^{3+}$ ,  $Cu^{2+}$ ) which can lower their energy by distorting the crystal environment. This is the [Jahn-Teller effect](#). If the local strain is  $\varepsilon$ , the energy change  $\Delta E = -A\varepsilon + B\varepsilon^2$ , where the first term is the crystal-field stabilization energy and the second term is the increased elastic energy.

## 5. Paramagnetism

In small fields, the average atomic moment is proportional to applied magnetic field. The paramagnetic Curie-law susceptibility  $\chi = C/T$  is calculated using either classical or quantum statistical mechanics.

## 5.1 Classical limit; Langevin theory

We study the response of a magnetic moment  $\mathbf{m}$  to an applied magnetic field  $\mathbf{H}$ . Each particle has a small moment  $\mathbf{m}$  which can adopt any orientation Relative to the applied field  $\mathbf{B} = \mu_0 \mathbf{H}$ . The energy is  $-\mathbf{m} \cdot \mathbf{B}$

$$E(\theta) = -m \mu_0 H \cos \theta$$

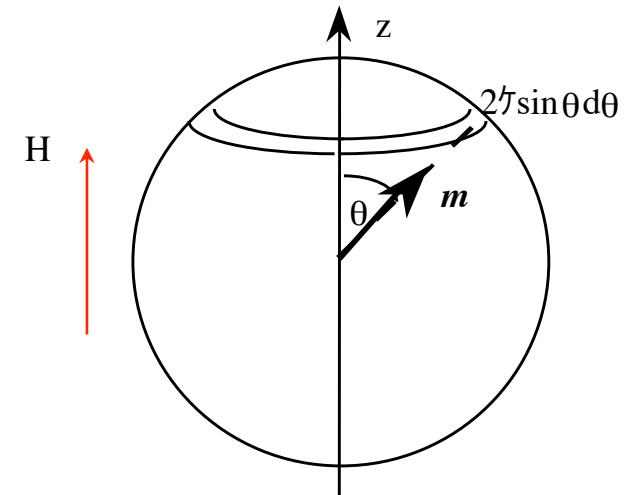
The probability  $P(\theta)$  of the moment making an angle  $\theta$  with  $z$  is the product of a Boltzmann factor  $\exp\{-E(\theta)/k_B T\}$  and a geometric factor  $2\pi \sin \theta d\theta$ .

Hence 
$$P(\theta) d\theta = \kappa 2\pi \sin \theta \exp\{-E(\theta)/k_B T\} d\theta$$

where  $\kappa$  is determined by the normalization condition

$$\kappa = \int_0^\pi P(\theta) d\theta = N, \quad \text{the number of moments per unit volume.}$$

$$\langle m \rangle = \int_0^\pi m \cos \theta P(\theta) d\theta / \int_0^\pi P(\theta) d\theta$$



To evaluate the integrals, let  $a = \cos \theta$ ;  $da = -\sin \theta d\theta$  and define  $x = -m \mu_0 H / k_B T$  which is the dimensionless ratio of magnetic to thermal energy.

$$\begin{aligned}\int_0^\pi P(\theta) d\theta &= \int_0^\pi \kappa 2\pi \sin \theta \exp[-E(\theta)/k_B T] d\theta = -\kappa 2\pi \int_1^{-1} \exp[ax] da \\ &= \kappa 2\pi \left|_1^{-1} (1/x) \exp[ax] \right. = \kappa 2\pi (1/x) \{ \exp[-x] - \exp[x] \}\end{aligned}$$

$$\begin{aligned}\int_0^\pi m \cos \theta P(\theta) d\theta &= -\kappa 2\pi m \int_1^{-1} a \exp[ax] da \\ &= \kappa 2\pi m \left\{ \left|_1^{-1} (a/x) \exp[ax] - \int_1^{-1} (1/x) \exp[ax] da \right. \right\} \\ &= \kappa 2\pi m \left\{ \left|_1^{-1} (a/x) \exp[ax] + \left|_1^{-1} (1/x)^2 \exp[ax] \right. \right\} \\ &= \kappa 2\pi m (1/x) \left\{ -\{ \exp[-x] + \exp[x] \} + (1/x) [ \exp[-x] - \exp[x] ] \right\} \\ \langle m \rangle &= m \left\{ -\{ \exp[-x] + \exp[x] \} / \{ \exp[-x] - \exp[x] \} - (1/x) \right\} \\ \langle m \rangle &= m \{ \coth x - (1/x) \} = m \mathcal{L}(x); \end{aligned}$$

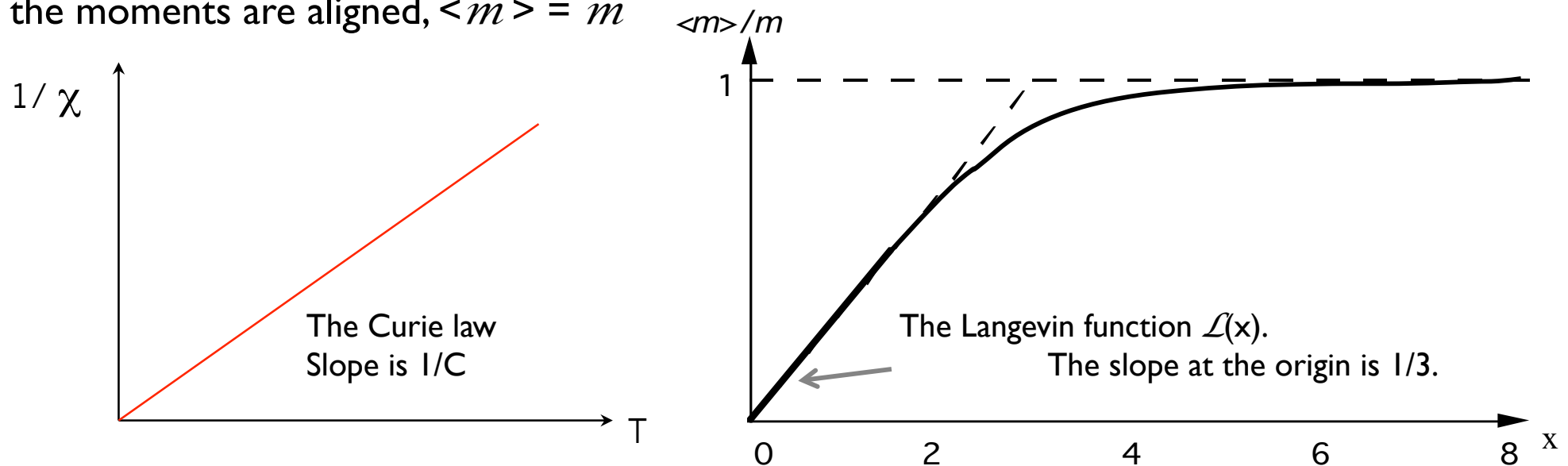
$\coth x - 1/x$  is the *Langevin function*

At low fields,  $\mathcal{L}(x) \approx x/3$ .

The susceptibility of an ensemble of  $N$  moments is  $\chi = N\langle m \rangle / H$ ,

$$\chi = \mu_0 N m^2 / 3 k_B T$$

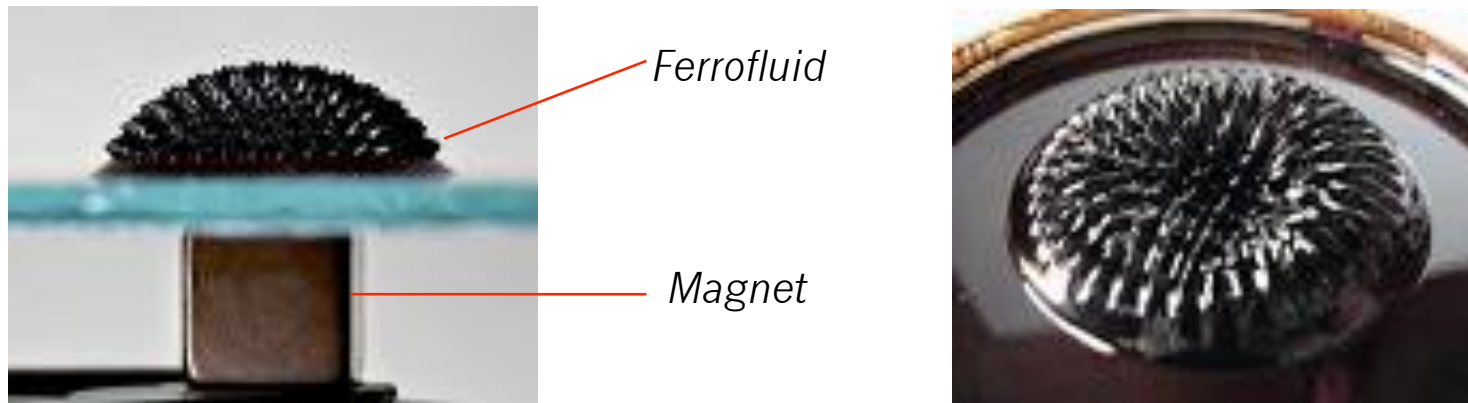
This is the *Curie law* it is also written as  $\chi = C/T$  where  $C = \mu_0 N m^2 / 3 k_B$  is the Curie constant. Units of  $C$  are kelvin. At high fields,  $x \gg 1$  the magnetization saturates;  $\mathcal{L}(x) \rightarrow 1$ ; the moments are aligned,  $\langle m \rangle = m$



Langevin theory is applied to tiny ferromagnetic nanoparticles whose direction of magnetization is randomized by thermal excitation (superparamagnetism).

### 5.1.1 Ferrofluids

These are colloidal suspensions of superparamagnetic particles,



Criterion for superparamagnetism:  $KV/k_B T < 25$     Particle size  $\leq 15$  nm.

*Applications:* Superparamagnetic iron oxide nanoparticles used for magnetic separation of biological species, hypothermia and for rotation seals in high-vacuum.



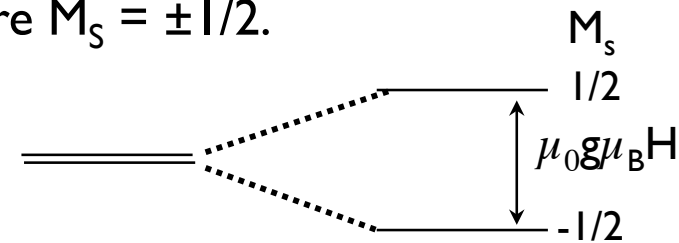
## 5.2 Quantum theory.

### 5.2.1 $S = 1/2$

The extreme quantum limit is the case  $J = 1/2$ .

This arises when  $S = 1/2, L = 0$

There are only two energy levels  $E_i = -\mu_0 g \mu_B M_S H$ , where  $M_S = \pm 1/2$ .



Two possible orientations of the moment relative to the applied field.

Moments of the two states are  $m_i = g \mu_B M_S$ .

The states are also known as 'spin up' ( $\uparrow$ ) and 'spin down' ( $\downarrow$ ).

A single, localized electron has  $s = 1/2$  and  $g = 2$ .

The spin angular momentum is  $s = 1/2, m_s = \pm 1/2$ .

Eigenvalues of  $\mathbf{s}_z$  are  $\pm \hbar/2$  so  $m_i = \mp \mu_B$

The electrons have only two eigenstates, ‘spin up’ ( $\uparrow, m_s = -1/2$ ) and ‘spin down’ ( $\downarrow, m_s = 1/2$ ), which correspond to two possible orientations of the spin moment relative to the applied field.

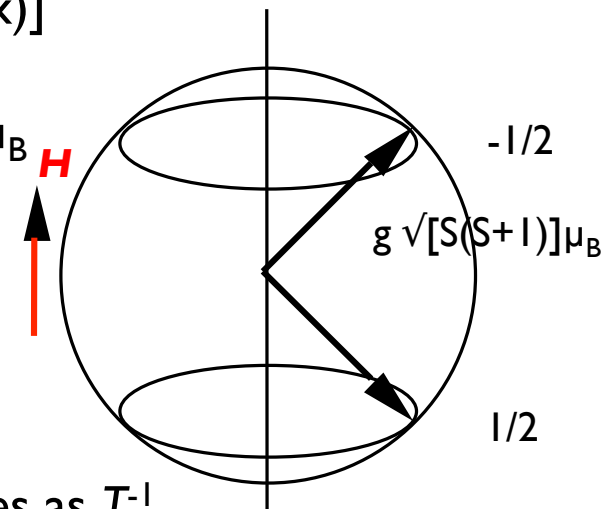
The population of an energy level is given by Boltzmann statistics; it is proportional to  $\exp\{-E_i/k_B T\}$ . The thermodynamic average  $\langle m \rangle$  is evaluated from these Boltzmann populations.

$$\langle m \rangle = [(1/2)g\mu_B \exp(x) - (1/2)g\mu_B \exp(-x)] / [\exp(x) + \exp(-x)]$$

$$\langle m \rangle = m \tanh(x) \quad \text{where } x = \mu_0 \mu_B H / k_B T; \quad m = g\mu_B s = \mu_B H$$

In small fields,  $\tanh(x) \approx x$ , hence the susceptibility  $\chi = N \langle m \rangle / H$

$$\chi = \mu_0 N \mu_B^2 / k_B T$$



This is again the famous *Curie law* for the susceptibility, which varies as  $T^{-1}$ .

In other terms  $\chi = C/T$ , where now  $C = \mu_0 N \mu_B^2 / k_B$  is a constant with dimensions of temperature; Assuming an electron density  $N$  of  $6 \times 10^{28} \text{ m}^{-3}$  gives  $C \approx 0.5 \text{ K}$ . The Curie law susceptibility at room temperature is of order  $10^{-3}$ .

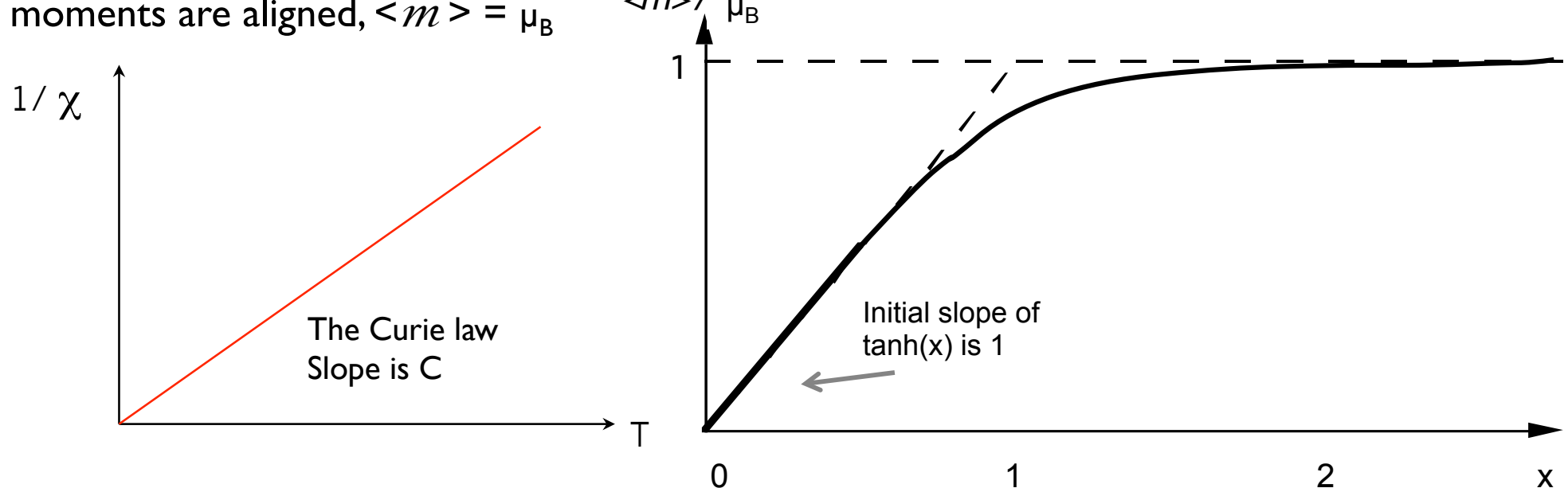
Many ‘two-level systems’ in physics are treated by assigning them a ‘pseudospin’  $s = 1/2$ .

At low fields,  $\tanh(x) \approx x$ .

The susceptibility of an ensemble of  $N$  moments is  $\chi = N\langle m \rangle / H$ ,

$$\chi = \mu_0 N \mu_B^2 / k_B T$$

This is the *Curie law* it is also written as  $\chi = C/T$  where  $C = \mu_0 N \mu_B^2 / k_B$  is the Curie constant. Units of  $C$  are kelvin. At high fields,  $x \gg 1$  the magnetization saturates;  $\tanh(x) \rightarrow 1$ ; the moments are aligned,  $\langle m \rangle = \mu_B$



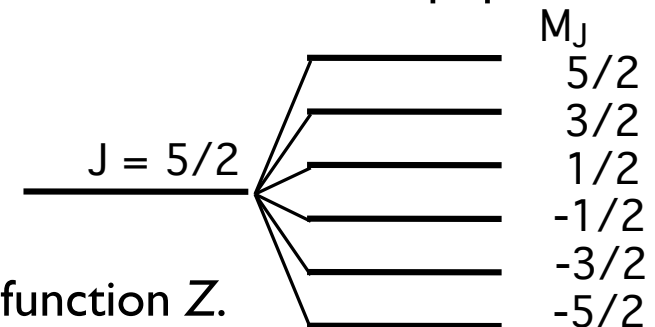
Many 'two-level systems' in physics are treated by assigning them a 'pseudospin'  $s = 1/2$ .

## 5.2.2 General case

The general quantum case was treated by Brillouin;  $m$  is  $g\mu_B J$ , and  $x$  is defined as  $x = m \mu_0 H / k_B T$ . There are  $2J+1$  energy levels  $E_i = -g\mu_B M_J \mu_0 H$ , with moment  $m_i = g\mu_B M_J$  where  $M_J = J, J-1, J-2, \dots -J$ . The sums over the energy levels include  $2J+1$  terms.

The population of an energy level is given by Boltzmann statistics; it is proportional to  $\exp\{-E_i/k_B T\}$ . The thermodynamic average  $\langle m \rangle$  is evaluated from the Boltzmann populations of the levels  $E_i$ .

$$\langle m \rangle = \frac{\sum_i m_i \exp\{-E_i/k_B T\}}{\sum_i \exp\{-E_i/k_B T\}}$$



The normalization factor in the denominator is the partition function  $Z$ .

**a) Susceptibility** To calculate the susceptibility, we take  $x \ll 1$ , because the susceptibility is defined as the linear response in small fields. We expand exponentials  $\exp(x) \approx 1 + x + \dots$ ,

$$\langle m \rangle = \frac{\sum_{-J}^J g\mu_B M_J (1 + g\mu_B M_J \mu_0 H / k_B T)}{\sum_{-J}^J (1 + g\mu_B M_J \mu_0 H / k_B T)}$$

Recall  $\sum_{-J}^J 1 = 2J+1$ ;  $\sum_{-J}^J M_J = 0$ ;  $\sum_{-J}^J M_J^2 = J(J+1)(2J+1)/3$

Hence  $\langle m \rangle = g^2 \mu_B^2 B J(J+1) / 3(2J+1) k_B T$

The susceptibility is  $N\langle m \rangle / H$ , where  $N$  is the number of atoms/m<sup>3</sup>.

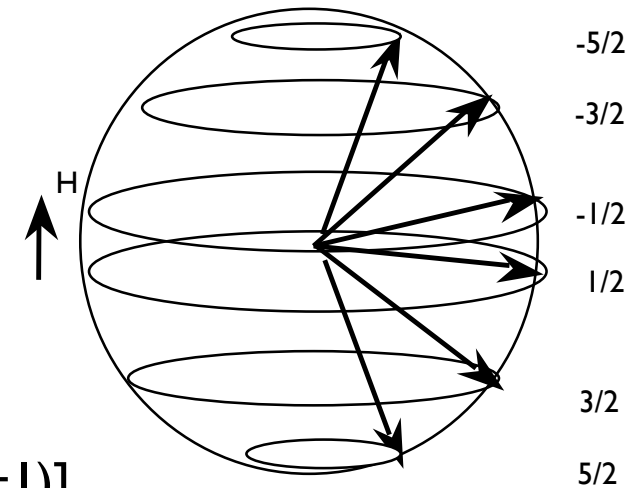
$$\chi = \mu_0 N g^2 \mu_B^2 J(J+1) / 3 k_B T$$

This is the general form of the Curie law.

It can be written  $\chi_r = C/T$  where the *Curie constant*

$$C = \mu_0 N g^2 \mu_B^2 J(J+1) / 3 k_B$$

or  $C = \mu_0 N m_{\text{eff}}^2 / 3 k_B$  where  $m_{\text{eff}} = g \mu_B \sqrt{J(J+1)}$ .



A typical value of  $C$  for  $J = 1$ ,  $N = 8.10^{28} \text{ m}^{-3}$  is 3.5 K.

Note that the previous results for  $S = 1/2$  are obtained for  $J = 1/2$ .

The classical limit  $J \rightarrow \infty$  ( $m = g \mu_B J$ ) gives

$$\chi = \mu_0 N m^2 / 3 k_B T$$

Ion 3d	$2S+1L_J$	L	S	J	g	$m_{\text{eff}} = g\sqrt{J(J+1)}$ ( $\mu_B$ )	$m_s = 2\sqrt{S(S+1)}$ ( $\mu_B$ )	$m_{\text{eff}}^*$ ( $\mu_B$ )
Ti <sup>2+</sup> , V <sup>4+</sup> (3d <sup>1</sup> )	<sup>2</sup> D <sub>3/2</sub>	2	1/2	3/2	4/5	1.549	1.73	1.7
Ti <sup>2+</sup> , V <sup>3+</sup> (3d <sup>2</sup> )	<sup>3</sup> F <sub>2</sub>	3	1	2	2/3	1.633	2.83	2.8
V <sup>2+</sup> , Cr <sup>3+</sup> (3d <sup>3</sup> )	<sup>4</sup> F <sub>3/2</sub>	3	3/2	3/2	2/5	0.775	3.87	3.8
Cr <sup>2+</sup> , Mn <sup>3+</sup> (3d <sup>4</sup> )	<sup>5</sup> D <sub>0</sub>	2	2	0	-	-	4.90	4.9
Mn <sup>2+</sup> , Fe <sup>3+</sup> (3d <sup>5</sup> )	<sup>6</sup> S <sub>5/2</sub>	0	5/2	5/2	2	5.916	5.92	5.9
Fe <sup>2+</sup> , Co <sup>3+</sup> (3d <sup>6</sup> )	<sup>5</sup> D <sub>4</sub>	2	2	4	3/2	6.708	4.90	5.4
Co <sup>2+</sup> , Ni <sup>3+</sup> (3d <sup>7</sup> )	<sup>4</sup> F <sub>9/2</sub>	3	3/2	9/2	4/3	6.633	3.87	4.8
Ni <sup>2+</sup> (3d <sup>8</sup> )	<sup>3</sup> F <sub>4</sub>	3	1	4	5/4	5.590	2.83	3.2
Cu <sup>2+</sup> (3d <sup>9</sup> )	<sup>2</sup> D <sub>5/2</sub>	2	1/2	5/2	6/5	3.550	1.73	1.9

Ion 4f	$2S+1L_J$	L	S	J	g	$m_0 = gJ$ ( $\mu_B$ )	$m_{\text{eff}} = g\sqrt{J(J+1)}$ ( $\mu_B$ )	$m_{\text{eff}}$ ( $\mu_B$ )
Ce <sup>3+</sup> (4f <sup>1</sup> )	<sup>2</sup> F <sub>5/2</sub>	3	1/2	5/2	6/7	2.14	2.54	2.5
P <sup>3+</sup> (4f <sup>2</sup> )	<sup>3</sup> H <sub>4</sub>	5	1	4	4/5	3.20	3.58	3.5
Nd <sup>3+</sup> (4f <sup>3</sup> )	<sup>4</sup> I <sub>9/2</sub>	6	3/2	9/2	8/11	3.27	3.62	3.4
Pm <sup>3+</sup> (4f <sup>4</sup> )	<sup>5</sup> I <sub>4</sub>	6	2	4	3/5	2.40	2.68	-
Sm <sup>3+</sup> (4f <sup>5</sup> )	<sup>6</sup> H <sub>5/2</sub>	5	5/2	5/2	2/7	0.71	0.85	1.7
Eu <sup>3+</sup> (4f <sup>6</sup> )	<sup>7</sup> F <sub>0</sub>	3	3	0	-	0.00	0.00	3.4
Gd <sup>3+</sup> (4f <sup>7</sup> )	<sup>8</sup> S <sub>7/2</sub>	0	7/2	7/2	2	7.00	7.94	8.9
Tb <sup>3+</sup> (4f <sup>8</sup> )	<sup>7</sup> F <sub>6</sub>	3	3	6	3/2	9.00	9.72	9.8
Dy <sup>3+</sup> (4f <sup>9</sup> )	<sup>6</sup> H <sub>15/2</sub>	5	5/2	15/2	4/3	10.00	10.65	10.6
Ho <sup>3+</sup> (4f <sup>10</sup> )	<sup>5</sup> I <sub>8</sub>	6	2	8	5/4	10.00	10.61	10.4
Er <sup>3+</sup> (4f <sup>11</sup> )	<sup>4</sup> I <sub>15/2</sub>	6	3/2	15/2	6/5	9.00	9.58	9.5
Tm <sup>3+</sup> (4f <sup>12</sup> )	<sup>3</sup> H <sub>6</sub>	5	1	6	7/6	7.00	7.56	7.6
Yb <sup>3+</sup> (4f <sup>13</sup> )	<sup>2</sup> F <sub>7/2</sub>	3	1/2	7/2	8/7	4.00	4.53	4.5

## b) Magnetization

To calculate the complete magnetization curve, set  $y = g\mu_B\mu_0 H/k_B T$ , then

$$\langle m \rangle = g\mu_B \partial / \partial y [\ln \sum_j \exp\{M_j y\}] \quad [d(\ln z)/dy = (1/z) dz/dy]$$

The sum over the energy levels must be evaluated; it can be written as

$$\exp(Jy) \{1 + r + r^2 + \dots + r^{2J}\} \quad \text{where } r = \exp\{-y\}$$

The sum of a geometric progression  $(1 + r + r^2 + \dots + r^n) = (r^{n+1} - 1)/(r - 1)$

$$\therefore \sum_j \exp\{M_j y\} = (\exp\{-(2J+1)y\} - 1)\exp\{Jy\}/(\exp\{-y\} - 1)$$

multiply top and bottom by  $\exp\{y/2\}$

$$= [\sinh(2J+1)y/2]/[\sinh y/2]$$

$$\langle m \rangle = g\mu_B (\partial / \partial y) \ln \{ [\sinh(2J+1)y/2] / [\sinh y/2] \}$$

$$= g\mu_B/2 \{ (2J+1) \coth(2J+1)y/2 - \coth y/2 \}$$

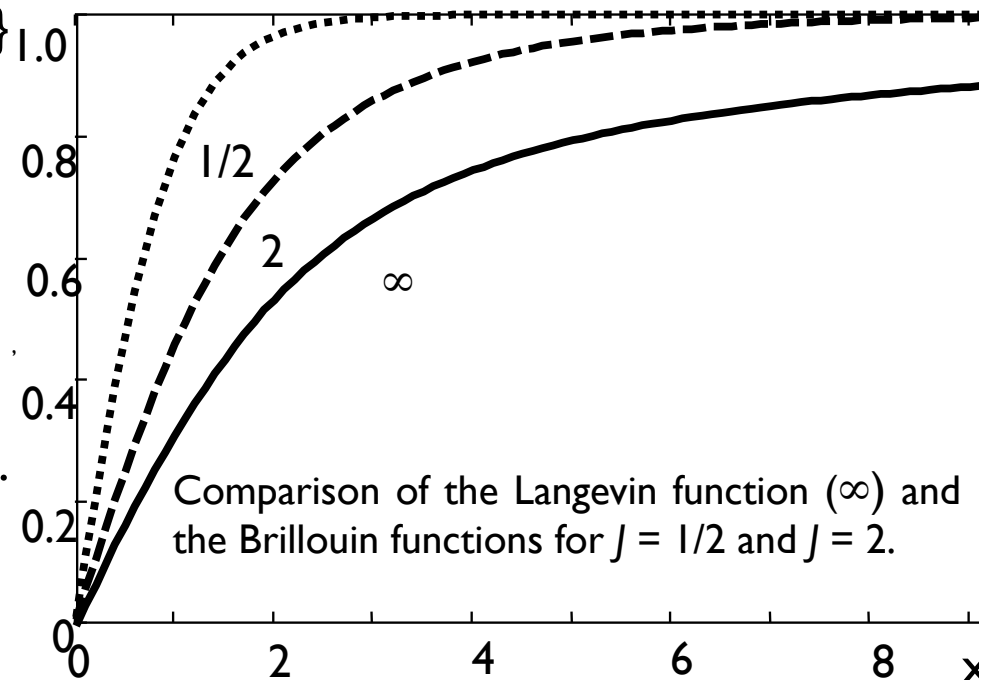
setting  $x = Jy$ , we obtain

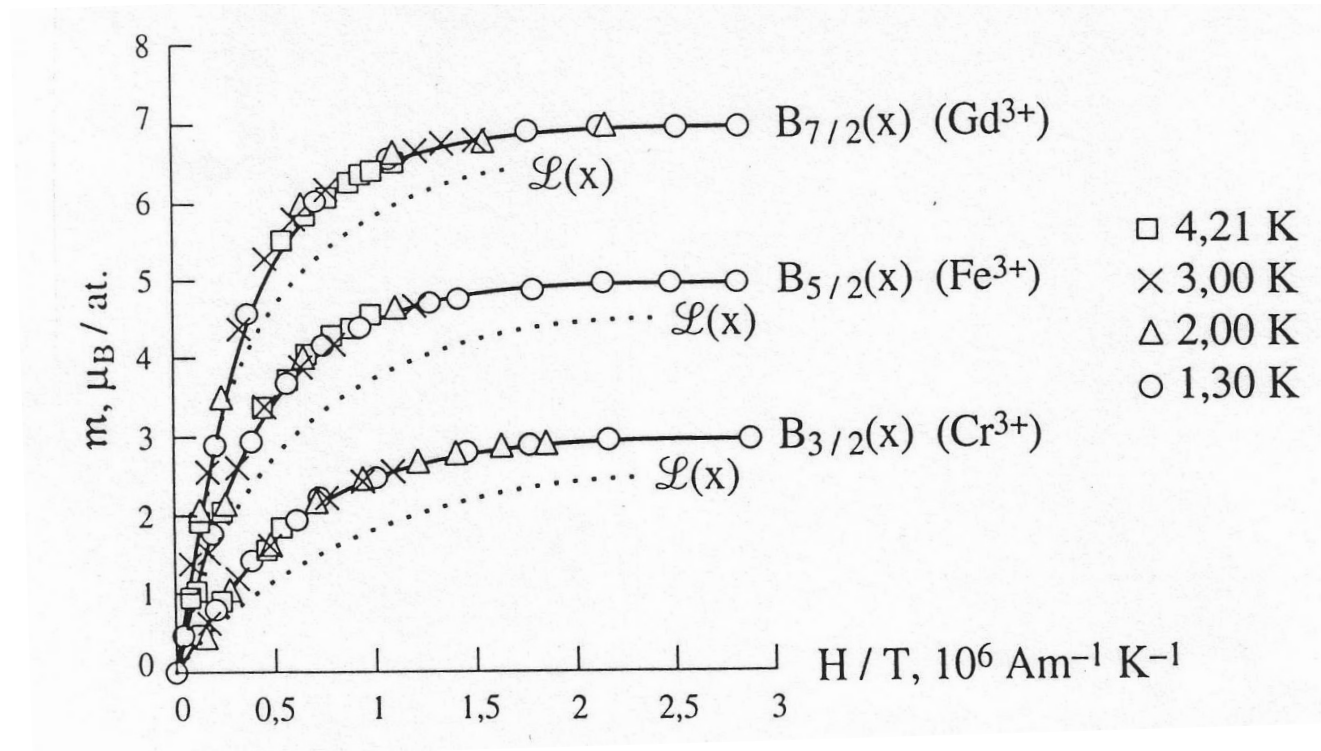
$$\langle m \rangle = m B_J(x)$$

where the Brillouin function

$$B_J(x) = \{(2J+1)/2J\} \coth(2J+1)x/2J - (1/2J) \coth(x/2J).$$

This reduces to  $\langle m \rangle = \mu_B \tanh(x)$   
in the limit  $J = 1/2$ ,  $g = 2$ .





Reduced magnetization curves for three paramagnetic salts, with Brillouin-theory predictions

The quantum theory of localized magnetism gives a good account of magnetically-dilute 3d and 4f salts where the magnetic moments do not interact with each other. Except in large fields or very low temperatures, the  $M(H)$  response is linear. Fields  $> 100 \text{ T}$  would be needed to approach saturation at room temperature.

The excellence of the theory is illustrated by the fact that data for quite different temperatures superpose on a single Brillouin curve plotted as a function of  $x \approx H/T$



## 5.3 Paramagnetism of Metals - band electrons

The calculation for metals proceeds on a quite different basis. The electrons are indistinguishable particles which obey Fermi-Dirac statistics. They are not localized, so Boltzmann statistics cannot be applied. The electrons have  $s = 1/2$ ,  $m = 1\mu_B$ . They partly-fill an energy band up to the Fermi level  $E_F$ .

A rough calculation gives the susceptibility as follows:

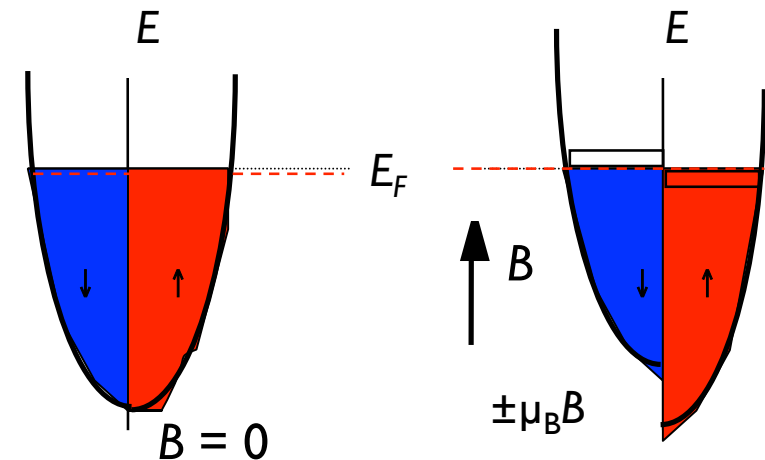
$$\chi = (N^\uparrow - N^\downarrow)\mu_B/H$$

$\approx 2[N(E_F)\mu_0 g\mu_B H]\mu_B/H$  where  $\mathcal{N}(E_F)$  is the density of states at the Fermi level for one spin direction.

$$\chi_{\text{Pauli}} \approx 2\mu_0 \mathcal{N}(E_F) \mu_B^2$$

This is known as the *Pauli* susceptibility. Unlike the Curie susceptibility, it is very small, and temperature independent.

The density of states  $\mathcal{N}(E_F)$  in a band is approximately  $N/2W$ , where  $W$  is the bandwidth (which is typically a few eV). Comparing the expression for the Pauli susceptibility with that for the Curie susceptibility  $\chi_{\text{Curie}} = \mu_0 N \mu_B^2 / k_B T$ , we see that the Pauli susceptibility is a factor  $k_B T / W$  smaller than the Curie susceptibility. The factor is of order 100 at room temperature.  $\chi_{\text{Pauli}}$  is of order  $10^{-5}$ .



## 6. Ferromagnetism.

An ordered ferromagnetic state forms when the atomic moments in a solid align spontaneously below the Curie temperature. It was originally explained by a huge fictitious internal magnetic field, but Heisenberg showed that the Coulomb interaction between electrons of adjacent atoms creates magnetic ‘exchange interaction’ between them. The ferromagnetic hysteresis loop is governed by magnetic dipole interactions, which lead to a ground state in ferromagnetic domains.

The characteristic features of ferromagnetic order are spontaneous magnetization  $M_s$  due to spontaneous alignment of the atomic magnetic moments, which disappears on heating above a critical temperature known as the *Curie point*. The magnetization tends to lie along certain *easy directions* determined by crystal structure or sample shape.

## 6.1 Mean field theory

Weiss (1907) supposed that in addition to any externally applied field  $\mathbf{H}$ , there is an internal ‘molecular’ field in a ferromagnet proportional to its magnetization.

$$\mathbf{H}^i = n_W \mathbf{M}$$

$\mathbf{H}^i$  must be immense in a ferromagnet like iron to be able to induce a significant fraction of saturation at room temperature;  $n_W \approx 100$ . The origin of these huge fields remained a mystery until Heisenberg introduced the idea of the exchange interaction in 1928.

Magnetization is given by the Brillouin function,

$$\langle m \rangle = m \mathcal{B}_J(x)$$

where now  $x = \mu_0 m H^i / k_B T$ .

The magnetization at zero temperature,  $M_0 = Nm$  where  $m = g\mu_B J$ . At nonzero temperature  $M_s = N\langle m \rangle$

In zero external field, we have

$$M_s/M_0 = \mathcal{B}_J(x) \quad (1)$$

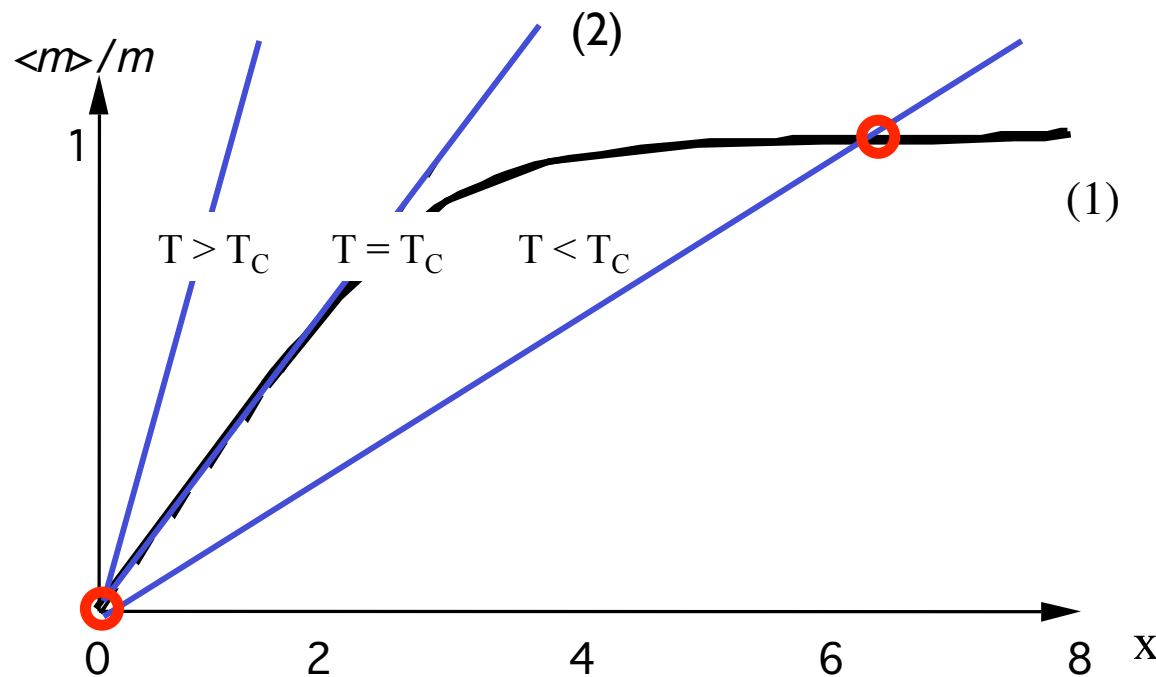
Also by eliminating  $H^i$  from the expressions for  $H^i$  ( $H^i = n_W M_s$ ) and  $x$  ( $H^i = k_B T x / \mu_0 m$ ); since  $M_0 = N m$

$$M_s/M_0 = (N k_B T / \mu_0 M_0^2 n_W) x$$

which can be rewritten in terms of the Curie constant  $C = \mu_0 N g^2 \mu_B^2 J(J+1) / 3 k_B$

$$M_s/M_0 = [T(J+1) / 3C] n_W x \quad (2)$$

The simultaneous solution of (1) and (2) is found *graphically*, or they can be solved numerically.



Graphical solution of (1) and (2) to find the spontaneous magnetization  $M_s$  when  $T < T_C$ .

Eq. (2) is also plotted for  $T = T_C$  and  $T > T_C$ .

At the Curie temperature, the slope of (2) is equal to the slope at the origin of the Brillouin function

For small  $x$ .

$$\mathcal{B}_J(x) \approx [(J+1)/3]x + \dots$$

hence

$$T_C = n_W C$$

where the Curie constant  $C = \mu_0 N g^2 \mu_B^2 J(J+1)/3k_B$ .

A typical value of  $T_C$  is a few hundred Kelvin. In practice,  $T_C$  is used to determine  $n_W$ .

In the case of Gd,  $T_C = 292$  K,  $J = S = 7/2$ ;  $g = 2$ ;  
 $N = 3.0 \times 10^{28} \text{ m}^{-3}$ ; hence  $C = 4.9$  K,  $n_W = 59$ .

The value of  $M_0 = Ng\mu_B J$  is  $1.95 \text{ MA m}^{-1}$ . Hence  $\mu_0 H_i = 144 \text{ T}$ .

This is an enormous 'effective' field

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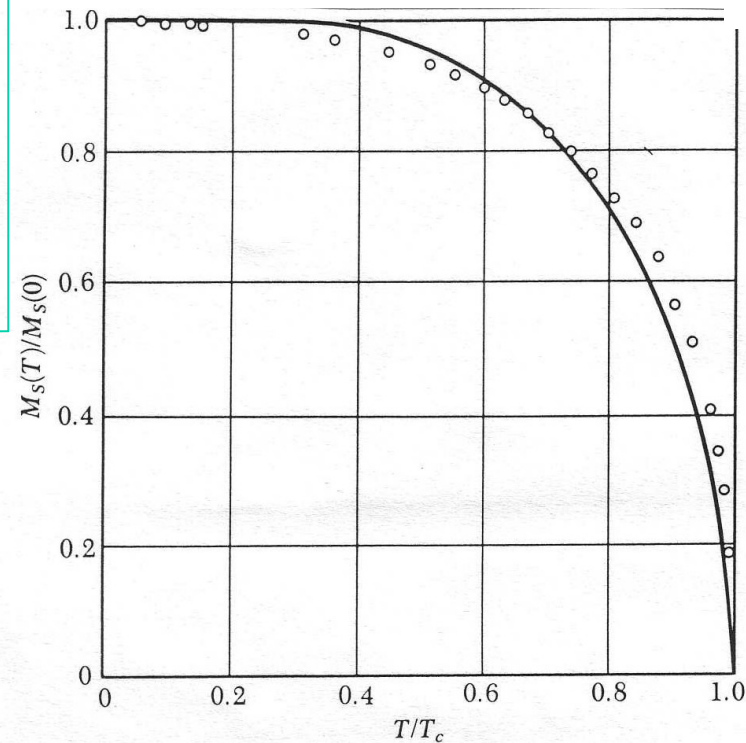
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The spontaneous magnetization for nickel, together with the theoretical curve for  $S = 1/2$  from the mean field theory. The theoretical curve is scaled to give correct values at either end.



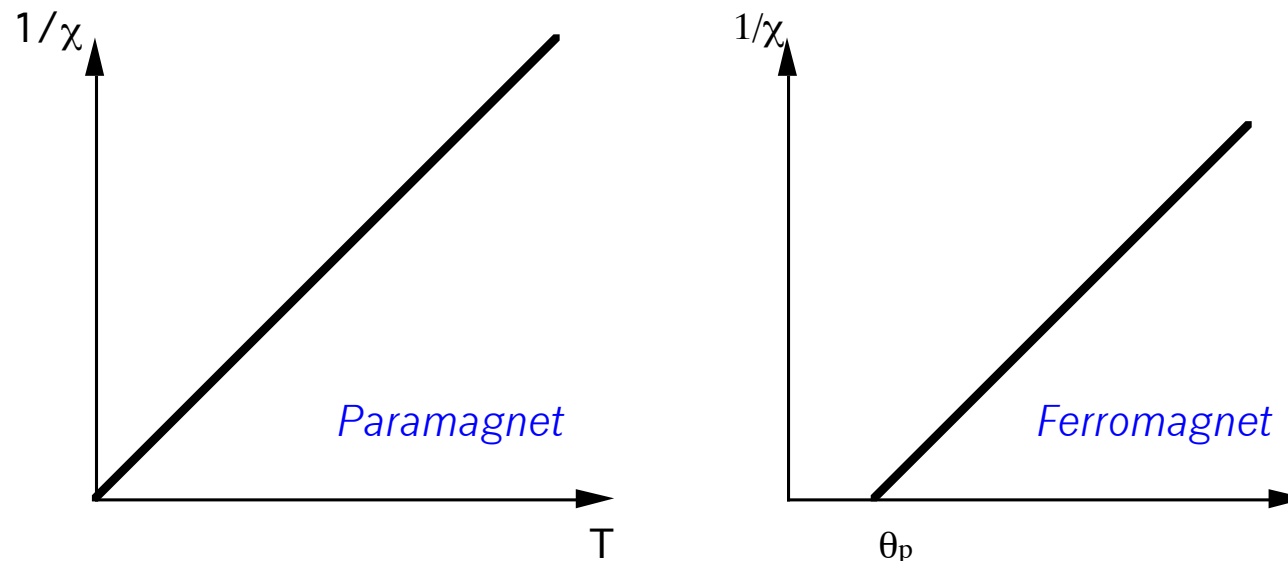
$$T > T_C$$

The paramagnetic susceptibility above  $T_C$  is obtained from the linear term  $\mathcal{B}_j(x) \approx [(j+1)/3j]x$  with  $x = \mu_0 m(n_W M + H)/k_B T$  and  $m = g\mu_B j$ .  $H$  is the applied field and  $H^i = n_W M$  is the internal field. The result is the *Curie-Weiss law*

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

where  $\theta_p = T_C = n_W C = \mu_0 n_W N g^2 \mu_B^2 j(j+1)/3k_B$

In this theory, the paramagnetic Curie temperature  $\theta_p$  is equal to the Curie temperature  $T_C$ , which is where the susceptibility *diverges*.



The Curie-law susceptibility of a paramagnet compared with the Curie-Weiss susceptibility of a ferromagnet for  $T > T_C$ . The slopes of both graphs are  $1/C$ . Hence the effective value of  $m$  can be deduced experimentally. See p. 128.

## 6.2 Exchange Interactions

What is the origin of the effective magnetic fields of  $\sim 100$  T which are responsible for ferromagnetism? They are *not* due to the atomic magnetic dipoles. The field at distance  $r$  due to a dipole  $\mathbf{m}$  is

$$\mathbf{B}_{\text{dip}} = (\mu_0 m / 4\pi r^3) [2\cos\theta \mathbf{e}_r + \sin\theta \mathbf{e}_\theta].$$

The order of magnitude of  $B_{\text{dip}} = \mu_0 H_{\text{dip}}$  is  $\mu_0 m / 4\pi r^3$ ; taking  $m = 1\mu_B$  and  $r = 0.1$  nm gives  $B_{\text{dip}} = 4\pi \cdot 10^{-7} \times 9.27 \cdot 10^{-24} / 4\pi \cdot 10^{-30} \approx 1$  tesla. Summing all the contributions of the neighbours on a lattice does *not* change this order of magnitude; in fact the dipole sum for a cubic lattice is exactly zero!

The origin of the internal field  $\mathbf{H}^i$  is the exchange interaction, which reflects the electrostatic Coulomb repulsion of electrons on neighbouring atoms and the Pauli principle, which forbids two electrons from entering the same quantum state. There is an energy difference between the  $\uparrow\downarrow$  and  $\uparrow\uparrow$  configurations for the two electrons. Inter-atomic exchange is one or two orders of magnitude weaker than the intra-atomic exchange which leads to Hund's first rule.

The Pauli principle requires the total wave function of two electrons 1,2 to be *antisymmetric* on exchanging two electrons

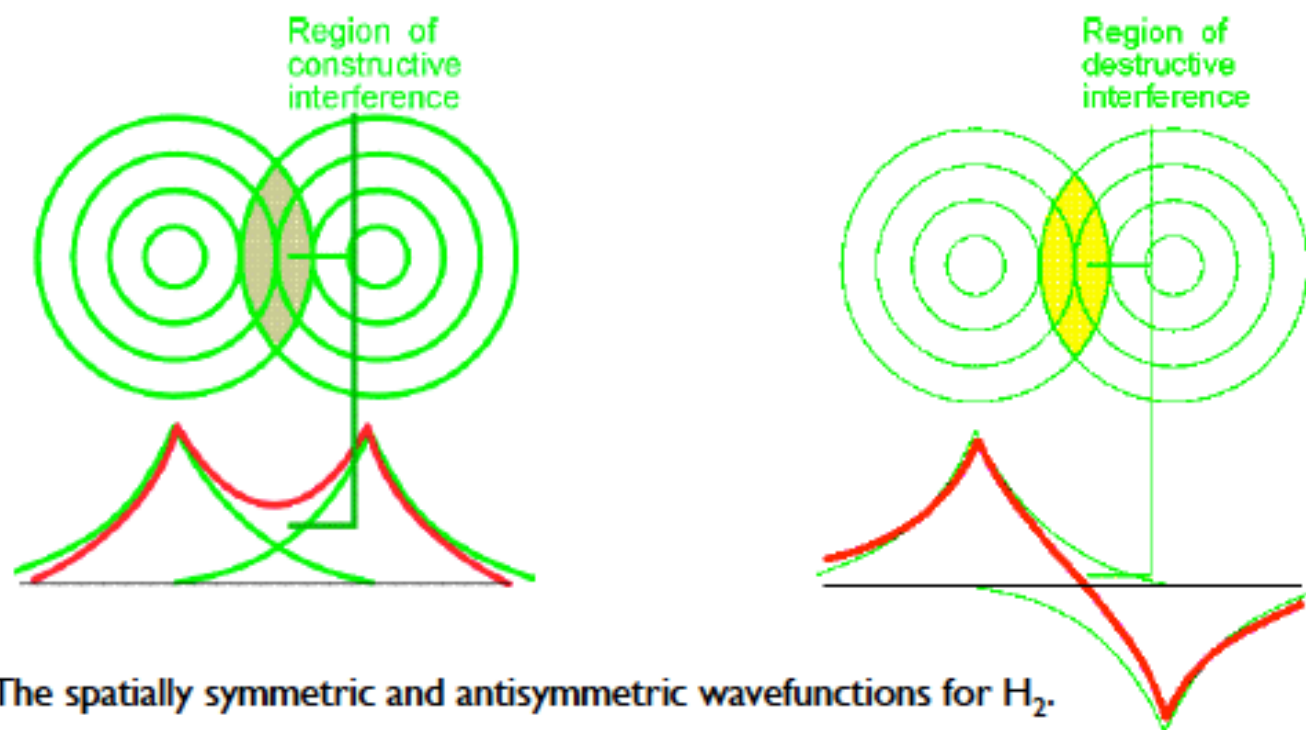
$$\Phi(1,2) = -\Phi(2,1)$$



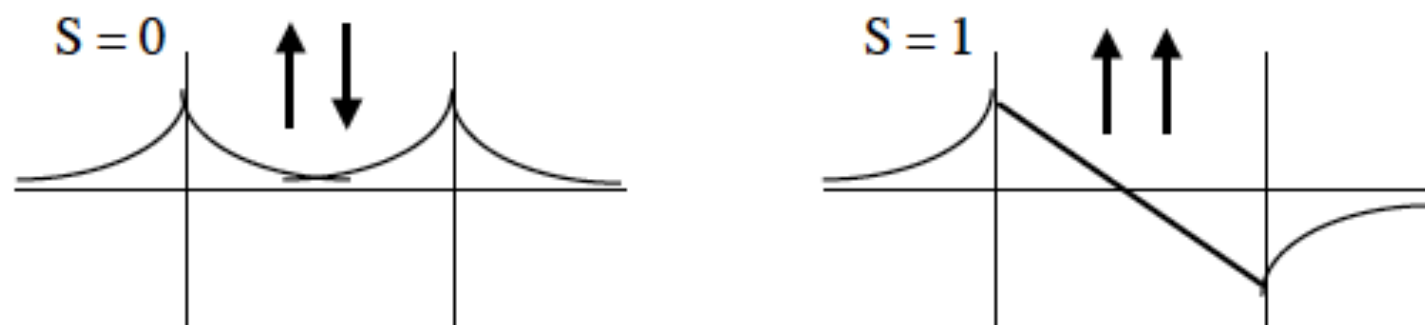
The total wavefunction is the product of functions of space and spin coordinates  $\Psi(\mathbf{r}_1, \mathbf{r}_2)$  and  $\chi(s_1, s_2)$ , each of which must be either symmetric or antisymmetric. This follows because the electrons are indistinguishable particles, and the number in a small volume  $dV$  can be written as  $\Psi^2(1,2)dV = \Psi^2(2,1)dV$ , hence  $\Psi(1,2) = \pm \Psi(2,1)$ .

The simple example of the **hydrogen molecule**  $H_2$  with two atoms  $a, b$  with two electrons  $1, 2$  in hydrogenic  $1s$  orbitals  $\psi_i$  gives the idea of the physics of exchange. There are two molecular orbits, one spatially symmetric  $\Psi_S$ , the other spatially antisymmetric  $\Psi_A$ .

$$\Psi_S(1,2) = (1/\sqrt{2})(\psi_{a1} + \psi_{b2}); \quad \Psi_A(1,2) = (1/\sqrt{2})(\psi_{a1} - \psi_{b2})$$



The spatially symmetric and antisymmetric wavefunctions for  $H_2$ .



The symmetric and antisymmetric spin functions are the spin triplet and spin singlet states

$$\chi_S = |\uparrow_1, \uparrow_2\rangle; (1/\sqrt{2})[|\uparrow_1, \downarrow_2\rangle + |\downarrow_1, \uparrow_2\rangle]; |\downarrow_1, \downarrow_2\rangle. \quad S = 1; M_S = 1, 0, -1$$

$$\chi_A = (1/\sqrt{2})[|\uparrow_1, \downarrow_2\rangle - |\downarrow_1, \uparrow_2\rangle] \quad S = 0; M_S = 0$$

According to Pauli, the symmetric space function must multiply the antisymmetric spin function, and vice versa. Hence the total wavefunctions are

$$\Phi_I = \Psi_S(1,2)\chi_A(1,2); \quad \Phi_{II} = \Psi_A(1,2)\chi_S(1,2)$$

The energy levels can be evaluated from the Hamiltonian  $H(\mathbf{r}_1, \mathbf{r}_2)$

$$E_{I,II} = \int \Psi_{S,A}^*(\mathbf{r}_1, \mathbf{r}_2) \mathcal{H}(\mathbf{r}_1, \mathbf{r}_2) \Psi_{S,A}(\mathbf{r}_1, \mathbf{r}_2) d\mathbf{r}_1 d\mathbf{r}_2$$

With no interaction of the electrons on atoms a and b,  $H(\mathbf{r}_1, \mathbf{r}_2)$  is just  $\mathcal{H}_0 = (-\hbar^2/2m)\{\nabla_1^2 + \nabla_2^2\} + V_1 + V_2$ .

The two energy levels  $E_I$ ,  $E_{II}$  are degenerate, with energy  $E_0$ . However, if the electrons interact via a term  $\mathcal{H} = e^2/4\pi\epsilon_0 r_{12}^2$ , we find that the perturbed energy levels are  $E_I = E_0 + 2J$ ,  $E_{II} = E_0 - 2J$ . The exchange integral is

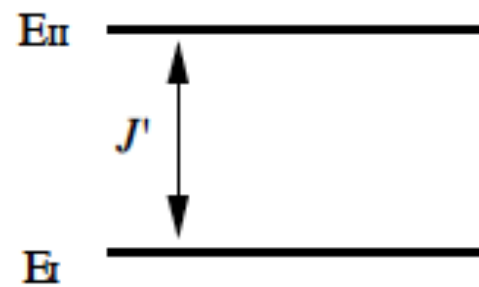
$$J = \int \psi_{a1}^* \psi_{b2}^*(\mathbf{r}) \mathcal{H}(r_{12}) \psi_{a2} \psi_{b1} d\mathbf{r}_1 d\mathbf{r}_2$$

and the separation  $(E_{II} - E_I)$  is  $4J$ . For the  $H_2$  molecule,  $E_I$  lies lower than  $E_{II}$ , the *bonding* orbital singlet state lies below the *antibonding* orbital triplet state  $J$  is negative. The tendency for electrons to pair off in bonds with opposite spin is everywhere evident in chemistry; these are the covalent interactions. We write the spin-dependent energy in the form

$$E = -2(J'/\hbar^2) \mathbf{s}_1 \cdot \mathbf{s}_2$$

The operator  $\mathbf{s}_1 \cdot \mathbf{s}_2$  is  $1/2[(\mathbf{s}_1 + \mathbf{s}_2)^2 - \mathbf{s}_1^2 - \mathbf{s}_2^2]$ . According to whether  $S = s_1 + s_2$  is 0 or 1, the eigenvalues are  $-(3/4)\hbar^2$  or  $-(1/4)\hbar^2$ . The splitting between the  $\uparrow\downarrow$  singlet state (I) and the  $\uparrow\uparrow$  triplet state (II) is then  $J'$ .

Energy splitting between the singlet and triplet states for hydrogen.



Heisenberg generalized this to many-electron atomic spins  $S_1$  and  $S_2$ , writing his famous Hamiltonian, where  $\hbar$  is absorbed into the  $J$ .

$$\mathcal{H} = -2J\mathbf{S}_1 \cdot \mathbf{S}_2$$

$J > 0$  indicates a ferromagnetic interaction (favouring  $\uparrow\uparrow$  alignment).

$J < 0$  indicates an antiferromagnetic interaction (favouring  $\uparrow\downarrow$  alignment).

When there is a lattice, the Hamiltonian is generalized to a sum over all pairs  $i,j$ ,  $-2\sum_{i>j} J_{ij} \mathbf{S}_i \cdot \mathbf{S}_j$ . This is simplified to a sum with a single exchange constant  $J$  if only nearest-neighbour interactions count.

The Heisenberg exchange constant  $J$  can be related to the Weiss constant  $n_W$  in the molecular field theory. Suppose the moment  $g\mu_B S_i$  interacts with an effective field  $H^i = n_W M = n_W N g \mu_B S$  and that in the Heisenberg model only the nearest neighbours of  $S_i$  have an appreciable interaction with it. Then the site Hamiltonian is

$$\mathcal{H}_i = -2(\sum_j J_{ij}) \cdot \mathbf{S}_i \approx -H^i g \mu_B S_i$$

The molecular field approximation amounts to neglecting the local correlations between  $\mathbf{S}$  and  $\mathbf{S}_j$ . If  $Z$  is the number of nearest neighbours in the sum, then  $J = n_W N g^2 \mu_B^2 / 2Z$ . Hence from the expression for  $T_C$  in terms of the Weiss constant  $n_W$

$$T_C = 2ZJ(J+1)/3k_B$$

Taking the example of Gd again, where  $T_C = 292$  K,  $J = 7/2$ ,  $Z = 12$ , we find  $J/k_B = 2.3$  K.

## 6.2.1 Exchange in Metals

The Heisenberg theory describes the exchange coupling of electrons in *localized* orbitals. It does not apply in metals, where there are partly-filled bands.

Generally, the energy of any electronic system is lowered as the wavefunctions spread out. This follows from the uncertainty principle  $\Delta p \Delta x \approx \hbar$ .

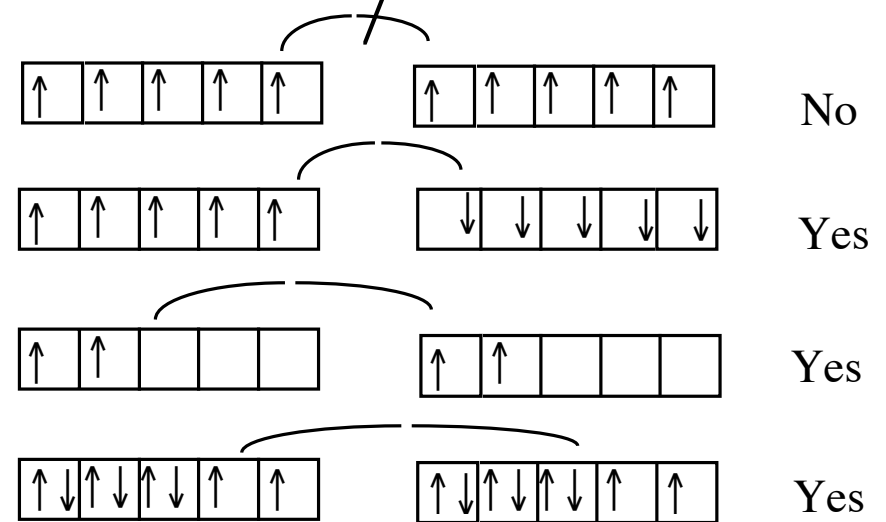
When many more-or-less delocalized electrons are present in different orbitals, the calculation of exchange is a delicate matter. Energies involved are only  $\approx 0.01$  eV, compared with bandwidths  $W$  of order 1 - 10 eV. There are competing exchange mechanisms with different signs of coupling.

The principal exchange mechanism in ferromagnetic and antiferromagnetic metals involves direct overlap of the partly-localized atomic orbitals of adjacent atoms. Other exchange mechanisms involve the interaction of localized and delocalized moments in the metal.

Electrons in 3d metals are described by extended wave functions and spin-polarized density of states

The bandwidth is 2 - 3 eV. In a  $\sim$  half-filled band the exchange is antiferromagnetic, whereas in a nearly-filled or nearly empty band it is ferromagnetic.

The sign depends first on band occupancy, then on the interatomic spacing, with ferromagnetic exchange favoured at larger spacing.





# Magnetic Periodic Table

1H

1.00

3Li

6.94

1 + 2s<sup>0</sup>

4Be

9.01

2 + 2s<sup>0</sup>

11Na

22.99

1 + 3s<sup>0</sup>

12Mg

24.21

2 + 3s<sup>0</sup>

19K

38.21

1 + 4s<sup>0</sup>

20Ca

40.08

2 + 4s<sup>0</sup>

21Sc

44.96

3 + 3d<sup>0</sup>

22Ti

47.88

4 + 3d<sup>0</sup>

23V

50.94

3 + 3d<sup>2</sup>

24Cr

52.00

3 + 3d<sup>3</sup>

312

25Mn

55.85

2 + 3d<sup>5</sup>

96

26Fe

55.85

3 + 3d<sup>6</sup>

1043

27Co

58.93

2 + 3d<sup>7</sup>

1390

28Ni

58.69

2 + 3d<sup>8</sup>

629

29Cu

63.55

2 + 3d<sup>9</sup>

30Zn

65.39

2 + 3d<sup>10</sup>

31Ga

69.72

3 + 3d<sup>10</sup>

32Ge

72.61

33As

74.92

34Se

78.96

35Br

79.90

36Kr

83.80

37Rb

85.47

1 + 5s<sup>0</sup>

38Sr

87.62

2 + 5s<sup>0</sup>

39Y

88.91

2 + 4d<sup>0</sup>

40Zr

91.22

4 + 4d<sup>0</sup>

41Nb

92.91

5 + 4d<sup>0</sup>

42Mo

95.94

5 + 4d<sup>1</sup>

43Tc

97.9

44Ru

101.1

3 + 4d<sup>6</sup>

45Rh

102.4

3 + 4d<sup>6</sup>

46Pd

106.4

2 + 4d<sup>8</sup>

47Ag

107.9

1 + 4d<sup>10</sup>

48Cd

112.4

2 + 4d<sup>10</sup>

49In

114.8

3 + 4d<sup>10</sup>

50Sn

118.7

4 + 4d<sup>10</sup>

51Sb

121.8

52Te

127.6

53I

126.9

54Xe

83.80

55Cs

132.9

1 + 6s<sup>0</sup>

56Ba

137.3

2 + 6s<sup>0</sup>

57La

138.9

3 + 4f<sup>0</sup>

72Hf

178.5

4 + 5d<sup>0</sup>

73Ta

180.9

5 + 5d<sup>0</sup>

74W

183.8

6 + 5d<sup>0</sup>

75Re

186.2

4 + 5d<sup>3</sup>

76Os

190.2

3 + 5d<sup>5</sup>

77Ir

192.2

4 + 5d<sup>5</sup>

78Pt

195.1

2 + 5d<sup>8</sup>

79Au

197.0

1 + 5d<sup>10</sup>

80Hg

200.6

2 + 5d<sup>10</sup>

81Tl

204.4

3 + 5d<sup>10</sup>

82Pb

207.2

4 + 5d<sup>10</sup>

83Bi

209.0

84Po

209

85At

210

86Rn

222

87Fr

223

88Ra

226.0

2 + 7s<sup>0</sup>

89Ac

227.0

3 + 5f<sup>0</sup>

58Ce

140.1

4 + 4f<sup>0</sup>

13

59Pr

140.9

3 + 4f<sup>2</sup>

60Nd

144.2

3 + 4f<sup>3</sup>

19

61Pm

145

62Sm

150.4

3 + 4f<sup>6</sup>

105

63Eu

152.0

2 + 4f<sup>7</sup>

90

64Gd

157.3

3 + 4f<sup>7</sup>

292

65Tb

158.9

3 + 4f<sup>8</sup>

229 221

66Dy

162.5

3 + 4f<sup>9</sup>

179 85

67Ho

164.9

3 + 4f<sup>10</sup>

132 20

68Er

167.3

3 + 4f<sup>11</sup>

85 20

69Tm

168.9

3 + 4f<sup>12</sup>

56

70Yb

173.0

3 + 4f<sup>13</sup>

71Lu

175.0

3 + 4f<sup>14</sup>

90Th

232.0

4 + 5f<sup>0</sup>

91Pa

231.0

5 + 5f<sup>0</sup>

92U

238.0

4 + 5f<sup>2</sup>

93Np

238.0

5 + 5f<sup>2</sup>

94Pu

244

95Am

243

96Cm

247

97Bk

247

98Cf

251

99Es

252

100Fm

257

101Md

258

102No

259

103Lr

260

Atomic Number

Atomic symbol

Atomic weight

Typical ionic charge

Antiferromagnetic T<sub>N</sub>(K)

Ferromagnetic T<sub>C</sub>(K)

66Dy

162.5

3 + 4f<sup>9</sup>

179

85

Nonmetal

Metal

Radioactive

Diamagnet

Paramagnet

**BOLD**

Magnetic atom

Ferromagnet T<sub>C</sub> > 290K

Antiferromagnet with T<sub>N</sub> > 290K

Antiferromagnet/Ferromagnet with T<sub>N</sub>/T<sub>C</sub> < 290 K

### 6.2.2. Stoner Criterion

Ferromagnetic *exchange* in metals need not lead to spontaneous ferromagnetic *order*.

The Pauli susceptibility must exceed a certain threshold. Ferromagnetic metals have an exceptionally large density of states at the Fermi level  $\mathcal{N}(E_F)$ .

Stoner applied Weiss' s molecular field idea to the free electron model.

$$H_i = n_S M$$

Here  $n_S$  is the Stoner molecular field constant;  
Bare Pauli susceptibility  $\chi_p = M/(H + n_{SM}M)$   
enhanced:

$$\chi = M/H = \chi_p/(1 - n_S \chi_p)$$

Hence the susceptibility diverges when

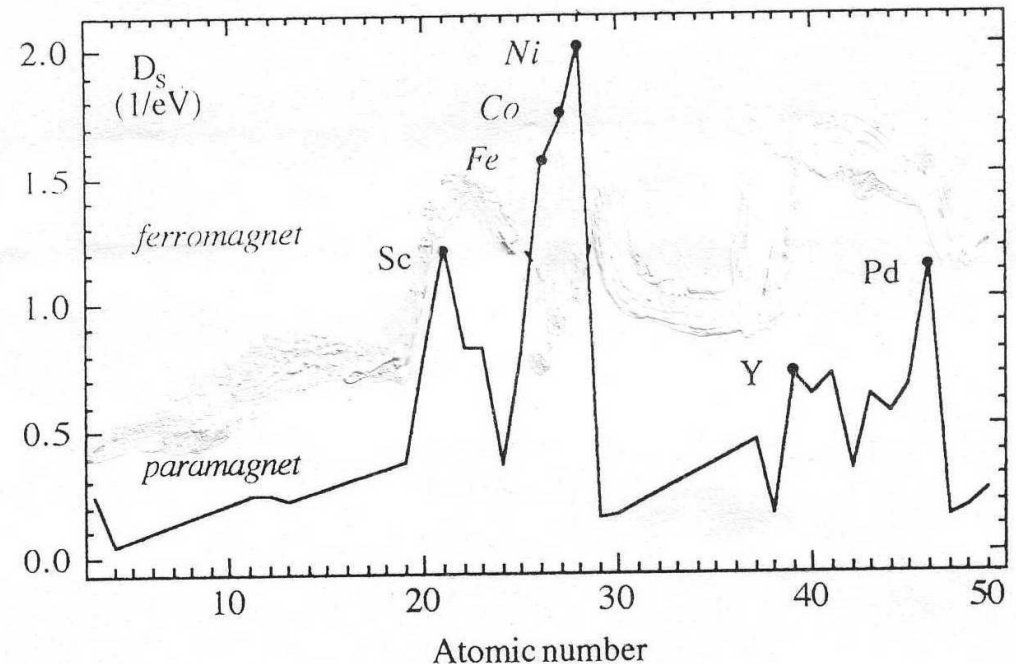
$$n_S \chi_p = 1$$

The value of  $n_S$  is about 10,000 in 3d metals.

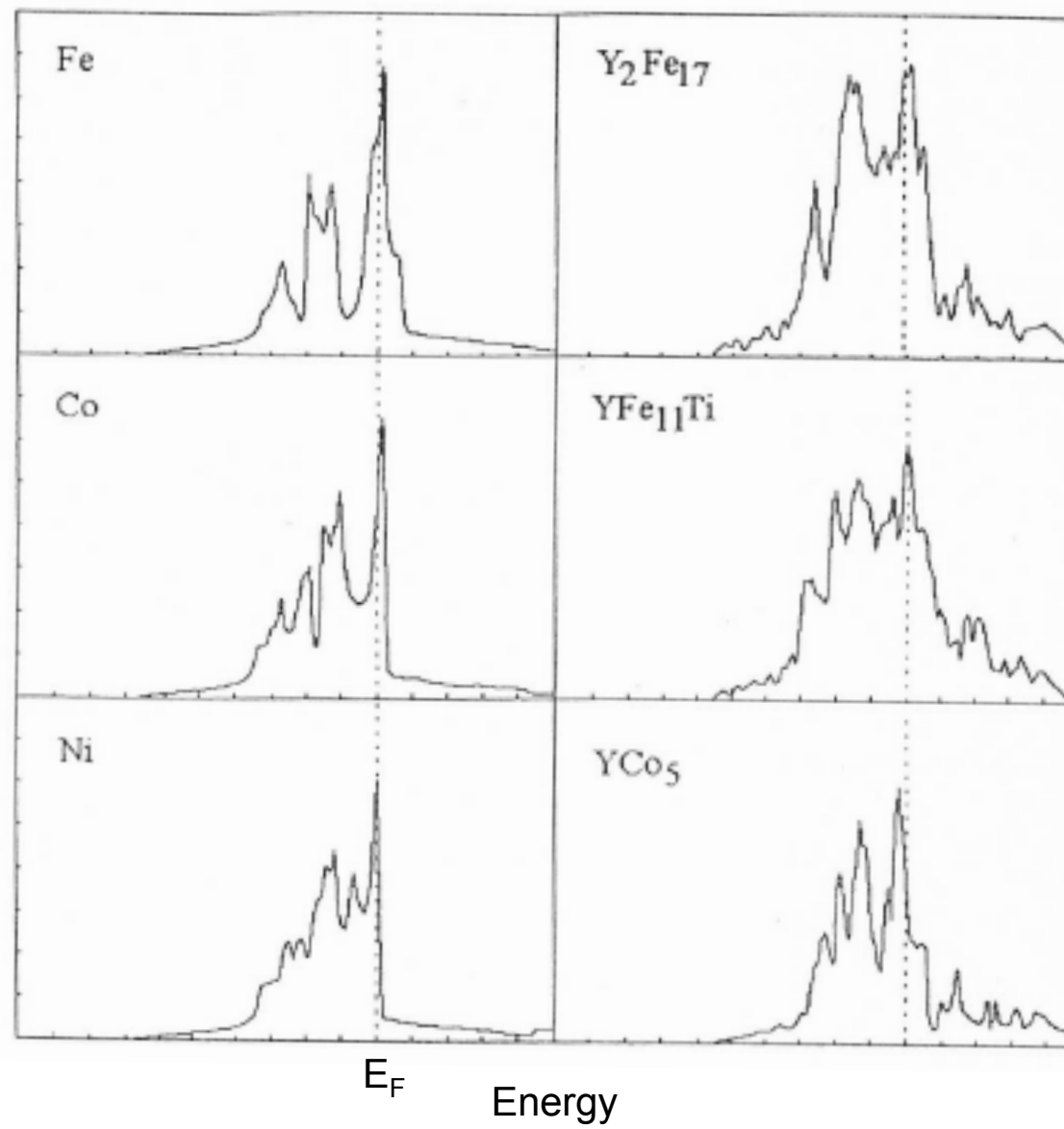
The Pauli susceptibility is proportional  
to the density of states  $\mathcal{N}(E_F)$ .

Only metals with a large  $\mathcal{N}(E_F)$  can order ferromagnetically. A big peak at the Fermi level is needed. Hence the late 3d elements Fe, Co, Ni are ferromagnetic, but the early 3d or 4d elements Ti, V, Cr are not. Elements in the middle of the series Cr, V are antiferromagnetic because the 3d band is approximately half-full.

If the Stoner criterion is satisfied, the  $\uparrow$  and  $\downarrow$  bands split spontaneously.



Density of states





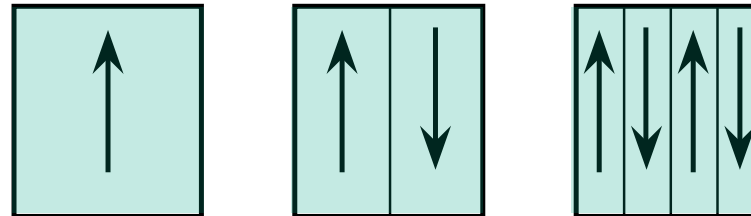
## 6.3 Ferromagnetic domains

Weiss also explained why most lumps of iron, for example, do not appear ferromagnetic. They actually contain many ferromagnetic *domains*, magnetized in different directions. The domains form in order to reduce the magnetostatic self-energy. This self-energy  $E_{\text{ms}}$  can be written in two equivalent forms

$$E_{\text{ms}} = (1/2) \int_{\text{all space}} \mu_0 H^2 dV \quad \text{or} \quad E_{\text{ms}} = -(\mu_0/2) \int_{\text{magnet}} \mathbf{M} \cdot \mathbf{H} dV$$

The value of  $\mathbf{H}$  inside the magnet is the demagnetizing field  $\mathbf{H}_d = -\mathcal{N}\mathbf{M}$  where  $\mathcal{N}$  is the demagnetizing factor. Hence

$$E_{\text{ms}} = (1/2) \mu_0 \mathcal{N} M^2 V$$



Reduction of the demagnetizing energy of a ferromagnet by splitting up into domains. The values of  $E_{\text{ms}}$  are approximately 0.20, 0.10 and 0.05 in units of  $\mu_0 M^2 V$

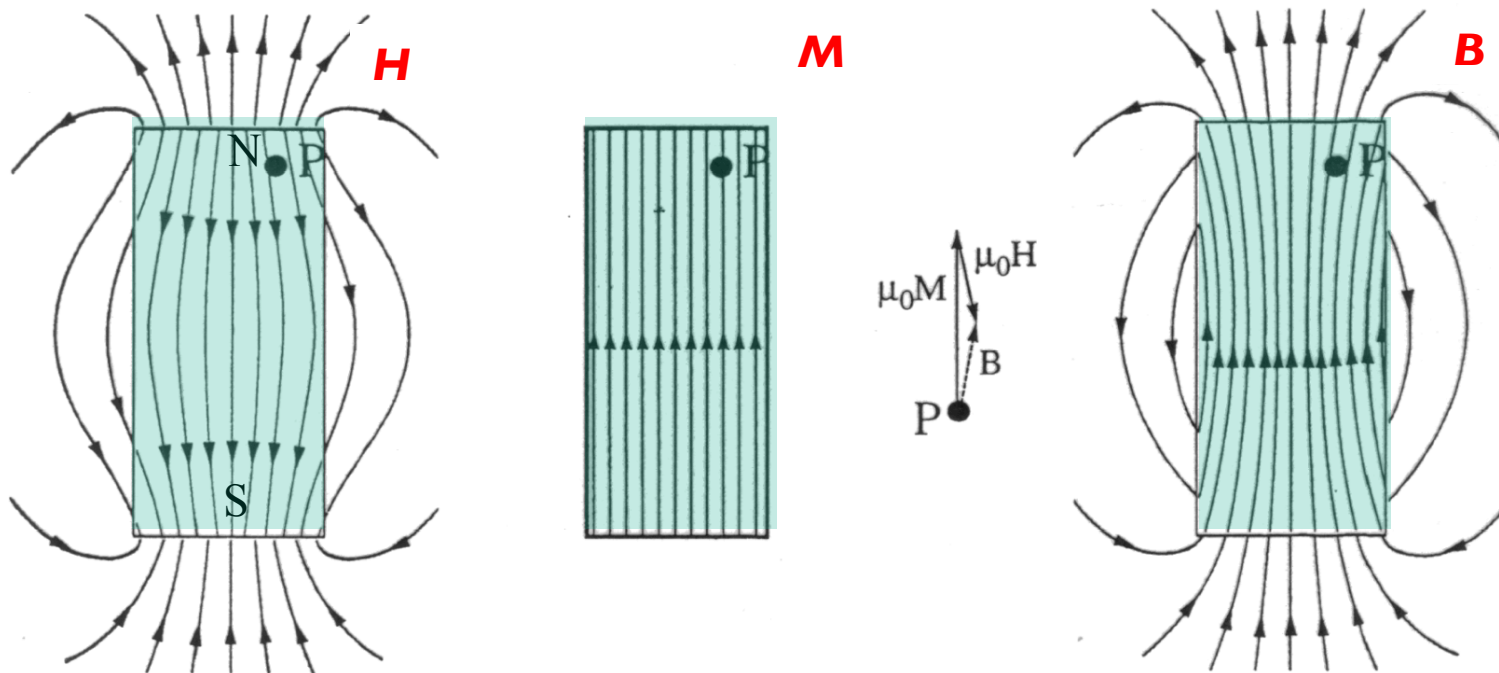
The particular domain structure adopted by a piece of ferromagnetic material is the result of minimizing the total energy, which is the sum of four terms

$$E_{\text{tot}} = E_{\text{ms}} + E_{\text{ex}} + E_{\text{a}} + E_{\text{Z}}$$

$E_{\text{ex}}$  is the exchange energy.  $E_{\text{a}}$  is the anisotropy energy.  $E_{\text{Z}}$  is the Zeeman energy in an external field

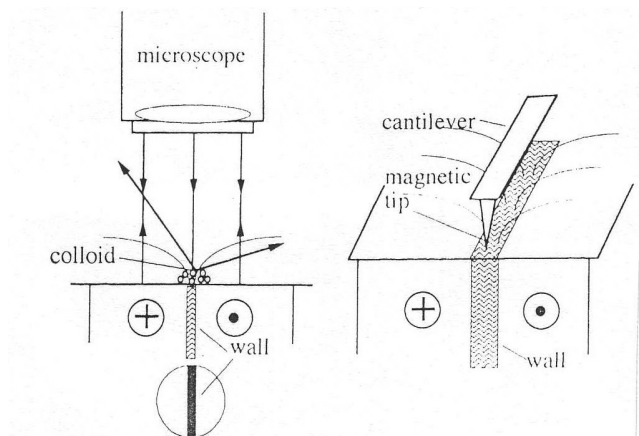
## ***B, H and M again***

- The distinction between the  $B$ -field and the  $H$ -field in *free space* is trivial. They are proportional, but with different units. Thus  $\mathbf{B} = \mu_0 \mathbf{H}$ .
- *Inside* a magnetic material,  $B$  and  $H$  are completely different, as shown below for a uniformly magnetized bar magnet. The relation  $\mathbf{B} = \mu_0(\mathbf{H} + \mathbf{M})$  at a point  $P$  is illustrated by the little vector diagram. Note that inside the magnet,  $\mathbf{B}$  and  $\mathbf{H}$  are oppositely directed, and  $\mathbf{H}$  is also opposite to  $\mathbf{M}$ . Hence the term *demagnetizing field*.
- $\mathbf{H}$  is important in solids because the magnetization state is determined by  $\mathbf{H}(\mathbf{r})$

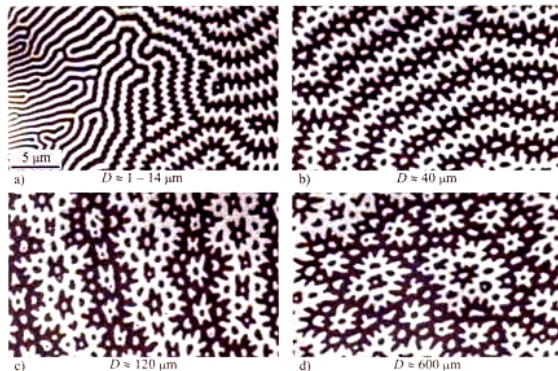


## Some ways of visualizing domains:

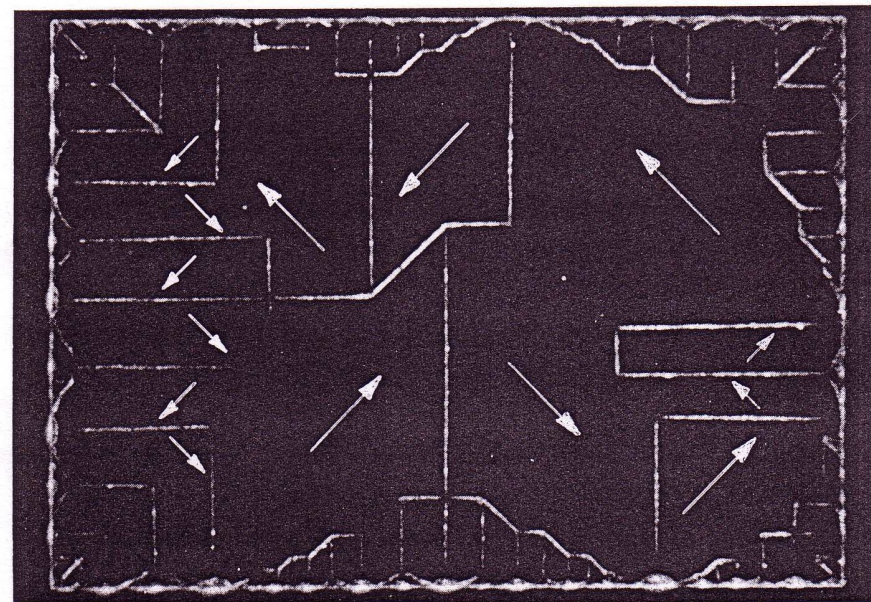
- Bitter pattern (spread ferrofluid on the surface) [depends on stray field]
- Atomic force microscope with a magnetic tip [depends on stray field]
- Magneto-optic Kerr effect [depends on  $\mathbf{M}$  in the surface region]
- Lorentz (transmission electron) microscopy [depends on  $\mathbf{B}$  in a thin foil]



Bitter method (left) and MFM (right)  
— Barkhausen heard them first !



Kerr images  
of domains



Domain pattern on the surface of a nickel crystal revealed  
by the Bitter method.

## 6.3.1 Anisotropy

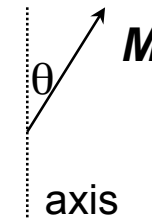
The tendency for the ferromagnetic axis of a domain to lie along some fixed *easy axes* in a crystal is known as the phenomenon of *magnetic anisotropy*.

Strong uniaxial anisotropy is a prerequisite for hard magnetism.

Near-zero anisotropy is needed for soft magnets.

Generally, the tendency for magnetization to lie along some easy axis is represented by an energy expression of which the leading term is

$$E_a = K_1 \sin^2 \theta$$



where  $\theta$  is the angle between  $\mathbf{M}$  and the anisotropy axis.

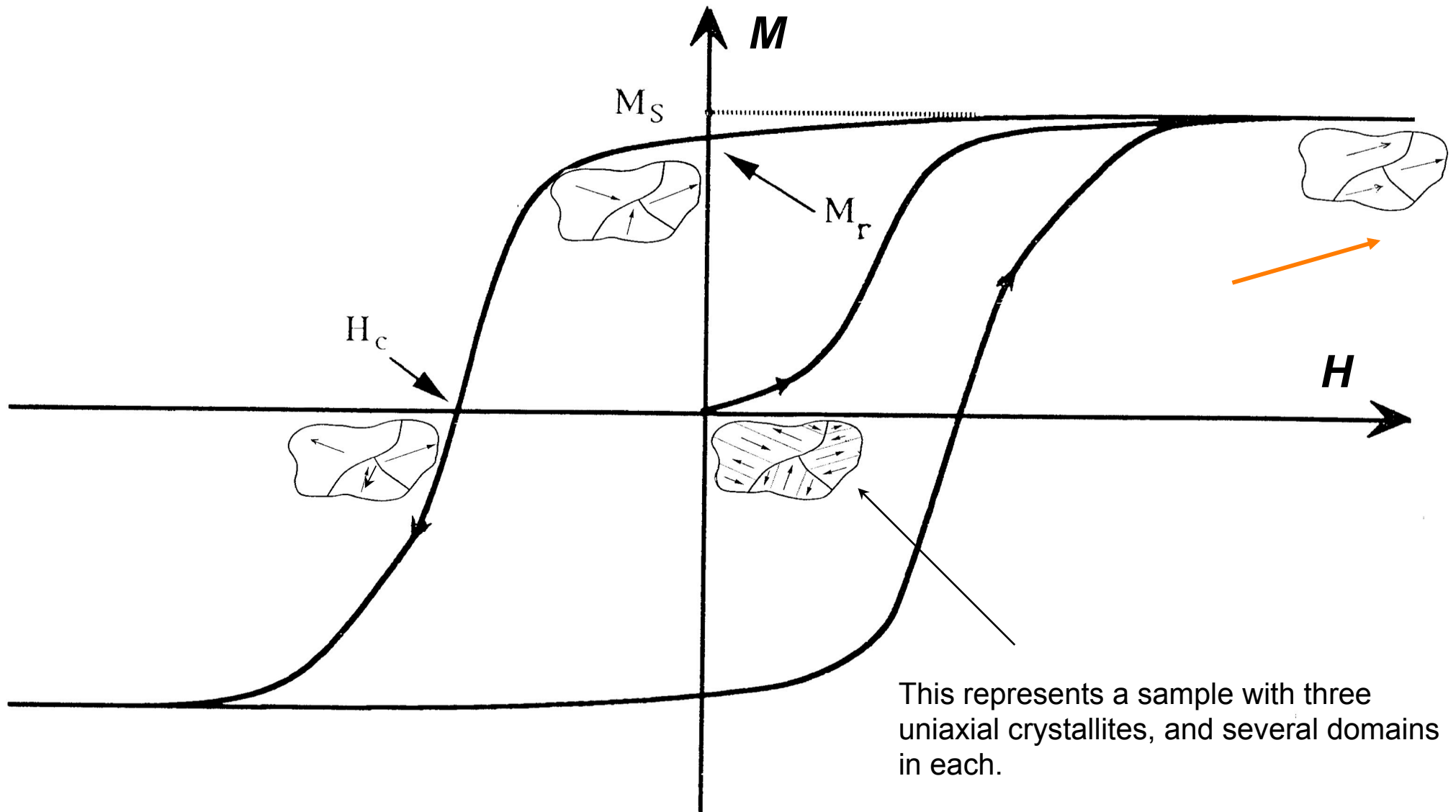
The anisotropy constant  $K_1$  depends on temperature, and the anisotropy energy goes to zero at  $T_C$ . Units are  $\text{J m}^{-3}$ . Values typically range from  $10^2$  to  $10^6 \text{ J m}^{-3}$ .

Most common source of anisotropy is magnetocrystalline anisotropy due to the crystal field, where the magnetization process is different along different crystallographic directions. This depends on spin-orbit coupling. The expression  $E_a = K_1 \sin^2 \theta$  is valid for *uniaxial* crystal structures (hexagonal, tetragonal, trigonal).

In cubic symmetry, a different expression is necessary to reflect the symmetry of the crystal.

Sample *shape* will also contribute to the anisotropy.  $K_1^{\text{shape}} = \frac{1}{4} \mu_0 M_s^2 (1 - 3\mathcal{N})$

## The magnetization curve and hysteresis loop

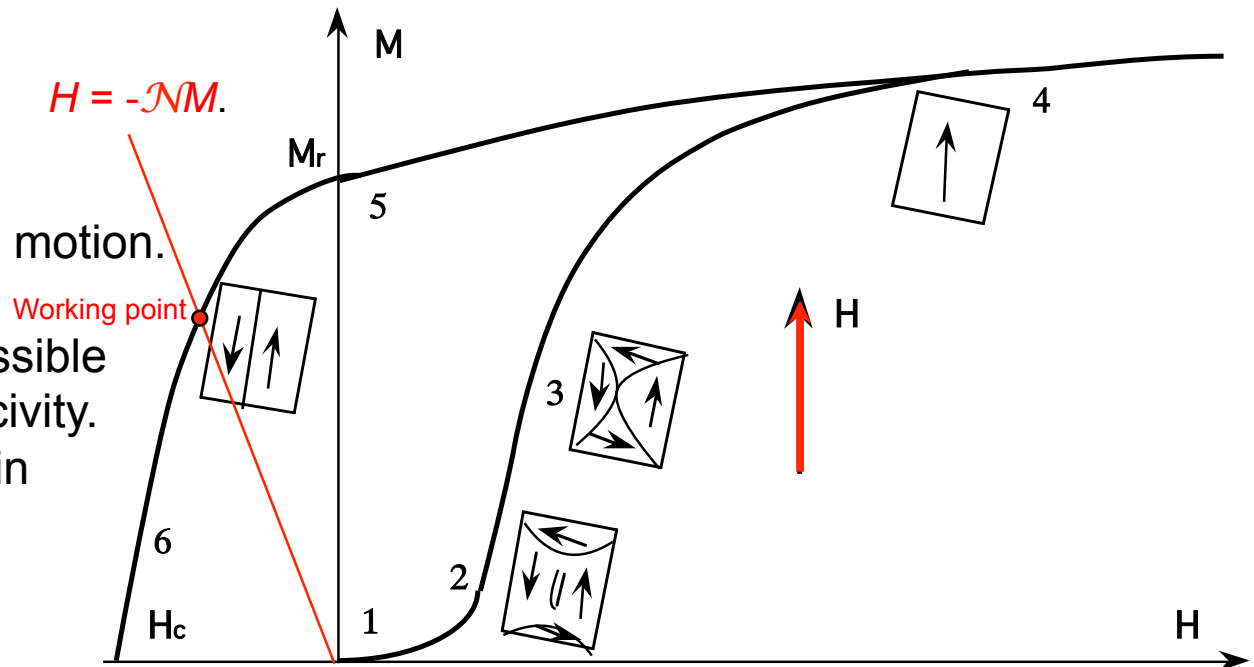




Starting from the thermally-demagnetized state, the following magnetization processes are involved around the hysteresis curve

- 1 - 2 Reversible wall motion
- 3 irreversible wall motion
- 4 coherent rotation
- 5 - 6 nucleation, irreversible wall motion.

In bulk material it is practically impossible to calculate the hysteresis and coercivity. An exception are small single-domain particles where the magnetization reverses coherently



The first two quadrants of the hysteresis loop

The energy loss on cycling the the  $M(H)$  loop is  $\int_{\text{loop}} \mu_0 H dM$ .

For minimum losses in ac applications the coercivity must be as small as possible.

The other extreme is needed for a permanent magnet, where the hysteresis loop should be broad to avoid self demagnetization in the demagnetizing field  $-\mathcal{NM}$ .

If the magnet is to remain fully magnetized no matter what its shape, it should have a square loop with  $H_c > M$

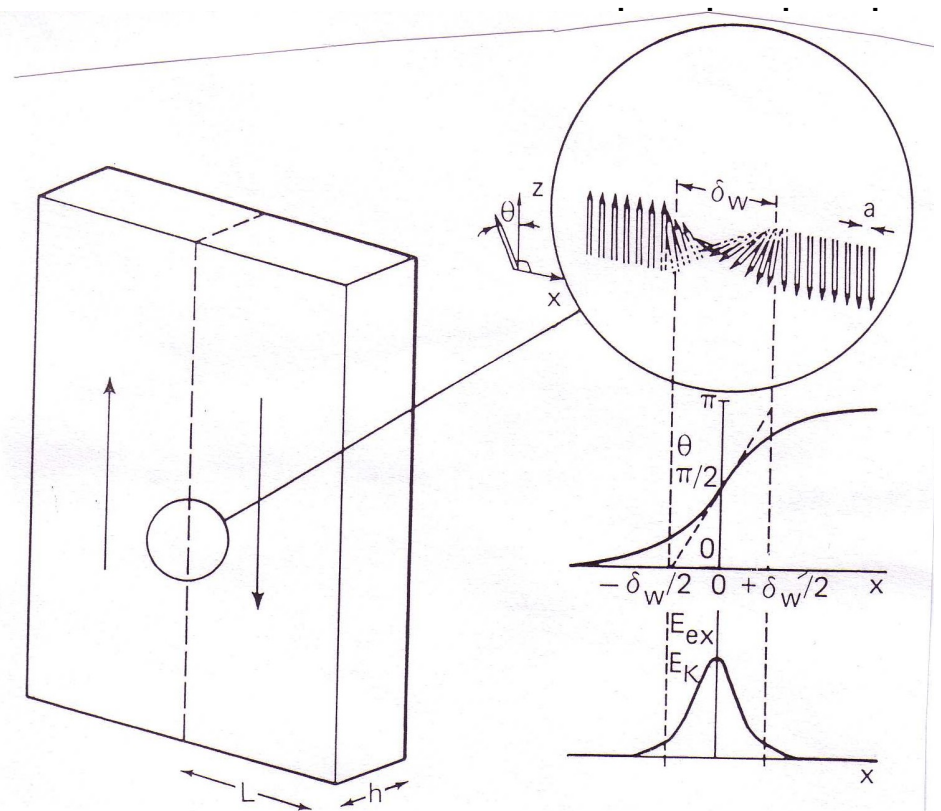
### 6.3.2 Domain walls

The region separating two oppositely-magnetized domains is a  $180^\circ$  domain wall, known as a *Bloch wall*. The structure is obtained by minimizing the energy

$$E_{\text{tot}} = E_{\text{ms}} + E_{\text{ex}} + E_{\text{a}}.$$

We give an approximate treatment which illustrates the physics.

Granted we need to create a wall to reduce  $E_{\text{ms}}$ , we seek a compromise between a wide wall, which would minimize  $E_{\text{ex}}$  and a narrow one which would minimize  $E_{\text{a}}$ . Suppose we have a ferromagnet with the sites on a cubic lattice with side  $a$ , and suppose also that magnetization turns by an angle  $\varphi$  from one site to the next across the wall, as shown in the figure.



A  $180^\circ$  Bloch wall between oppositely-magnetized domains in a sample with uniaxial anisotropy.

The wall width  $\delta_w$  is related to  $a$  and  $\varphi$ ,  $\delta_w = \pi a / \varphi$

Exchange energy for a neighbouring pair of spins is

$$-2J\mathbf{S}_i \cdot \mathbf{S}_j = -2JS^2 \cos \varphi \approx -2JS^2(1 - \varphi^2/2 + \dots)$$

The extra energy due to misalignment is  $JS^2\varphi^2$ . For a line of  $n = \pi/\varphi$  spins across the wall, this is  $JS^2\pi\varphi$ , and per unit area of wall  $E'_{\text{ex}} = JS^2\pi\varphi/a^2$

If this were the *only* term,  $\varphi$  would be very small,  $\delta_w \rightarrow \infty$ . But the spins in the wall are pointing away from the easy axis. The anisotropy cost is about  $(1/2)K_1a^3$  per spin or

$$E'_a = (1/2)K_1a\pi/\varphi \text{ per unit area.}$$

The wall energy  $\gamma_{\text{wall}} = E'_{\text{ex}} + E'_a$  is minimum with respect to  $\varphi$  when

$$\partial E_w / \partial \varphi = JS^2\pi/a^2 - (1/2)K_1a/\varphi^2 = 0. \quad \varphi^2 = (1/2)K_1a^3/JS^2$$

$$\delta_w = \pi\sqrt{(2JS^2/K_1a)}$$

$$\gamma_w = \pi\sqrt{(2K_1JS^2/a)}$$

Taking the example of cobalt,  $K_1 = 500 \text{ kJ m}^{-3}$ ,  $J = S \approx 1$  and using  $T_C = 1390 \text{ K}$  and  $Z = 12$  to deduce  $J$  from the expression  $T_C = 2ZJ/(j+1)/3k_B$  gives  $J = 1.2 \cdot 10^{-21} \text{ J}$ .  $a \approx 0.2 \text{ nm}$ ; hence  $\delta_w \approx 15 \text{ nm}$ , about 75 atomic spacings;  $\gamma_w = 8 \text{ mJ m}^{-2}$ .



## Domain wall pinning

The domain wall acts like an elastic membrane with energy  $\gamma_w$  J m<sup>-2</sup>. It will be strongly pinned at defects, especially planar defects, with different  $J$  or  $K_1$  to the bulk, especially when these defects have dimension comparable to the domain wall width  $\delta_w$ .

Weaker pinning occurs when there are many defects distributed throughout the wall width.

Generally, there is always some distribution of defects in any sample of magnetic material. Suppose the energy of the system depends just on the wall position  $x$ , and applied field  $H$ , where  $f(x)$  represents the effects of the pinning sites

$$E_{\text{tot}} = f(x) + 2\mu_0 MHx$$

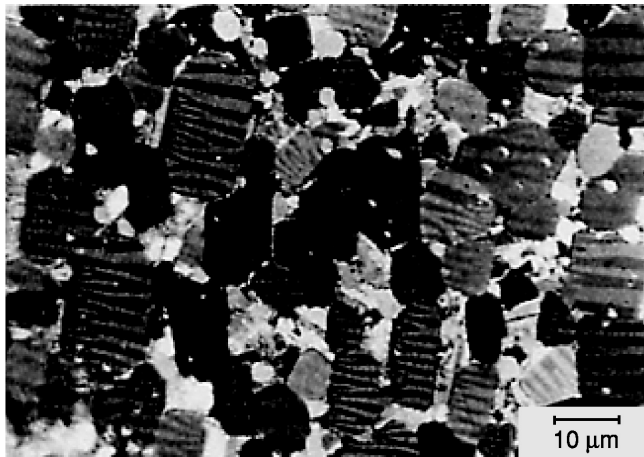
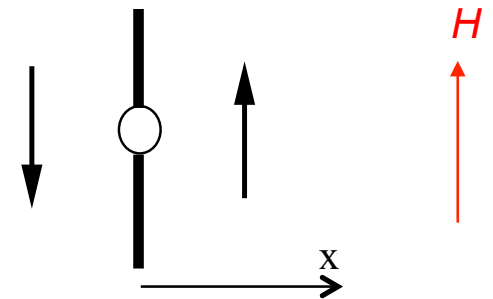
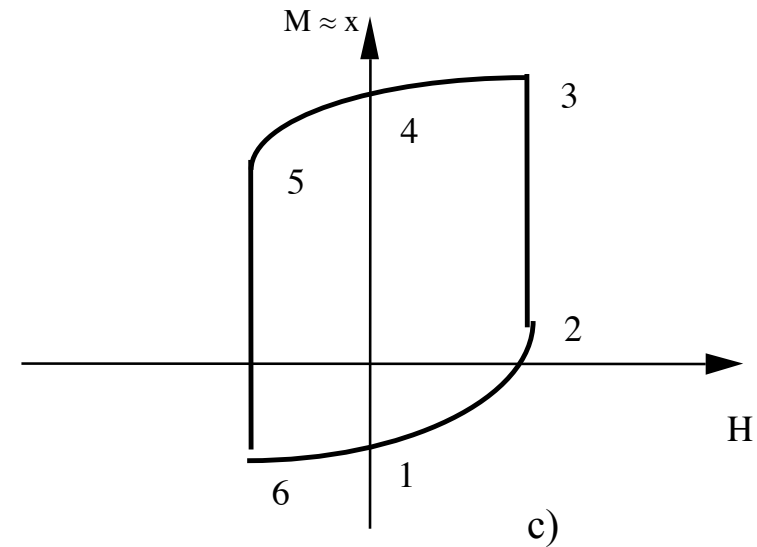
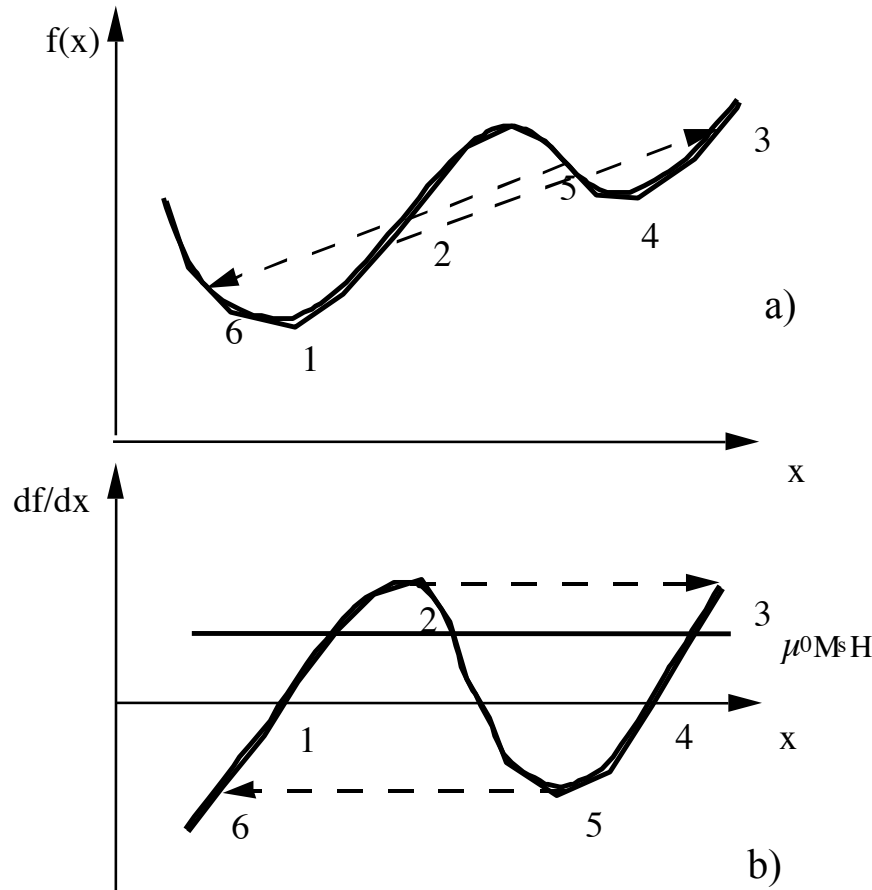


Image of the polished surface of a Nd-Fe-B sintered magnet in the Kerr microscope. The magnet is in the virgin state, and the oriented Nd<sub>2</sub>Fe<sub>14</sub>B crystallites are unmagnetized multidomains. The domain contrast is due to Kerr rotation observed between crossed polarizers. Domain walls are trapped between the grains

We show how a hysteresis loop results from the energy landscape with several minima due to pinning. At local energy minimum  $df(x)/dx = 2\mu_0 M_s H$ . As the wall jumps from points with the same  $df(x)/dx$  on increasing field, the magnetization changes discontinuously in a *Barkhausen* jump. The hysteresis loop of a macroscopic sample consists of many such jumps.



a) Energy as a function of wall position. b) The equilibrium condition  $df(x)/dx = 2\mu_0 M_s H$  c) a hysteresis loop due to field cycling.

### 6.3.3 Single-domain particles.

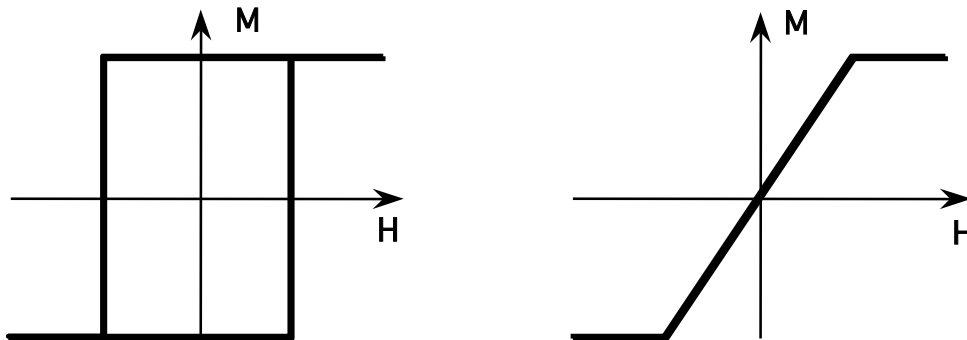
When ferromagnetic particles are no bigger than a few tens of nanometers, it does not pay to form a domain wall. The energy gain is of order  $(1/2)\mu_0 M^2 V \sim \mu_0 M^2 r^3$ , whereas the cost of forming the wall is  $\gamma_w \pi r^2$ . When the particle radius  $r$  is sufficiently small, the latter outweighs the former.

When the particle is very small, reversal takes place by *coherent rotation* of the magnetic moment  $\mathbf{m}$ .

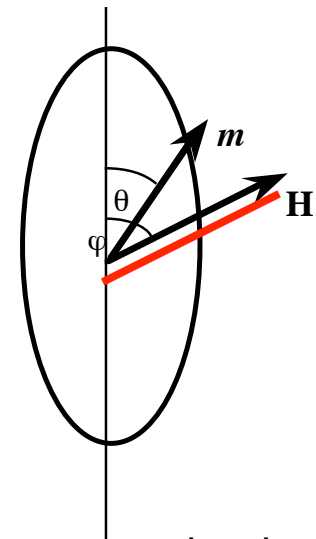
If an external field  $\mathbf{H}$  is applied at an angle  $\varphi$  to the easy direction, and the magnetization is at an angle  $\theta$  to the easy direction, the energy is  $E_{\text{tot}} = E_{\text{ms}} + E_a + E_Z$  the sum of magnetostatic (shape anisotropy), magnetocrystalline and Zeeman terms. The first two are given by a term  $K_u \sin^2 \theta$ , hence

$$E_{\text{tot}} = K_u V \sin^2 \theta - \mu_0 m H \cos(\varphi - \theta)$$

The energy can be minimized, and the hysteresis loop calculated numerically for a general angle  $\varphi$ . This is the *Stoner-Wohlfarth* model.



Two special cases of great interest: are  $\varphi = 0$  and  $\varphi = \pi/2$ . In the first case  $\theta = 0$  or  $\pi$ , and a square loop is observed with a flip from  $\theta = 0$  to  $\theta = \pi$  at  $H_c = 2K_u/M$ , ( $M = m/V$ ). These square loops are valuable for magnetic memory. In the second case, the magnetization rotates continuously with no hysteresis



A single domain particle where the magnetization rotates coherently.

## 6.4 Magnetic measurements

Methods of measuring magnetization, and hence susceptibility or hysteresis, of magnetic materials depend either on the force on a magnetic moment in a nonuniform field  $\mathbf{F} = -\nabla \mathbf{m} \cdot \mathbf{B}$ , or on Faraday's law  $\varepsilon = -d\Phi/dt$ , where  $\Phi$  is the flux threading a circuit and  $\varepsilon$  is the induced emf. We consider three examples:

### *Force method (Faraday balance)*

Considering one component of the force equation; ( $\mathbf{m}$  is constant)

$$F_z = -(m_x \partial B_x / \partial z + m_y \partial B_y / \partial z + m_z \partial B_z / \partial z)$$

If the field is in the x-direction,  $F_z = -m_x \partial B_x / \partial z$ . The field gradient may be produced using shaped pole-pieces, or by special field gradient coils. The gradient is calibrated with a sample of known magnetization or susceptibility. Sensitivity may be improved by applying an alternating current to the gradient coils, and using lock-in detection.

### *Extraction method.*

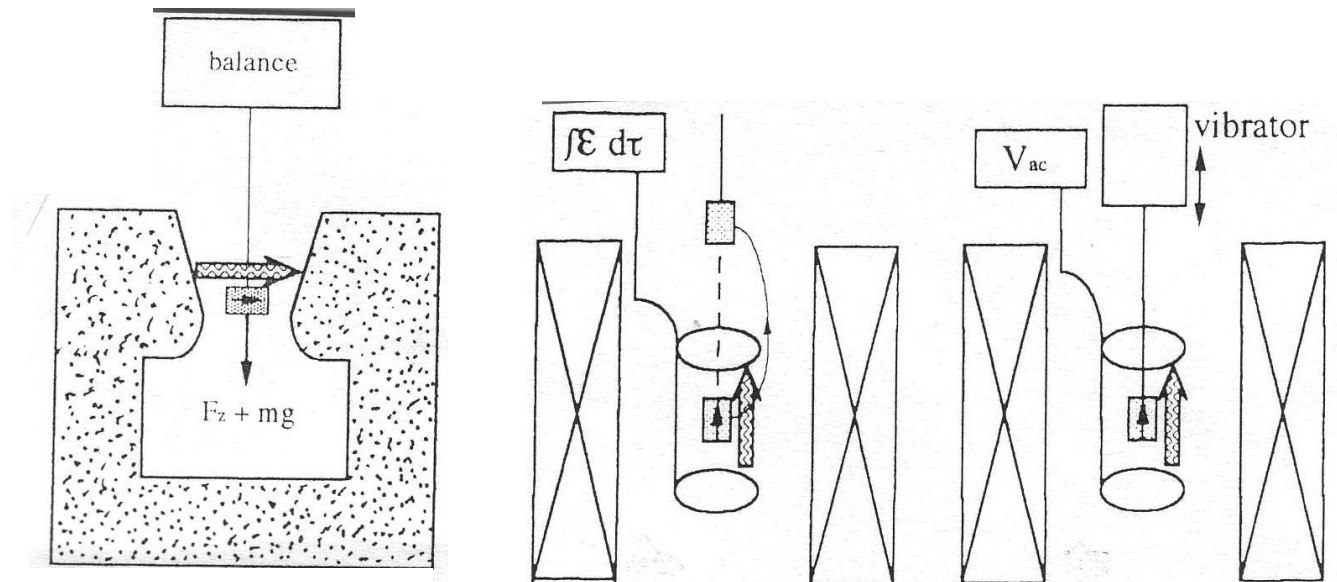
Here the sample is first located in a pickup coil in the field, and then removed to a distant point. An emf  $\varepsilon$  is induced in the coil, and

$$\int \varepsilon dt = \Phi$$

The flux  $\Phi$  produced by the dipole  $\mathbf{m}$  is proportional to its magnetization. A SQUID detector can be used to achieve great sensitivity in the measurement of  $\Phi$ . Sensitivity of  $10^{-11}$  A m<sup>2</sup> in  $\mathbf{m}$  is achievable.

### *Vibrating-sample magnetometer (Foner magnetometer)*

This is an ac variant of the extraction method. The sample vibrates with an amplitude of a few hundred microns at about 100 Hz, and an alternating voltage is induced in pickup coils. A reference signal is generated in another pickup coil or with a capacitor, and both signal and reference are fed into a lock-in amplifier. Typical sensitivity is  $10^{-8} \text{ A m}^2$ .



Methods of measuring magnetization or susceptibility. a) Faraday balance, b) extraction magnetometer and c) Vibrating-sample magnetometer

### Data on some ferromagnets

material	$\rho$ (kg/m <sup>3</sup> )	T <sub>C</sub> (K)	$\mu_0 M$ (290 K) (T)	$m_0$ ( $\mu_B$ /formula)	K <sub>1</sub> (kJ/m <sup>3</sup> )
Fe	7874	1044	2.15	2.2	50
Co	8836	1390	1.81	1.7	530
Ni	8902	628	0.62	0.6	-5
Fe <sub>65</sub> Co <sub>35</sub> *	8110	1240	2.34	2.5	40
Ni <sub>80</sub> Fe <sub>20</sub> ‡	8715	843	1.04	1.1	<1
Gd	7886	292	0.8	7.0	
CrO <sub>2</sub>	4870	396	0.50	2.0	20

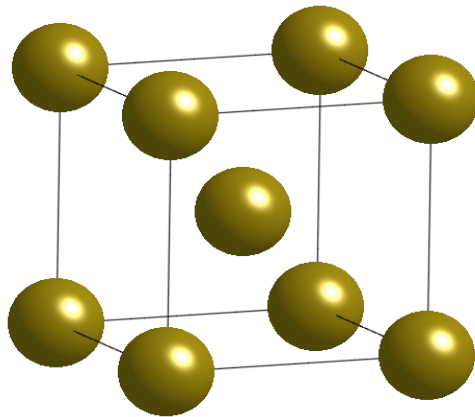
\* permendur ‡ permalloy

## 6.5 Hard and soft ferromagnets

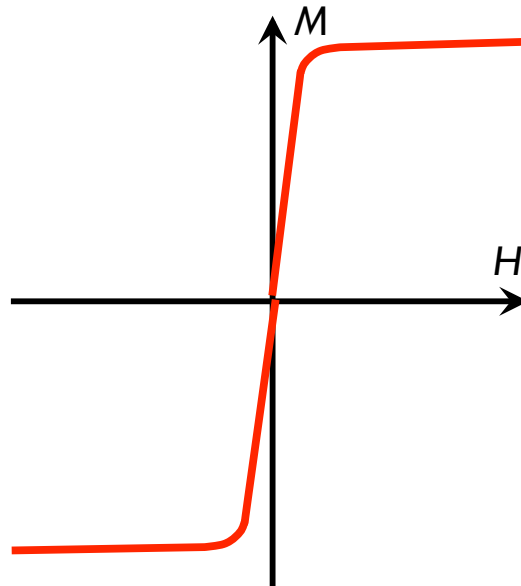
Two categories of useful ferromagnets are distinguished by their hysteresis loops.

*Soft ferromagnets* have narrow loops with as little hysteresis as possible (Energy loss is proportional to the area of the loop). Good examples are bcc iron with 3% Si substitution, and 'permalloy' — fcc  $\text{Fe}_{20}\text{Ni}_{80}$

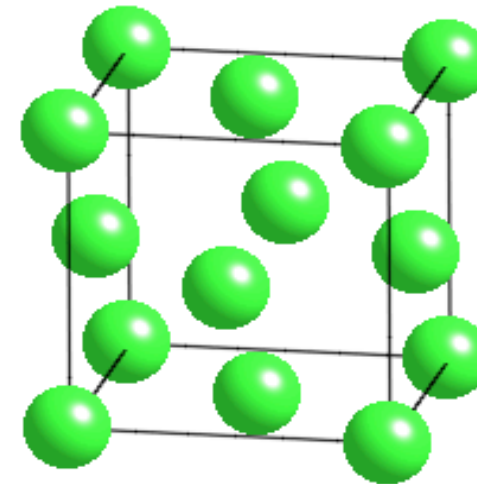
*Iron*



$$\begin{array}{ll} J_s = 2.1 \text{ T} & M_s = 1.73 \text{ MA m}^{-1} \\ K_{lc} \approx 48 \text{ kJ m}^{-3} & \langle 100 \rangle \text{ directions easy} \\ \lambda_s = -7 \cdot 10^{-6} & T_C = 1044 \text{ K} \end{array}$$



*Permalloy*



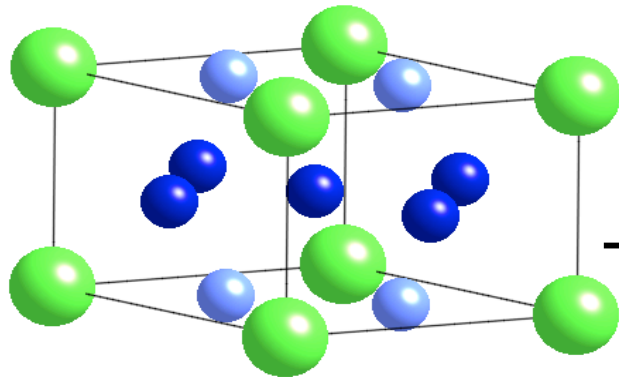
$$\begin{array}{ll} J_s = 1.0 \text{ T} & M_s = 0.8 \text{ MA m}^{-1} \\ K_l \approx 2 \text{ kJ m}^{-3} & \\ \lambda_s = 2 \cdot 10^{-6} & T_C = 843 \text{ K} \end{array}$$

**Hard ferromagnets** have broad square loops with  $H_c > (1/2)M_s$ . They always have a uniaxial crystal structure (hexagonal, tetragonal ...) with one *easy axis* of magnetization.

Once magnetized they remain in their metastable, fully magnetized state creating a stray field around them with no expenditure of energy.

Good examples are  $\text{SmCo}_5$  and  $\text{Nd}_2\text{Fe}_{14}\text{B}$ .

$\text{SmCo}_5$



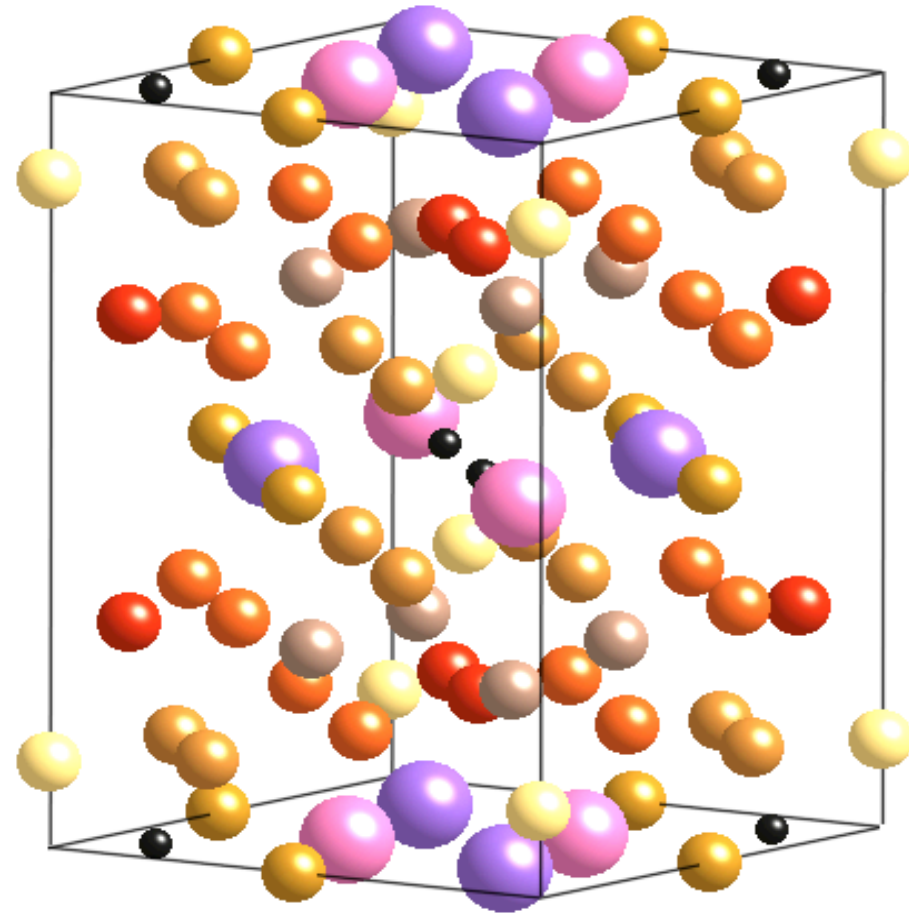
$$J_r = 1.0 \text{ T}; M_s = 0.8 \text{ MA m}^{-1}$$

$$K_1 = 17 \text{ MJ m}^{-3} \text{ (hexagonal)}$$

$$T_C = 1020 \text{ K}$$

$$(BH)_{\max} = 200 \text{ kJ/m}^3$$

$\text{Nd}_2\text{Fe}_{14}\text{B}$

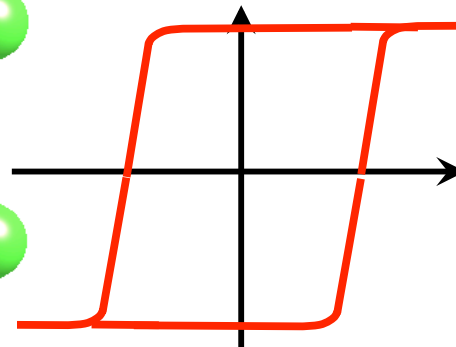


$$J_r = 1.4 \text{ T}; M_s = 1.1 \text{ MA m}^{-1}$$

$$K_1 = 4.9 \text{ MJ m}^{-3} \text{ (tetragonal)}$$

$$T_C = 878 \text{ K}$$

$$(BH)_{\max} \approx 400 \text{ kJ/m}^3$$





## 7. Miscellaneous Topics

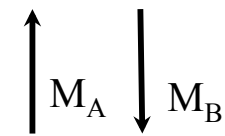
Other types of magnetic order arise from antiferromagnetic exchange interactions, or competing ferromagnetic and antiferromagnetic interactions. The elementary excitations from the magnetic ground state are spin waves (magnons.) which are described by a dispersion relation  $E = D_{\text{sw}} q^2$  in the ferromagnetic case.

A

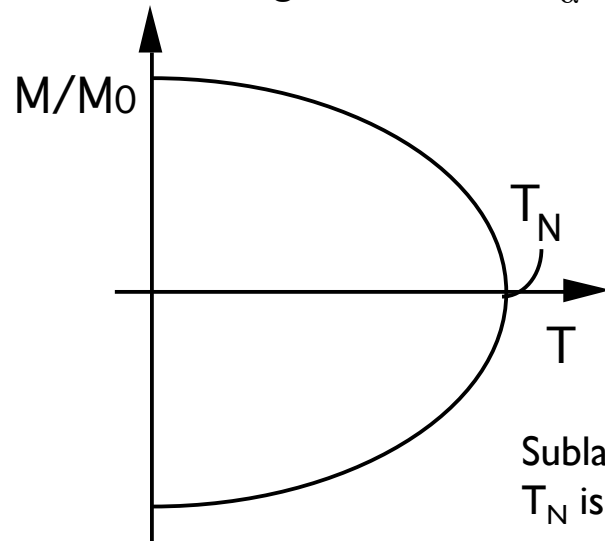
## 7.1 Antiferromagnetism

In many structures, the atoms can be assigned to two equal sublattices A and B. These materials may have two oppositely-directed magnetic sublattices  $M_A$  and  $M_B$ ;  $\mathbf{M}_A = -\mathbf{M}_B$ . Two Weiss coefficients  $n_W$  and  $n'_W$  represent the inter- and intrasublattice interactions. Usually  $n_W$  is negative.

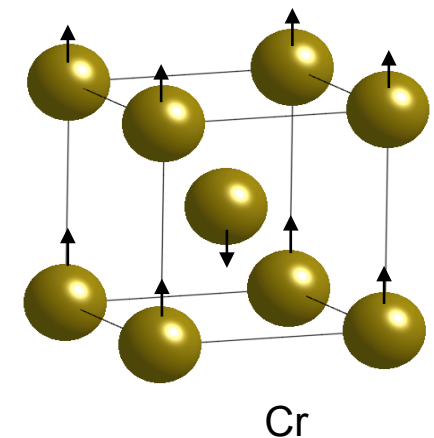
$$\begin{aligned}\mathbf{H}_A^i &= n'_W \mathbf{M}_A + n_W \mathbf{M}_B + \mathbf{H} \\ \mathbf{H}_B^i &= n'_W \mathbf{M}_B + n_W \mathbf{M}_A + \mathbf{H}\end{aligned}$$



The net magnetization  $\mathbf{M} = \mathbf{M}_A + \mathbf{M}_B$  is zero when  $\mathbf{H} = 0$ . The magnetization of each sublattice is represented by a Brillouin function, and each falls to zero at a critical temperature, the Néel temperature  $T_N$ . The sublattice magnetization  $\langle M_\alpha \rangle = M_0 \mathcal{B}_J(x_\alpha)$  where  $\alpha = A, B$  and  $x_\alpha = \mu_0 m H_\alpha / k_B T$ ,



Sublattice magnetization of an antiferromagnet.  
 $T_N$  is the Néel temperature



Above  $T_N$   $M_\alpha = \chi_r H_\alpha$  where  $\chi = C'/T$  with  $C' = \mu_0(N/2)m_{\text{eff}}^2/3k_B$ . Here  $N/2$  is the number of atoms per  $\text{m}^3$  of each sublattice. Hence

$$\begin{aligned} M_A &= (C'/T)(n_W' M_A + n_W M_B + H) \\ M_B &= (C'/T)(n_W M_A + n_W' M_B + H) \end{aligned}$$

The condition for the appearance of spontaneous sublattice magnetization is that these equations have a nonzero solution in zero applied field. The determinant of the coefficients is zero, hence  $[(C/T)n_W' - 1]^2 - [(C/T)n_W]^2 = 0$ , which yields

$$T_N = C' (n_W' - n_W).$$

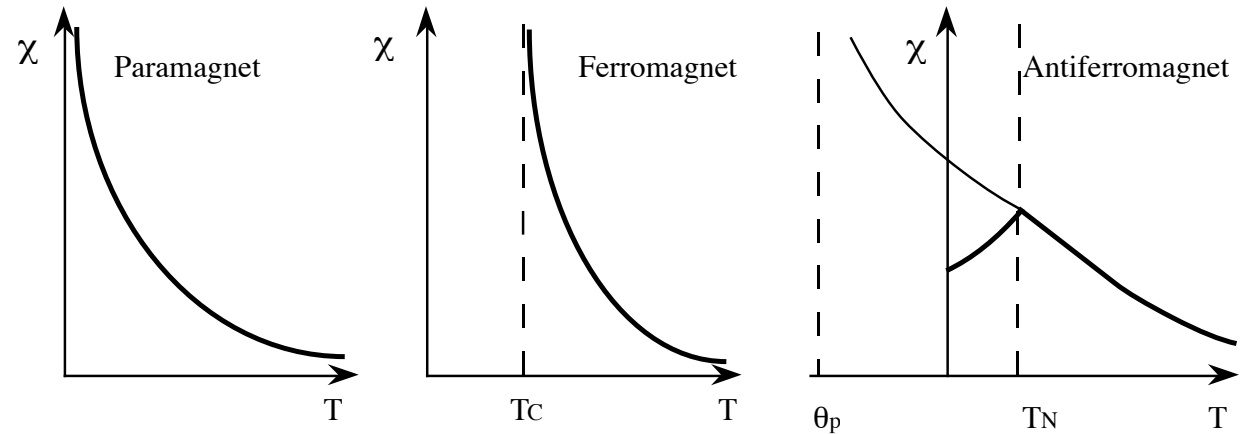
To calculate the susceptibility above  $T_N$  we evaluate  $\chi_r = (M_A + M_B)/H$ . Adding the equations for  $M_A$  and  $M_B$ , we find the Curie-Weiss law

$$\chi_r = C/(T - \theta_p)$$

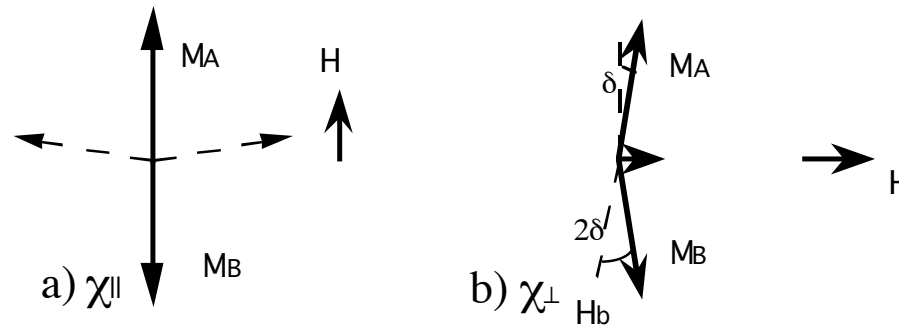
where  $C = 2C'$  and  $\theta_p = C' (n_W' + n_W)$ . In the two-sublattice model, we can therefore evaluate both  $n_W$  and  $n_W'$  from  $T_N$  and  $\theta_p$ . Since  $n_W < 0$ ,  $\theta_p < T_N$ , and it is usually negative. Normally  $1/\chi_r$  is plotted versus  $T$  to determine  $m_{\text{eff}}$  from  $C$ , and  $\theta_p$ .

.

Comparison of the susceptibility of a paramagnet, a ferromagnet and an antiferromagnet.



The antiferromagnetic axis along which the sublattice magnetizations lie is determined by magnetocrystalline anisotropy, and the response below  $T_N$  depends on the direction of  $\mathbf{H}$  relative to this axis.



Calculation of the susceptibility of an antiferromagnet below  $T_N$ . In a) the dashed lines show the configuration after a spin flop.

If a small field is applied parallel to the axis, we can calculate  $\chi_{||}$  by expanding the Brillouin functions about  $x_0$ , their arguments in zero applied field. For simplicity we take  $n_{W'} = 0$ , and the result for  $\chi_{||} = [M_A(H) + M_B(H)]/H$  is

$$\chi_{||} = Nm^2 \mathcal{B}_J'(x_0) / [k_B T + N' n_W m^2 \mathcal{B}_J'(x_0)]$$

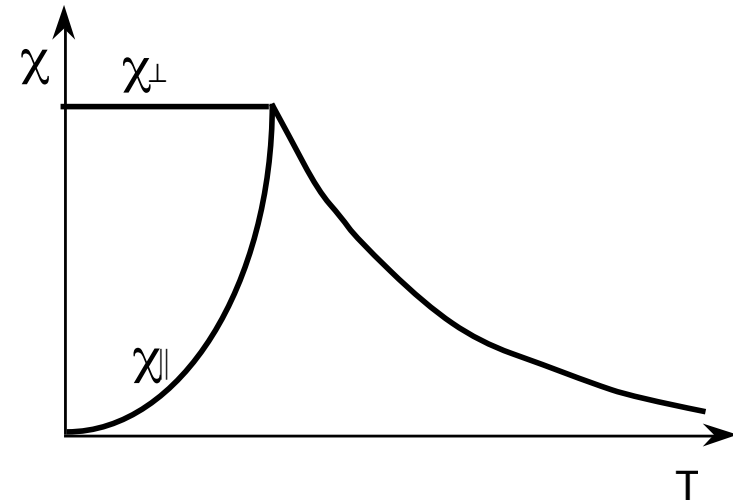
This rises from 0 at  $T = 0$  to  $C/(T - \theta_p)$  at  $T_N$ , where  $\mathcal{B}_J'(0) = (J+1)/3J$ .  $x_0$  is  $\mu_0 m n_W M / k_B T$ , where  $M$  is the sublattice magnetization in zero field.

The perpendicular susceptibility can be calculated assuming the sublattices are canted by a small angle  $\delta$ , as in Fig 7.3. In equilibrium the torque on each one is zero, hence  $M_\alpha H = M_\alpha n_W M_\beta \sin 2\delta$ . Since  $M = 2M_\alpha \sin \delta$ ,

$$\chi_\perp = 1/n_W$$

The perpendicular susceptibility is therefore constant and independent of temperature up to  $T_N$ . For a powder, the average is  $(1/3)\chi_{||} + (2/3)\chi_\perp$ , or  $2/3n_W$  at low temperature.

Parallel and perpendicular susceptibility of an antiferromagnet.



Since  $\chi_\perp > \chi_{||}$  for all  $T < T_N$ , we might expect that an antiferromagnet will always adopt the transverse, flopped configuration. That it doesn't is due to magneto-crystalline anisotropy, represented by an effective anisotropy field  $H_K$ , which acts on each sublattice along the antiferromagnetic axis. When  $H$  is applied parallel to  $M_\alpha$  the spin flop occurs when the energies of the parallel and perpendicular configurations are equal;

$$-2M_a H_K - (1/2)\chi_{||} H_{sf}^2 = - (1/2)\chi_\perp H_{sf}^2$$

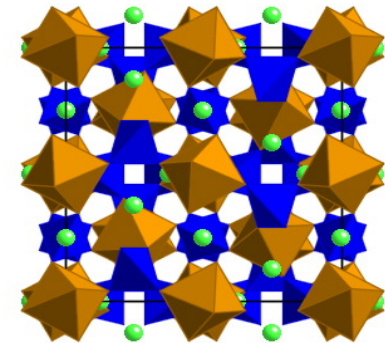
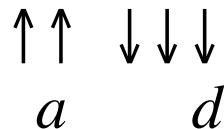
$$H_{sf} = [4M_\alpha H_K / (\chi_\perp - \chi_{||})]^{1/2}$$

When  $T \ll T_N$ , this reduces to  $H_{sf} = 2\sqrt{(H_K H_i)}$ . Orders of magnitude for the anisotropy field and the molecular field are 1 T and 100 T, respectively, hence  $H_{sf}$  is of order 10 T.

## 7.2 Ferrimagnetism.

A ferrimagnet may be regarded as an antiferromagnet with two unequal sublattices.

An example is yttrium-iron garnet (YIG)  $\text{Y}_3\text{Fe}_5\text{O}_{12}$ . The ferric iron in YIG occupies two different crystallographic sites, one ( $16a$ ) octahedrally coordinated by oxygen, the other ( $24d$ ) tetrahedrally coordinated. Neighbouring sites share a common oxygen ligand, and there is a strong antiferromagnetic  $a$ - $d$  interaction. The ferrimagnetic configuration is



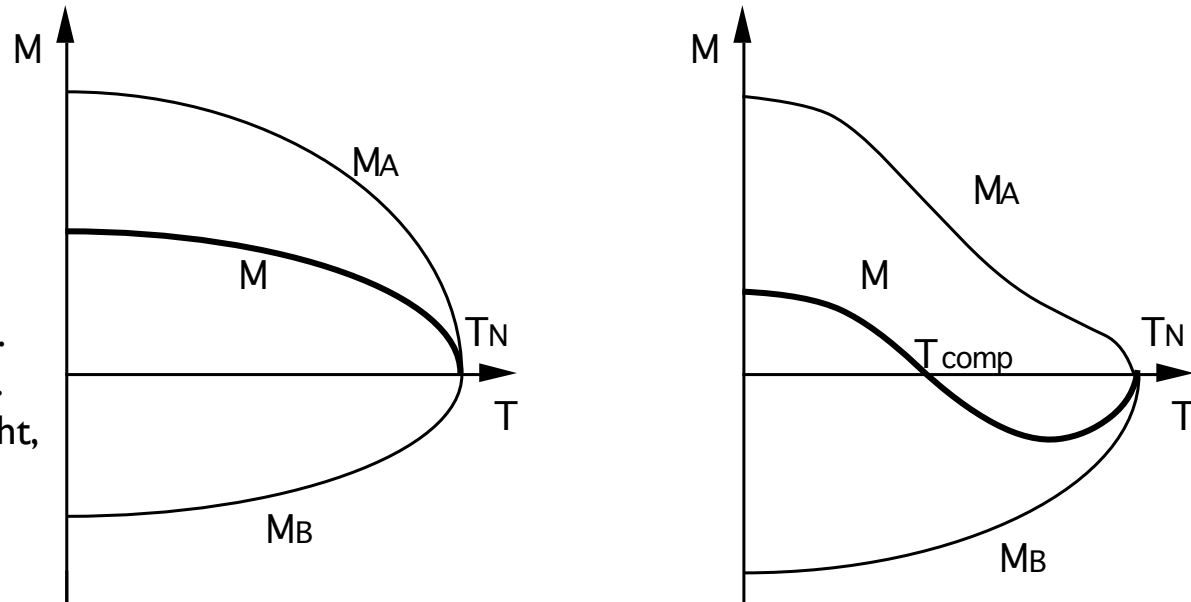
leading to a moment of  $5 \mu_B$ /formula at  $T = 0$ , due to a single uncompensated  $3d^5$  ion per formula unit.

Ferrimagnets have two unequal and oppositely-directed magnetic sublattices  $\mathbf{M}_A$  and  $\mathbf{M}_B$ ;  $|\mathbf{M}_A| \neq |\mathbf{M}_B|$ . The net magnetization  $\mathbf{M} = \mathbf{M}_A + \mathbf{M}_B$  is nonzero. Three Weiss coefficients  $n_{AA}$  and  $n_{BB}$  and  $n_{AB}$  represent the inter- and intrasublattice interactions. The essential interaction  $n_{AB}$  is negative

$$\begin{aligned} \mathbf{H}_A^i &= n_{AA}\mathbf{M}_A + n_{AB}\mathbf{M}_B + \mathbf{H} \\ \mathbf{H}_B^i &= n_{AB}\mathbf{M}_A + n_{BB}\mathbf{M}_B + \mathbf{H} \end{aligned}$$

when  $\mathbf{H} = 0$ . The magnetization of each sublattice is represented by a Brillouin function, and each falls to zero at a critical temperature, the ferrimagnetic Néel temperature  $T_N$ . The sublattice magnetization  $\langle M_\alpha \rangle = M_{\alpha 0} \mathcal{B}_J(x_\alpha)$  where  $\alpha = A, B$  and  $x_\alpha = \mu_0 m_\alpha H_\alpha / k_B T$ ,

Sublattice magnetization of an ferrimagnet.  
 $T_N$  is the ferrimagnetic Néel temperature.  
 On the left,  $|n_{AB}| \gg |n_{AA}|, |n_{BB}|$ ; on the right,  
 $|n_{BB}| \gg |n_{AB}|, |n_{AA}|$ .  $T_{comp}$  is the  
 compensation temperature.



Above  $T_N$ ,  $M_\alpha = \chi_\alpha H_\alpha$  where  $\chi_\alpha = C_\alpha/T$  with  $C_\alpha = \mu_0 N_\alpha m_{eff}^2/3k_B$ . Here  $N_\alpha$  is the number of atoms per  $m^3$  on each sublattice. Hence

$$M_A = (C_A/T)(n_{AA}M_A + n_{AB}M_B + H)$$

$$M_B = (C_B/T)(n_{AB}M_A + n_{BB}M_B + H)$$

The condition for the appearance of spontaneous sublattice magnetization is that these equations have a nonzero solution in zero applied field. The determinant of the coefficients is zero, hence  $[(C_A/T)n_{AA} - 1][(C_B/T)n_{BB} - 1] - (C_A C_B/T^2)n_{AB}^2 = 0$ , which yields

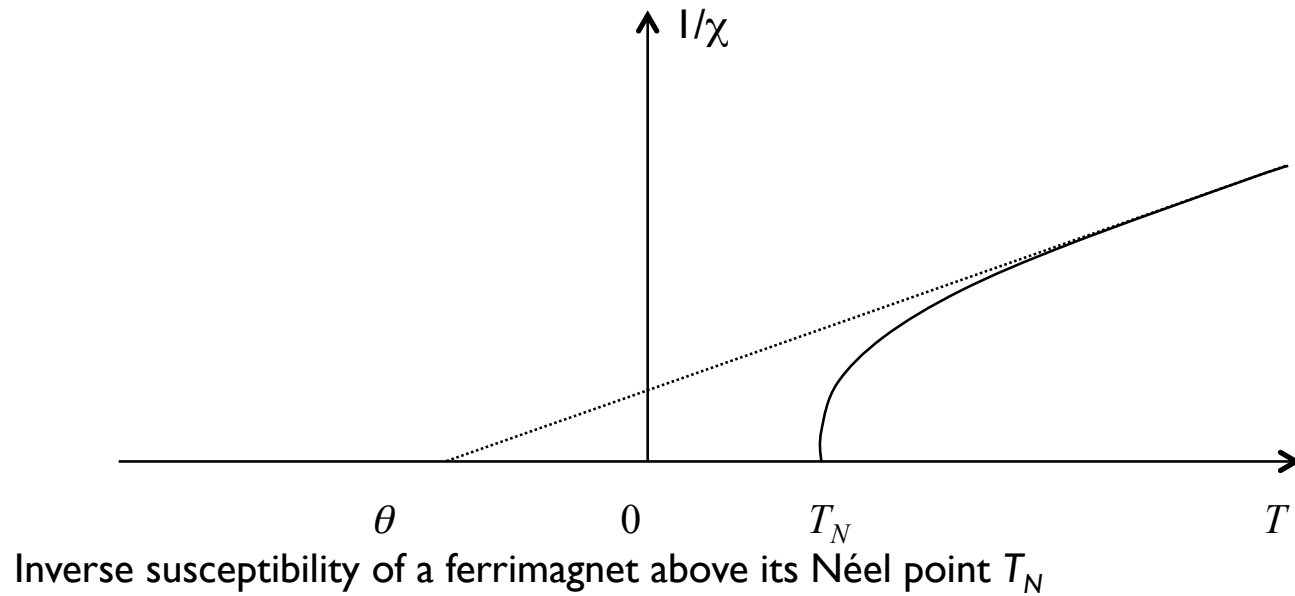
$$T_N = (1/2)[(C_A n_{AA} + C_B n_{BB}) - \sqrt{(C_A n_{AA} - C_B n_{BB})^2 + 4C_A C_B n_{AB}^2}]$$

The expression for the susceptibility above  $T_N$  is obtained,

$$1/\chi = (T - \theta)/(C_A + C_B) - C'/(T - \theta')$$

where  $C' = C_A C_B n_{AB}^2 / (C_A + C_B)[C_A(1 + n_{AA}) - C_B(1 + n_{BB})]^2$ ,  $\theta = C_A C_B n_{AB} / (C_A + C_B)[n_{AA} C_A / C_B - n_{BB} C_B / C_A - 2]$   
 and  $\theta' = C_A C_B n_{AB} / (C_A + C_B)[n_{AA} + n_{BB} + 2]$

This is the equation of an hyperbola.



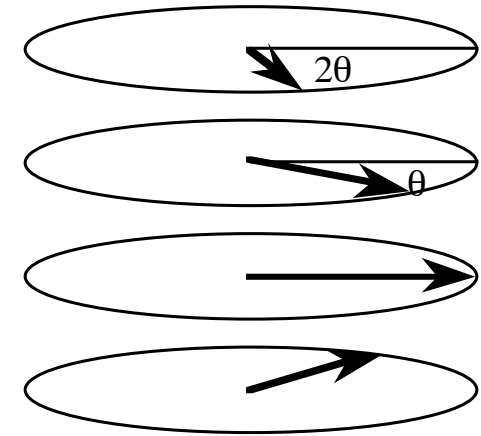
Give expressions for  $T_N$  and  $\chi$  when  $n_{AA} = n_{BB} = 0$ .



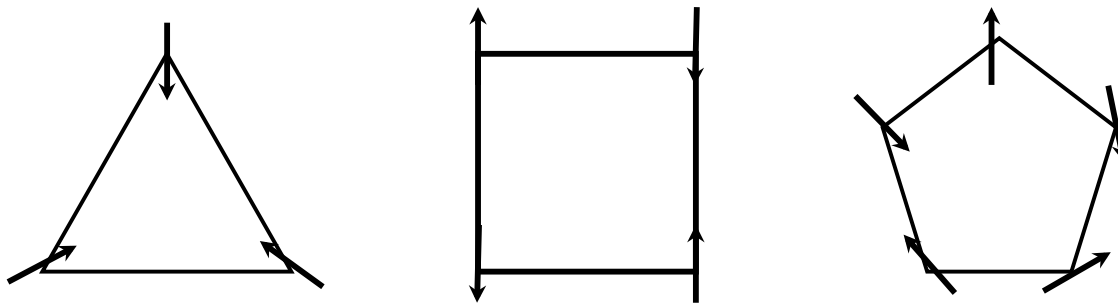
## 7.3 Other forms of magnetic order

Various other forms of magnetic order can arise in solids. When ferromagnetic and antiferromagnetic interactions compete, and cannot all be satisfied simultaneously, the system is said to be *frustrated*. A noncollinear spin structure may then arise, such as a helimagnetic structure where there are ferromagnetic planes, but the ferromagnetic axis turns by an angle  $\theta$  from one plane to the next.

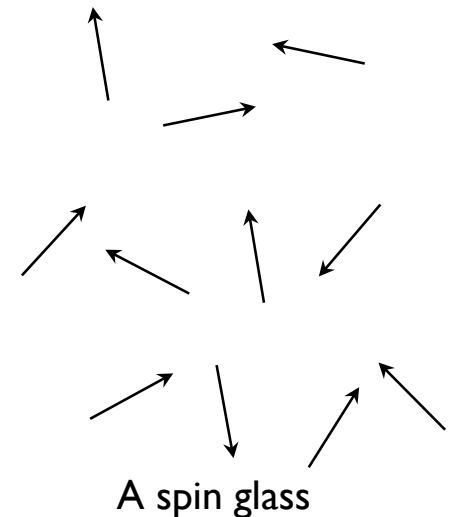
A helimagnet



Frustration may also arise with purely antiferromagnetic interactions, when there are odd-membered rings. Some examples are shown below.



In disordered and amorphous solids, frustrated antiferromagnetic interactions, or competing ferromagnetic and antiferromagnetic interactions may give rise to spin freezing in random directions. Such materials are known as *spin glasses*.



A spin glass

## 7.4 Spin waves (magnons).

The exchange energy in the ferromagnetic ground state is  $-2ZJS^2$  per site. Elementary excitations from the ferromagnetic ground state are spin waves, illustrated below. These extended spin deviations are also known as *magnons* by analogy with phonons, the quantized lattice waves. A single localized spin reversal  $\uparrow\uparrow\uparrow\uparrow\downarrow\uparrow\uparrow\uparrow$  costs  $8JS^2$  ( $2J$ ) for  $S = 1/2$ , which is greater than  $k_B T_C$  for a chain.  $T_C = 2ZS(S+1)/3$  (for  $J = S = 1/2$ ,  $Z = 2$ ). Such expensive excitations cannot occur at low temperature; instead the atoms all share the reversal, with periodic oscillation of spin orientation.

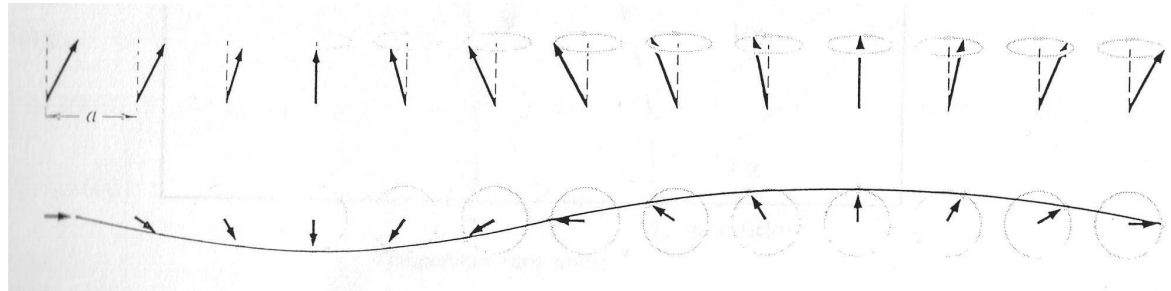


Illustration of a spin wave.

In one dimension, the relation between the frequency and wave-vector of a wave-like excitation of the spin system can be calculated classically

$$\hbar\omega_q = 4JS(1 - \cos qa)$$

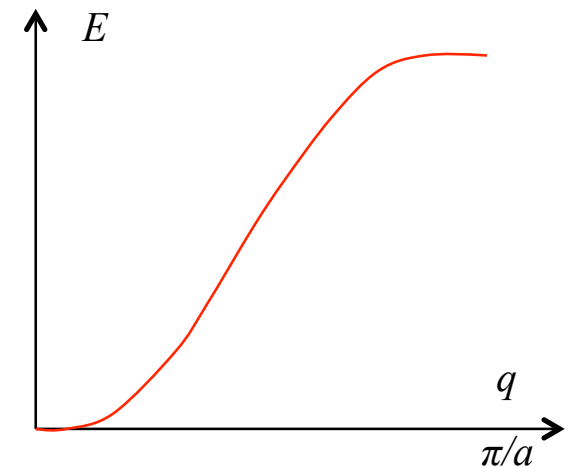
In the limit of small wave vectors, the dispersion relation becomes

$$E_q \approx D_{sw} q^2$$

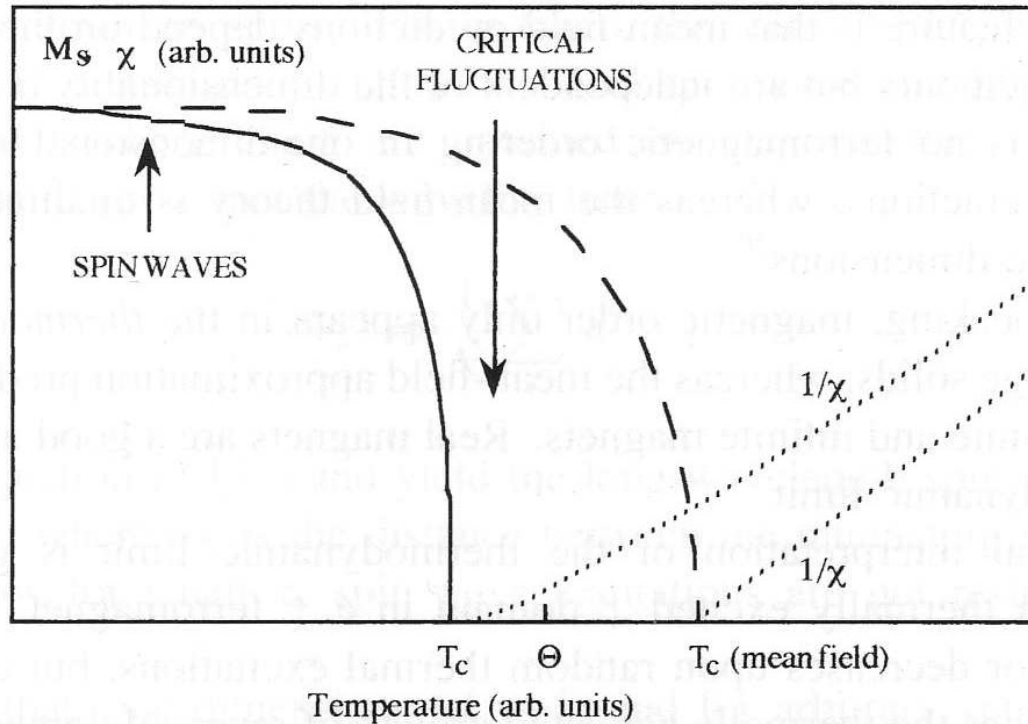
where  $E_q = \hbar\omega_q$ ,  $D_{sw} = 2JSa^2$ ;  $a$  is the interatomic spacing.

The expression in any of the three basic cubic lattices is the same, where  $a$  is the lattice parameter.

The spin-wave dispersion relation for a chain of atoms.



Excitation of spin waves is responsible for the fall of magnetization with increasing  $T$  which is much faster than expected from molecular-field theory, given  $J$ . They also contribute to resistivity and specific heat, giving a  $T^{3/2}$  variation of specific heat at low temperature.

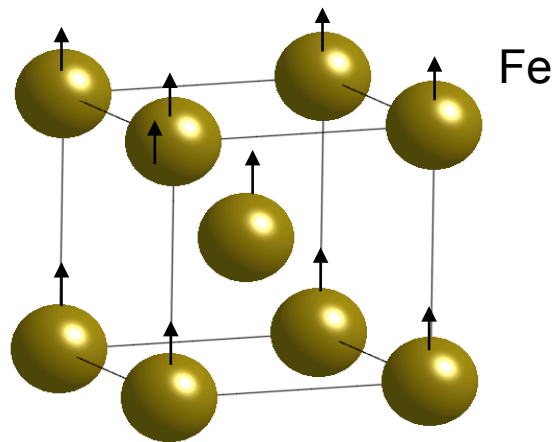


Spontaneous magnetization of a ferromagnet, compared with mean-field theory.

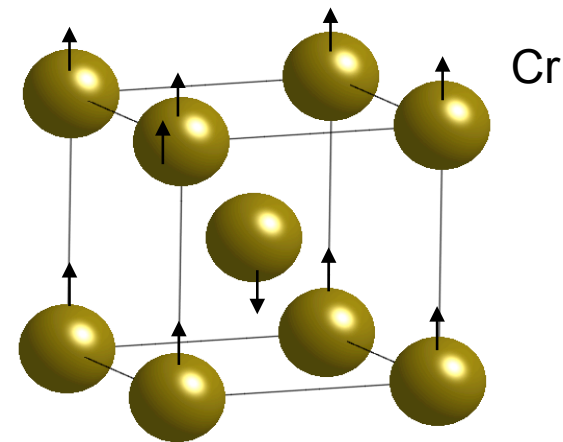
## 7.5 Magnetic neutron scattering

*Elastic (Bragg) scattering* The neutron possesses a small magnetic moment. In addition to nuclear scattering by the nuclear potential, it is also scattered by the unpaired electron spins in a solid. Extra Bragg peaks of magnetic origin may appear, from which the magnetic structure can be inferred. If the neutron, with incident wavevector  $\mathbf{K}$  is scattered into a state  $\mathbf{K}'$ , the Bragg condition is that the scattering vector  $\mathbf{\kappa} = \mathbf{K} - \mathbf{K}'$  should be a reciprocal lattice vector  $\mathbf{G}_{hkl}$ .

For example, magnetic Bragg scattering can be used to detect antiferromagnetic order



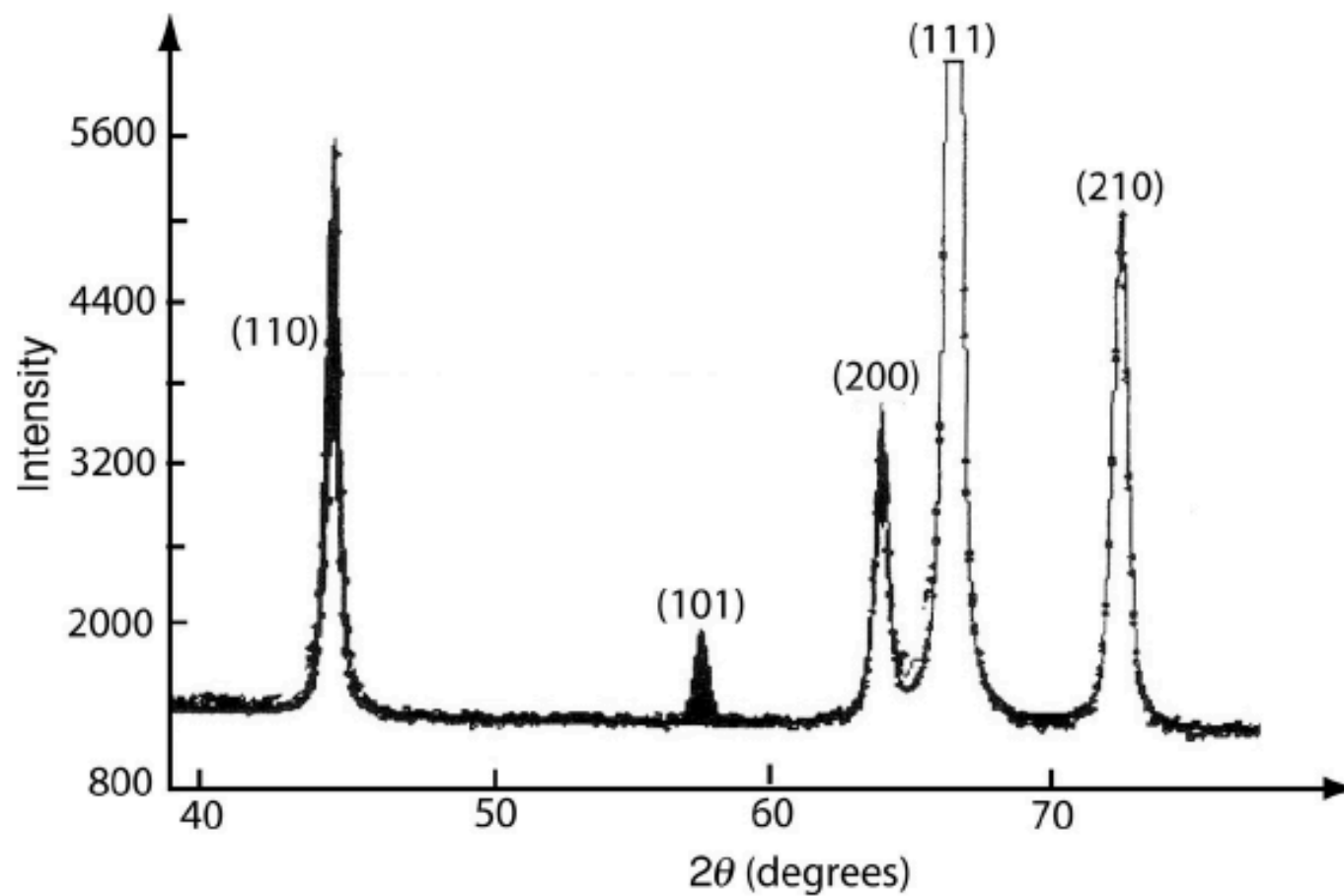
For iron, the magnetic Bragg reflections coincide with the nuclear reflection. The unit cell is body-centred, so there are no extra peak. The structure factor is zero when  $h + k + l$  is odd.



For chromium, the magnetic unit cell is simple cubic (not body centred). There are extra peaks with  $h + k + l$  odd which are entirely magnetic, and the antiferromagnetically-ordered Cr moment can be deduced from their intensity

**Figure 10.8**

Neutron powder diffraction pattern of  $\text{CrO}_2$ . Magnetic reflections are shaded.



### Inelastic scattering:

Inelastic neutron scattering, where the incident neutron loses (gains) energy by exciting an elementary excitation of energy  $E = \hbar\omega_q$  and wavevector  $\mathbf{q}$ , can be used to map spin wave dispersion relations.

For Fe,  $E = D_{sw}q^2$ , where  $D_{sw} = 8 \text{ Jm}^{-2}$ .

The energy in a mode of frequency  $\omega_q$  containing  $n_q$  magnons is  $(n_q + 1/2)\hbar\omega_q$

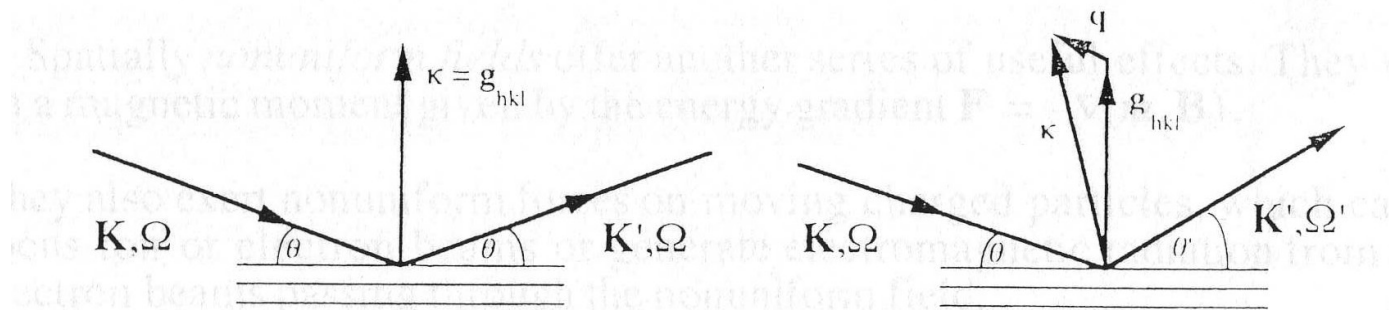


Illustration of elastic scattering,  $|\mathbf{K}| = |\mathbf{K}'|$  (left) and inelastic scattering.  $\mathbf{K} = \mathbf{K}' + \mathbf{q} + \mathbf{g}_{hkl}$  (right)

### Data on some antiferromagnets.

Material	$T_N$ (K)	$\theta$ (K)
Mn	96	-200
CoO	291	-330
NiO	525	-1300
MnF <sub>2</sub>	85	-113
$\alpha$ Fe <sub>2</sub> O <sub>3</sub>	950	-2000

### Data on some ferrimagnets.

Material	$T_C$ (K)	$m_0$ ( $\mu_B/\text{formula}$ )	$\mu_0 M$ at 290 K (T)
Fe <sub>3</sub> O <sub>4</sub>	840	4.0	0.63
$\gamma$ Fe <sub>2</sub> O <sub>3</sub>	1020	3.3	0.54
Y <sub>3</sub> Fe <sub>5</sub> O <sub>12</sub>	560	5.0	0.18
BaFe <sub>12</sub> O <sub>19</sub>	742	20.0	0.48

## Nickel Oxide; NiO

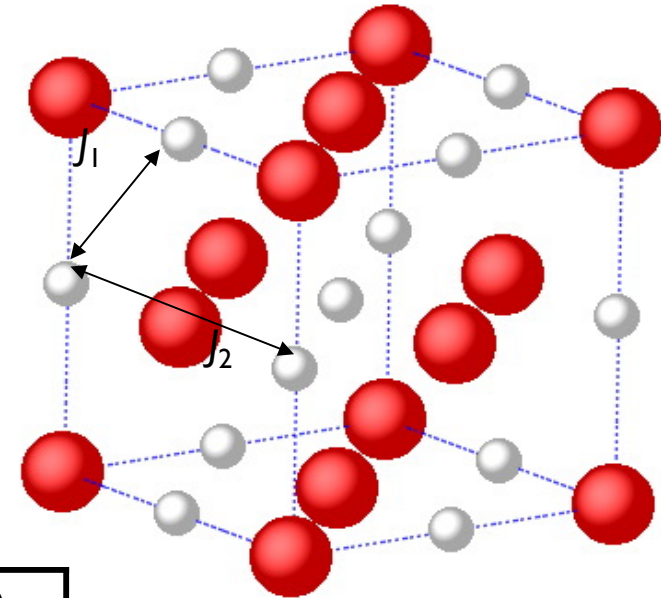
NaCl;  $a_0 = 418$  pm

A green Mott insulator.

$\text{Ni}^{2+}$  is in a  $^3F$  term.  $m_0 = 2.0 \mu_B/\text{atom}$

Antiferromagnetic  $T_N = 525$  K

Was used as an exchange bias layer in spin valves.



		$a_0$ (pm)	S	$T_N$ (K)	$\theta_p$ (K)	$J_1$ (K)	$J_2$ (K)
MnO	$3d^5$	445	5/2	117	-610	-7.2	-3.5
FeO	$3d^6$	431	2	198	-570	-7.8	-8.2
CoO	$3d^7$	426	3/2	291	-330	-6.9	-21.5
NiO	$3d^8$	418	1	525	-1310	-50	-85



## Hematite; $\text{Fe}_2\text{O}_3$

corundum;  $a = 504 \text{ pm}$ ,  $c = 1375 \text{ pm}$

Most common iron oxide mineral.

hcp oxygen array with  $\text{Fe}^{3+}$  in 2/3 of octahedral interstices..

Red insulator with localized  $d$  electrons.  
 $3d^5$   ${}^6A_1$  state.

Antiferromagnetic, but sublattices are slightly canted above the Morin transition by D-M interaction

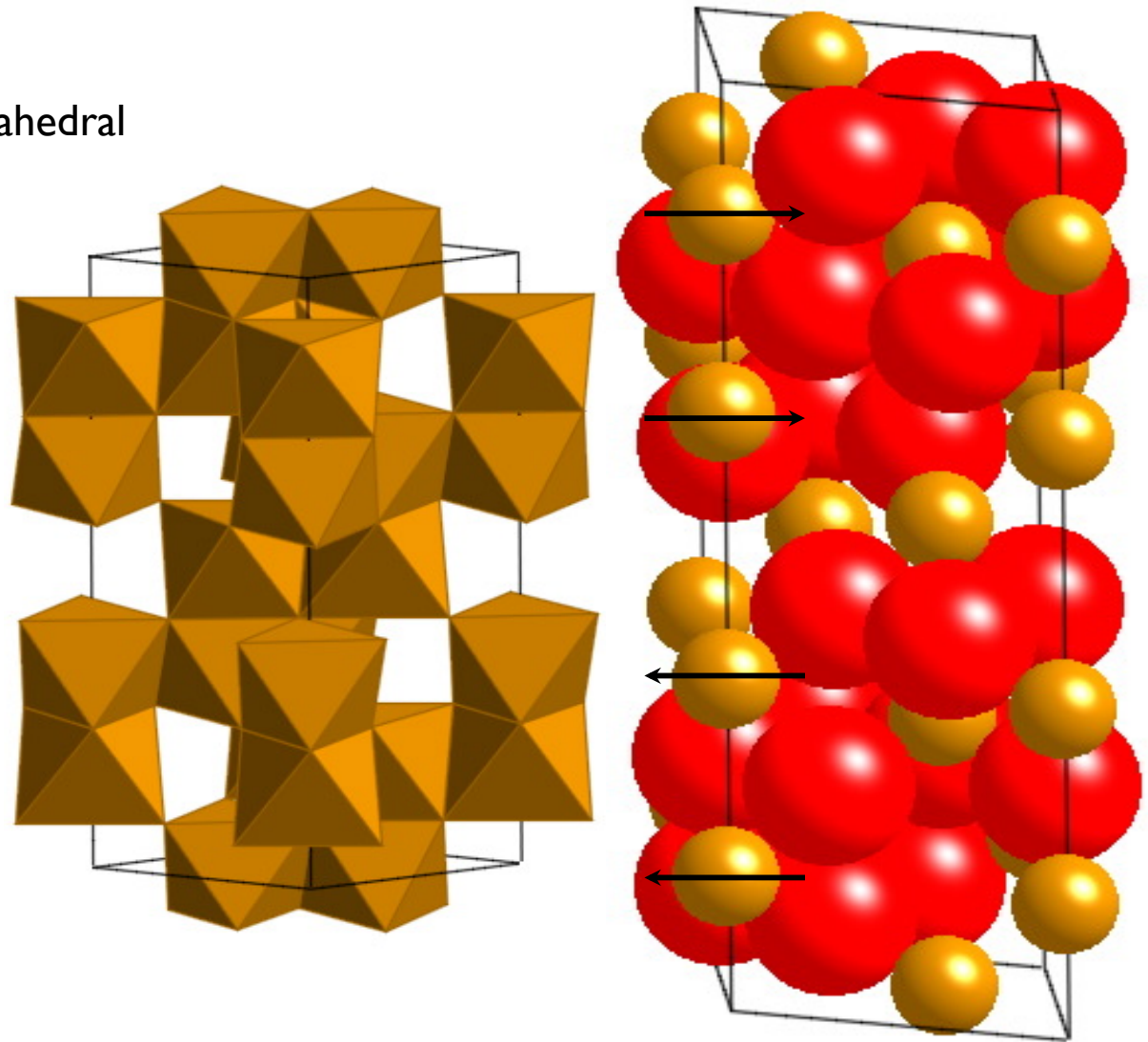
$$T_N = 960 \text{ K.}$$

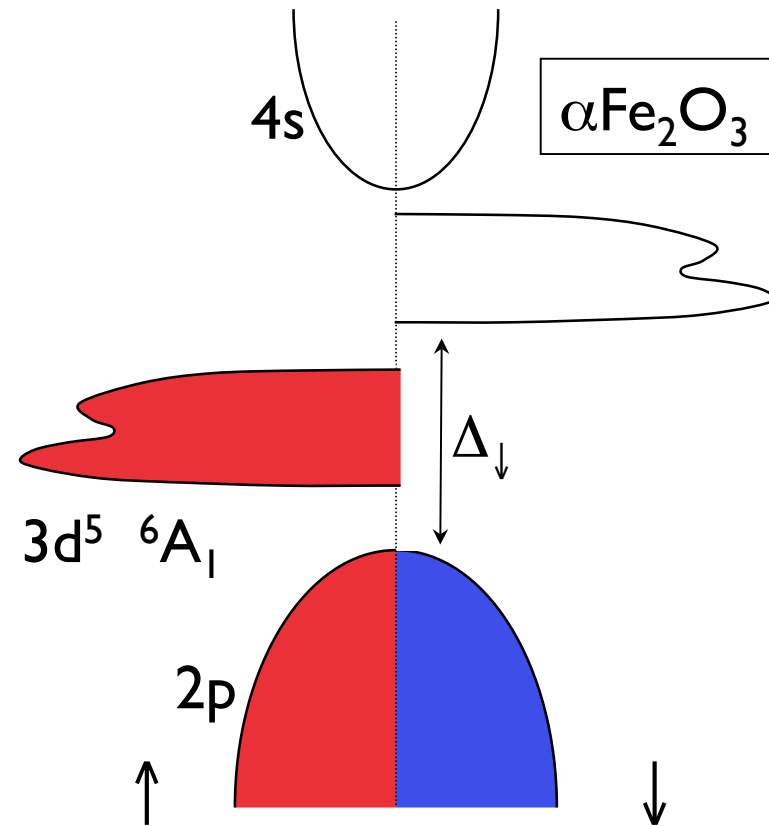
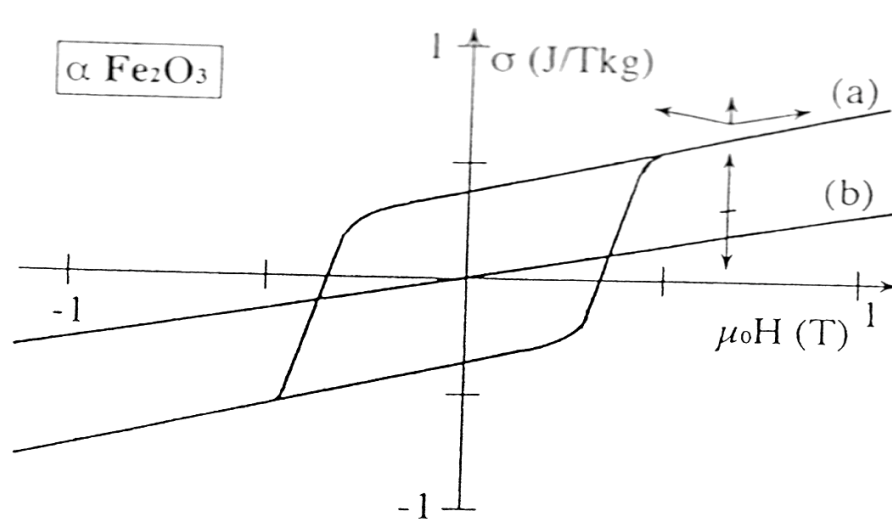
$$J_1 = 6.0 \text{ K}, J_2 = 1.6 \text{ K}$$

$$J_3 = -29.7 \text{ K}, J_4 = -23.2 \text{ K.}$$

$$J_s = 2.8 \cdot 10^{-3} \text{ T} \quad m_0 = 0.002 \mu_B / \text{fu}$$

$$K_1 = 23 \text{ kJ m}^{-3} \quad B_a = 2\mu_0 K_1 / J_s = 20 \text{ T}$$





At room temperature there is a weak ferromagnetic moment caused by canting of the sublattice magnetizations by the Dzialoshinski-Moria (D-M) interaction  $\mathcal{H}_{\text{DM}} = \mathcal{D} \cdot \mathbf{s}_i \times \mathbf{s}_j$ .



Below 260 K there is a spin reorientation to the c-axis.  $\mathcal{D}$  is then zero by symmetry, and the weak interaction disappears.

What causes the spin reorientation ?

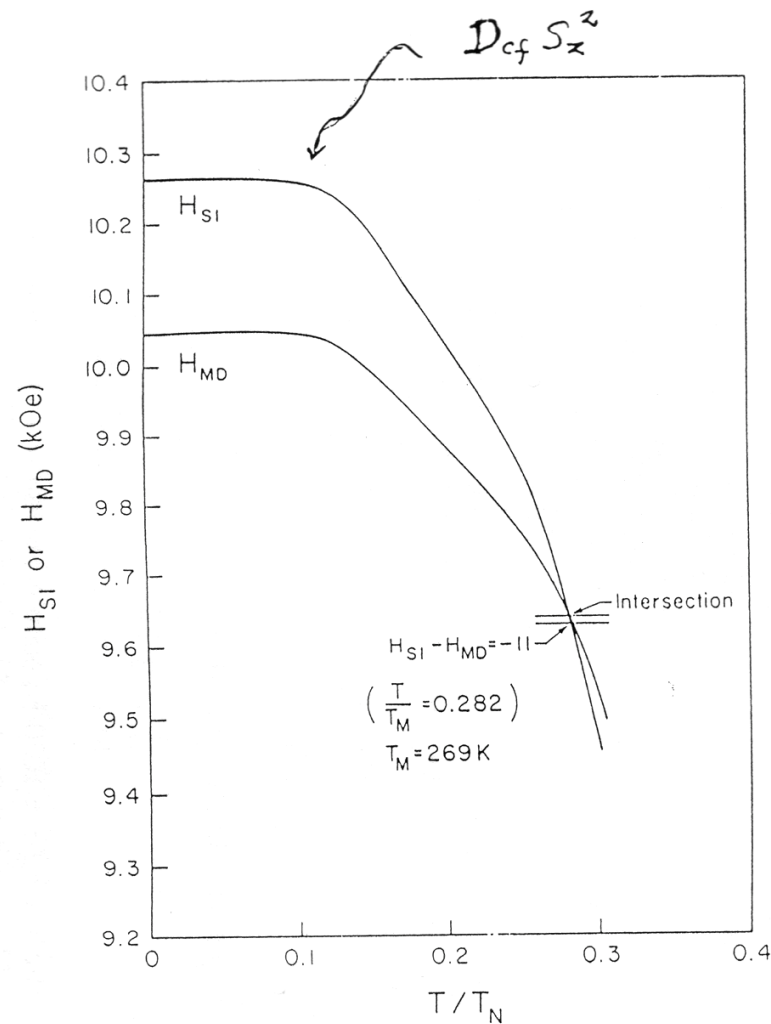


Figure 4.6: The temperature dependence of single-ion and magnetic-dipole fields to illustrate the prediction of the Morin temperature.

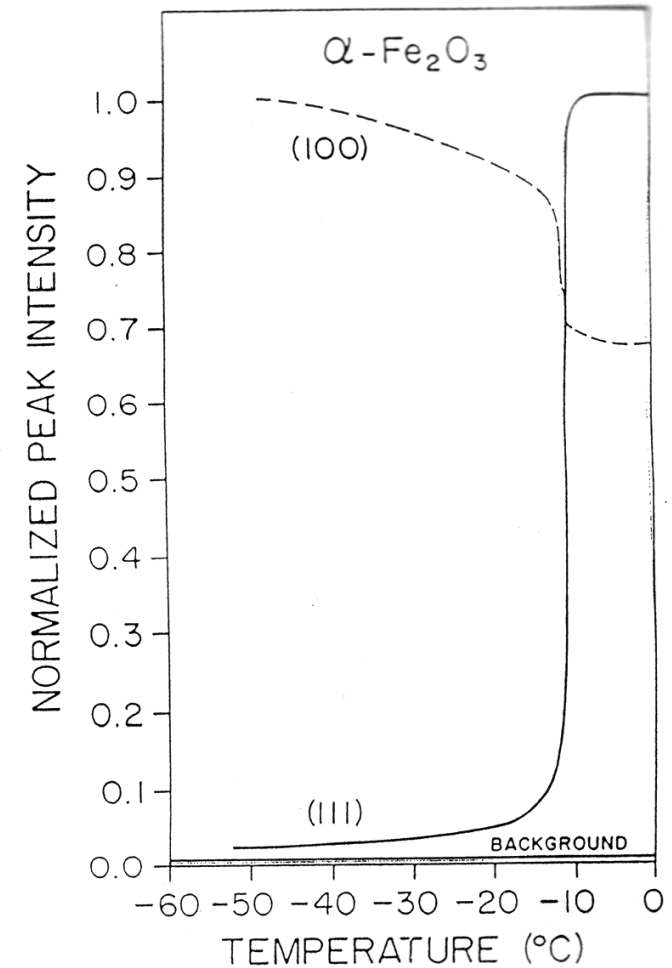


Figure 2.8: Neutron-diffraction intensities of the (111) and (100) lines as a function of temperature. The background intensity is also shown.

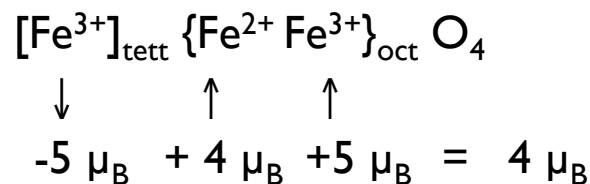
The spin direction is set by competing cf and dipole dipole interactions, which vary as  $\langle S_z^2 \rangle$  and  $\langle S_z \rangle^2$  respectively.  $B_{\text{dip}} = \mu_0/4\pi[3(\mathbf{m} \cdot \mathbf{r})\mathbf{r}/r^5 - \mathbf{m}/r^3]$

# Magnetite, $\text{Fe}_3\text{O}_4$

spinel;  $a_0 = 839 \text{ pm}$

Most common magnetic mineral, source of rock magnetism, main constituent of lodestones..

A ferrimagnet. with  $\text{Fe}^{2+}$  and  $\text{Fe}^{3+}$  disordered on B -sites above the Verwey transition at  $T_v = 120 \text{ K}$ , ordered below; A-B superexchange is the main magnetic interaction



A half-metal.  $\text{Fe(B)}$ ;  $\downarrow$  electrons hop in a  $t_{2g}$  band

Used as toner, and in ferrofluids.

Potential for spin electronics..

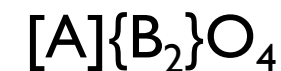
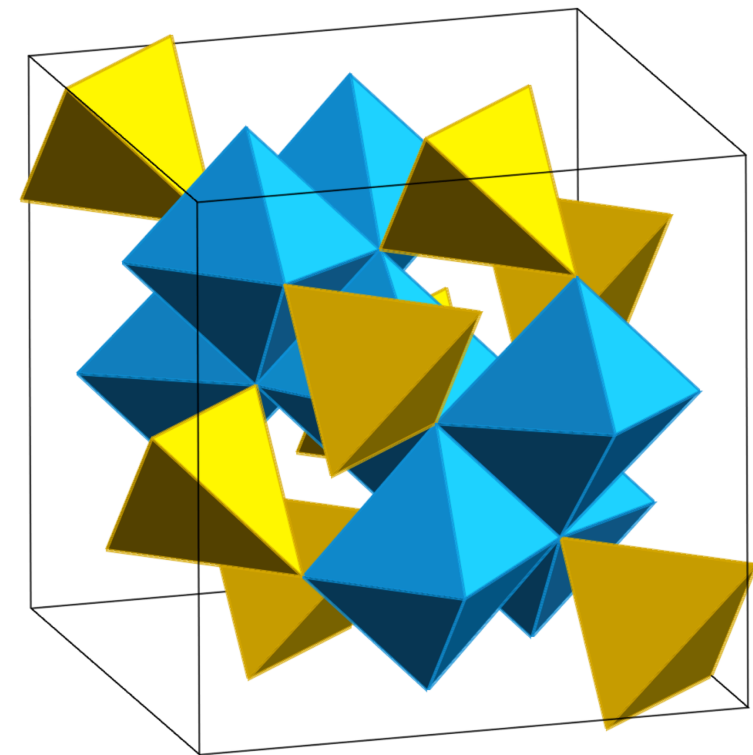
$$J_s = 0.60 \text{ T}$$

$$K_1 = -13 \text{ kJ m}^{-3}$$

$$T_C = 843 \text{ K}$$

$$m_0 = 4.0 \mu_B / \text{fu}$$

$$\lambda_s = 40 \cdot 10^{-6}$$

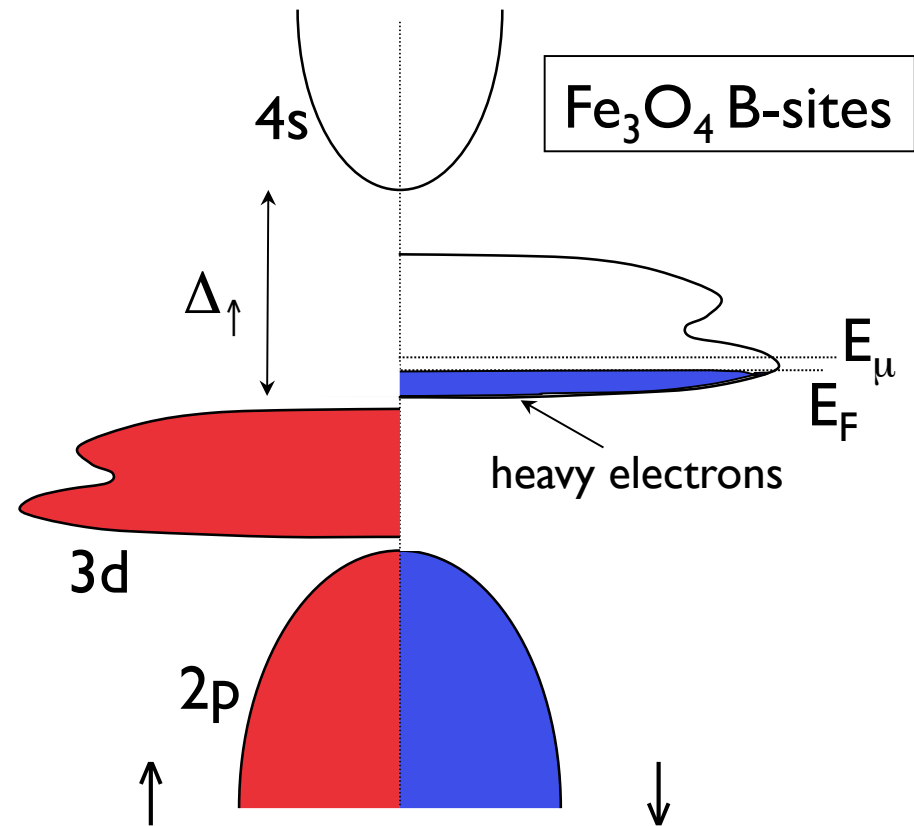


The B sites are populated by a mixture of  $\text{Fe}^{3+}(3d^5)$  and  $\text{Fe}^{2+}(3d^6)$  ions. At RT the  $t_{2g}\downarrow$  electrons hop in a narrow polaron band. Resistivity is  $\approx 50 \mu\Omega \text{ m}$ .

At the Verwey transition  $T_V = 119 \text{ K}$ , the interatomic Coulomb interactions lead to charge ordering – ‘Wigner crystallization’ Resistivity increases by 100x. Symmetry is reduced to monoclinic; details of charge order are still controversial

$$J_{AB} = -28 \text{ K} \quad J_{AA} = -18 \text{ K} \quad J_{BB} = +3 \text{ K}$$

Magnetite is the prototype for a family of spinel ferrites, which includes Ni-Zn ferrite for rf applications and  $\gamma\text{Fe}_2\text{O}_3$   $[\text{Fe}]\{\text{Fe}_{5/3}\text{V}_{1/3}\}\text{O}_4$  that was used for particulate magnetic recording.



## Room-temperature magnetic properties of oxide spinel ferrites

	<sup>a</sup>	$a_0$ (pm)	$T_C$ (K)	$M_s$ (MA/m)	$K_1$ (kJ/m <sup>3</sup> )	$\lambda_s$ (10 <sup>-6</sup> )	$\varrho$ ( $\Omega$ m)
MgFe <sub>2</sub> O <sub>4</sub>	I	836	713	0.18	-3	-6	10 <sup>5</sup>
Li <sub>0.5</sub> Fe <sub>2.5</sub> O <sub>4</sub>		829	943	0.33	-8	-8	1
MnFe <sub>2</sub> O <sub>4</sub>	I	852	575	0.50	-3	-5	10 <sup>5</sup>
Fe <sub>3</sub> O <sub>4</sub>	I	840	860	0.48	-13	40	10 <sup>-1</sup>
CoFe <sub>2</sub> O <sub>4</sub>	I	839	790	0.45	290	-110	10 <sup>5</sup>
NiFe <sub>2</sub> O <sub>4</sub>	I	834	865	0.33	-7	-25	10 <sup>2</sup>
ZnFe <sub>2</sub> O <sub>4</sub>	N	844	$T_N = 9$				1
$\gamma$ -Fe <sub>2</sub> O <sub>3</sub>		834	985 <sup>b</sup>	0.43	-5	-5	$\sim 1$

## $\text{SrFe}_{12}\text{O}_{19}$ - Hexagonal ferrite; also $\text{BaFe}_{12}\text{O}_{19}$

hexagonal;  $a = 589 \text{ pm}$ ,  $c = 2319 \text{ pm}$

A brown ferrimagnetic oxide, with an hcp lattice composed of oxygen and strontium (or barium), with iron in five different interstitial sites, three octahedral  $12k, 2a, 4f_2$  one tetrahedral  $4f_1$ , one trigonal  $2b$ . All magnetic ions are  $\text{Fe}^{3+}$ .

Structure is  $12k \uparrow 2a \uparrow 2b \uparrow 4f_1 \downarrow 4f_2 \downarrow$

Low-cost permanent magnet, the first to break the 'shape barrier'.

95 % by mass of all permanent magnets are hexagonal ferrite. Found on every fridge door and in innumerable catches, dc motors, microwave magnetrons, ...

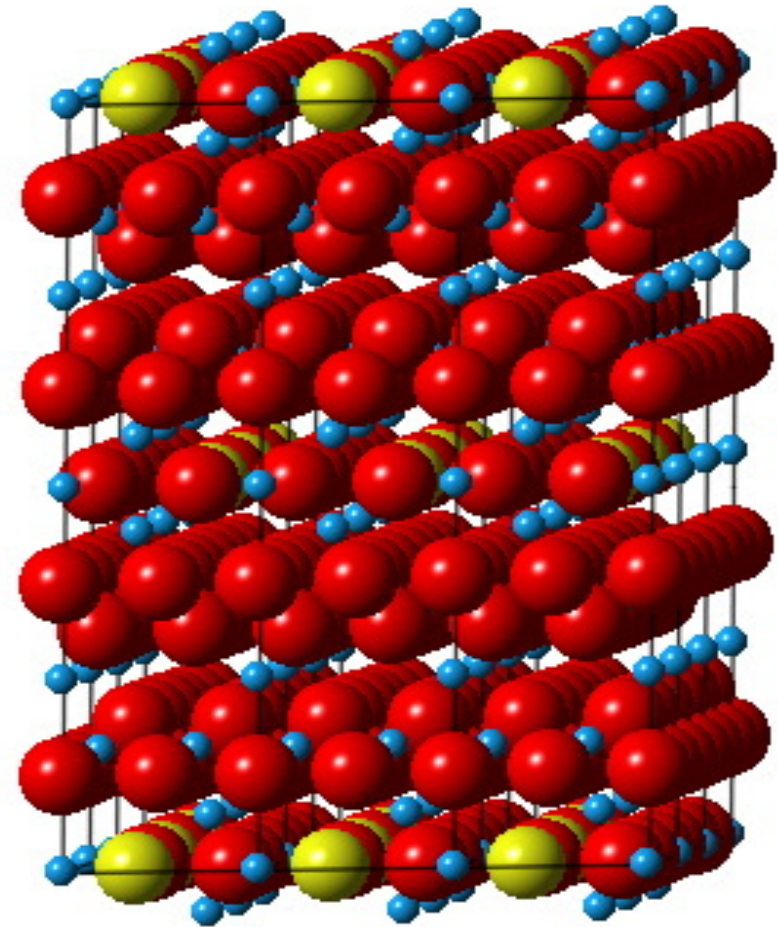
**150 g manufactured per year for everyone on earth**, mostly sintered magnets but some plastic bonded magnets.

$$J_r = 0.41 \text{ T}, \quad M_r = 0.33 \text{ MA m}^{-1}$$

$$K_1 = 330 \text{ kJ m}^{-3} \text{ (hexagonal)}$$

$$B_a = 1.7 \text{ T}$$

$$T_C = 467 \text{ }^\circ\text{C}.$$





## Ferrite magnets

	$J_r$ (T)	$(BH)_{\max}$ (kJ/m <sup>3</sup> )
Intrinsic (crystal)	0.48	[46]
Oriented sintered	0.41	34
Isotropic sintered	0.23	9
Oriented bonded	0.30	16
Isotropic bonded	0.13	5



Sintered magnets

Ferrite magnets are made from powder platelets, with a particle size of about 2  $\mu\text{m}$ .

The powder may be sintered or bonded in plastic or rubber, with or without prior orientation of the hexagonal crystallites.



Bonded magnets



## **8. Magnetic applications**

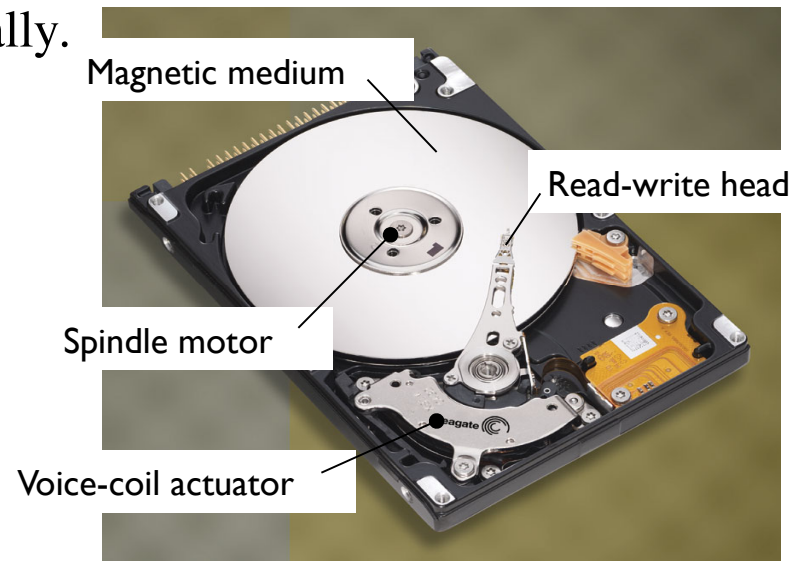
Magnets play a pivotal role in our civilization. Soft magnets are essential for electrical energy generation and conversion. Hard magnets generate magnetic fields with no continuous expenditure of energy. Magnetic recording and data storage have been the key to the information revolution.

## Magnetic applications

Magnets are classified as hard or soft according to their hysteresis. Soft magnets are used to generate electricity, and convert electrical energy into mechanical energy in motors and actuators. Hard magnets can generate magnetic fields with no continuous expenditure of energy, and are used to exert forces in static applications and in permanent magnet machines. Semi-hard material is used as the erasable recording medium on tapes and hard disc discs. Data is written using micron-scale electromagnets and read using tiny spin-valve sensors which respond to the stray field a few nanometers above the surface of the disc. All information downloaded from the internet is stored magnetically.

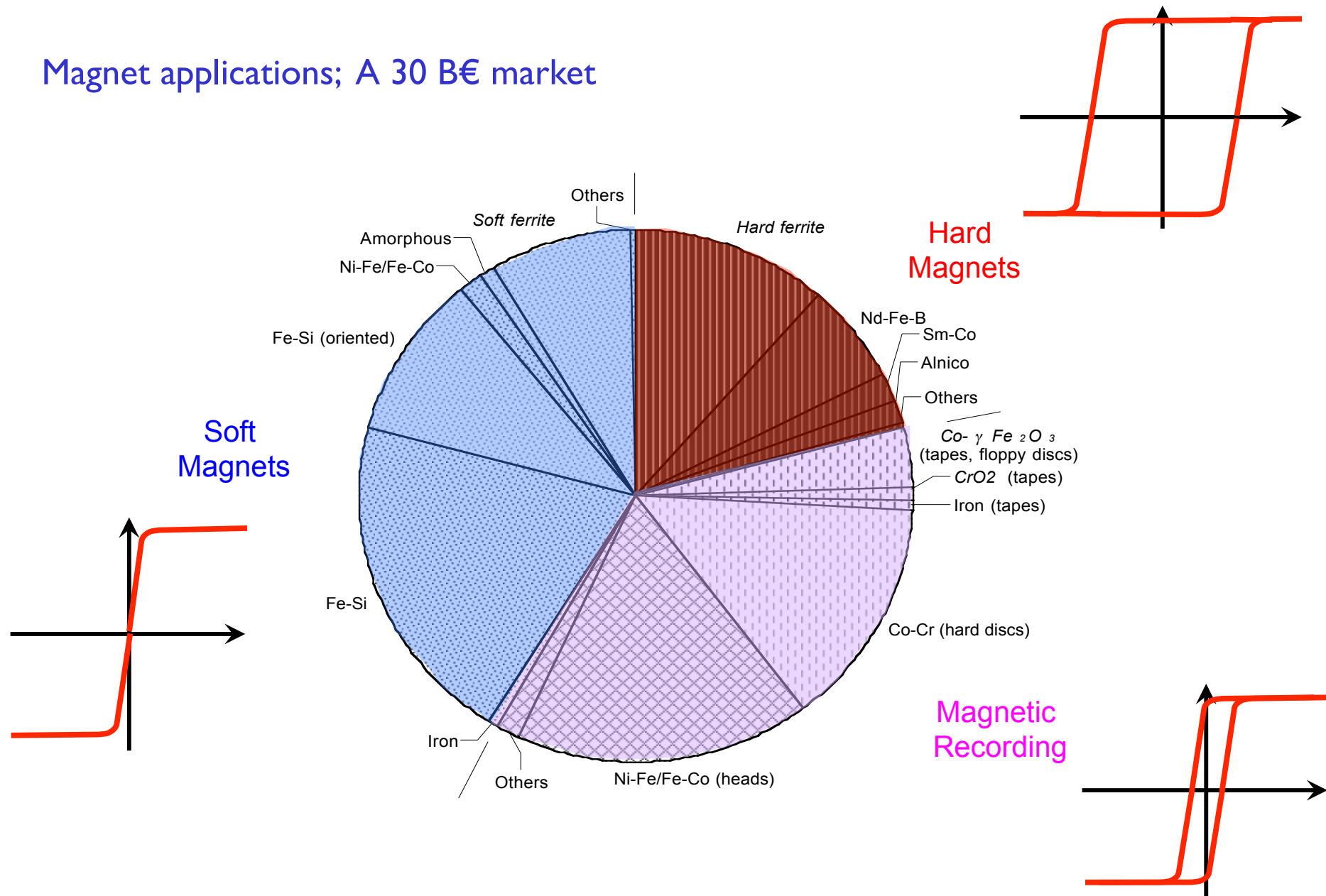


A server with thousands of hard disc drives



160 Gbit 2.5" perpendicular drive for laptops

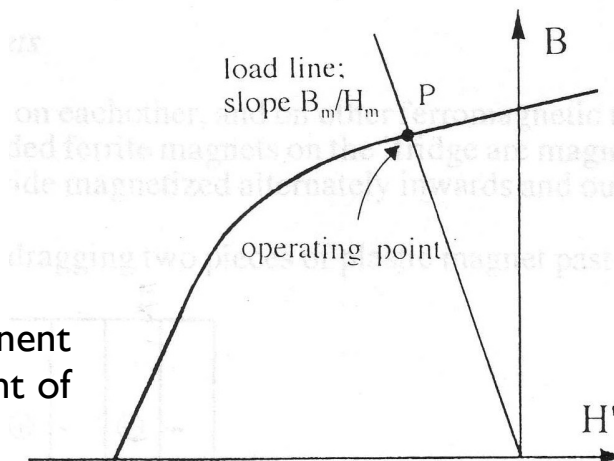
## Magnet applications; A 30 B€ market



## 8.1 Hard magnets

Permanent magnets are ferromagnets with a wide hysteresis loop. Once magnetized, they sit at a working point in the second quadrant of the loop which is determined by the magnet shape and the rest of the magnetic circuit.

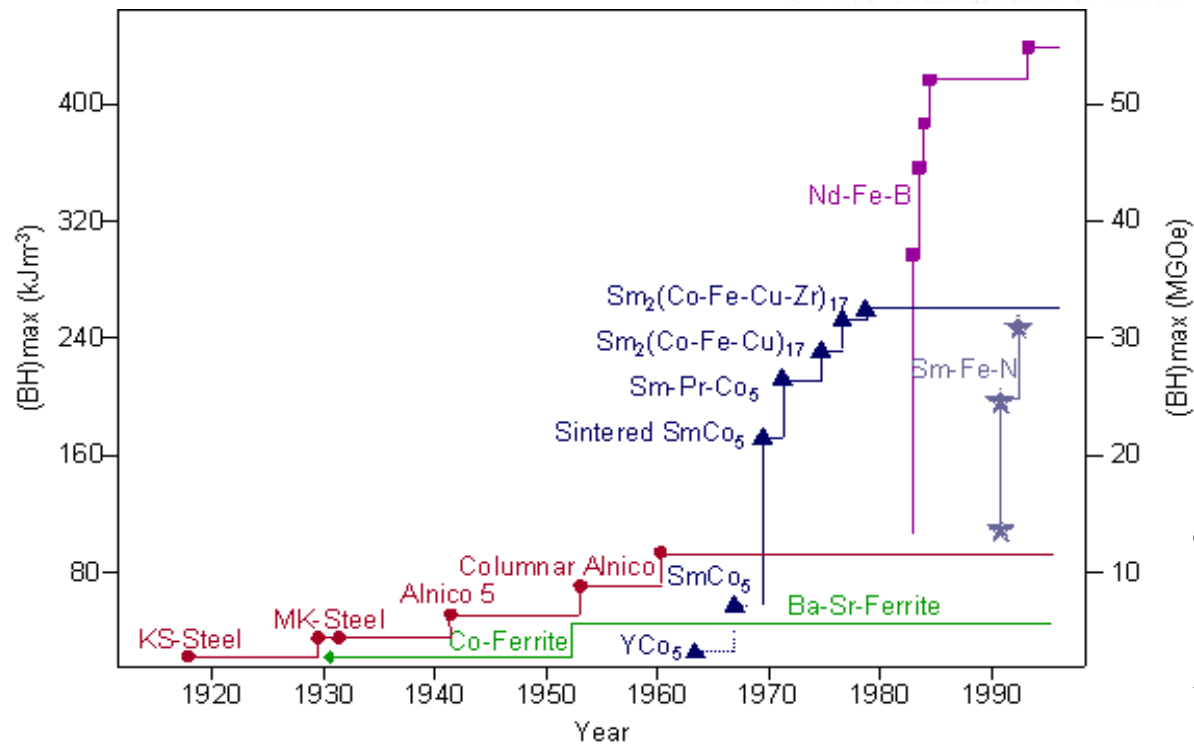
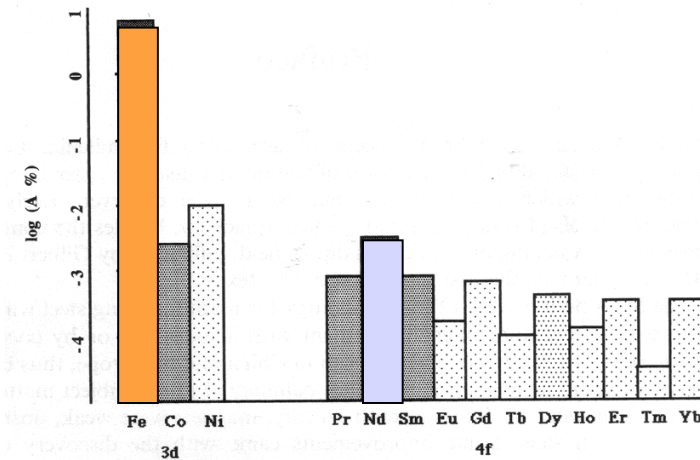
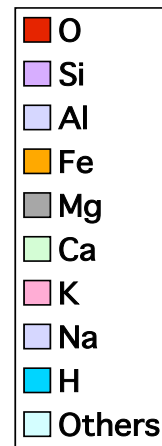
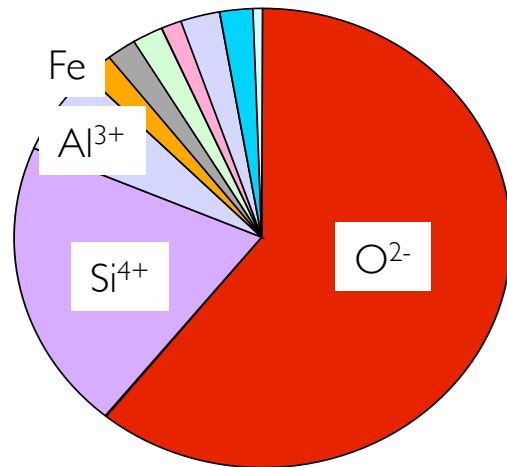
The working point of a permanent magnet in the second quadrant of the hysteresis loop.



Permanent magnets generate magnetic flux with no continual expenditure of energy!

The B-field may be uniform or nonuniform, static or time-dependent. The magnetic flux density  $\mathbf{B}_0$  in the airgap is the natural field to consider in permanent magnet applications because flux is conserved in a magnetic circuit, and forces on electric charges and magnetic moments all depend on  $\mathbf{B}$ .

The best permanent magnets are intermetallic compounds of a ferromagnetic 3d element and a 4f element; e.g.  $\text{SmCo}_5$  or  $\text{Nd}_2\text{Fe}_{14}\text{B}$ . Most common are the cheap hexagonal ferrites  $\text{BaFe}_{12}\text{O}_{19}$  and  $\text{SrFe}_{12}\text{O}_{19}$ . These powders are sometimes bonded in plastic



Global production ~80,000 t  
95% in China. Nd price  
increased from 8\$ to 25\$ in  
2006 to 125 \$/kg in 2011.



Lodestone  
1724

Ferrite 1956

Nd-Fe-B 1975

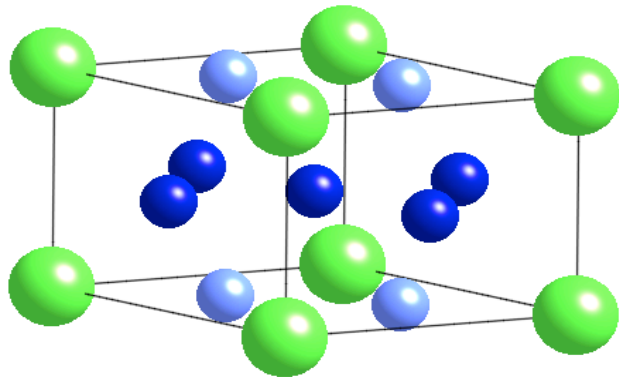
All three magnets contain  $\approx 70\%$  Fe and store  
 $\approx 0.4 \text{ J}$  of energy in their stray field

**Hard ferromagnets** have broad square loops with  $H_c > (1/2)M_s$ . They always have a uniaxial crystal structure (hexagonal, tetragonal ...) with one *easy axis* of magnetization.

Once magnetized they remain in their metastable, fully magnetized state creating a stray field around them with no expenditure of energy.

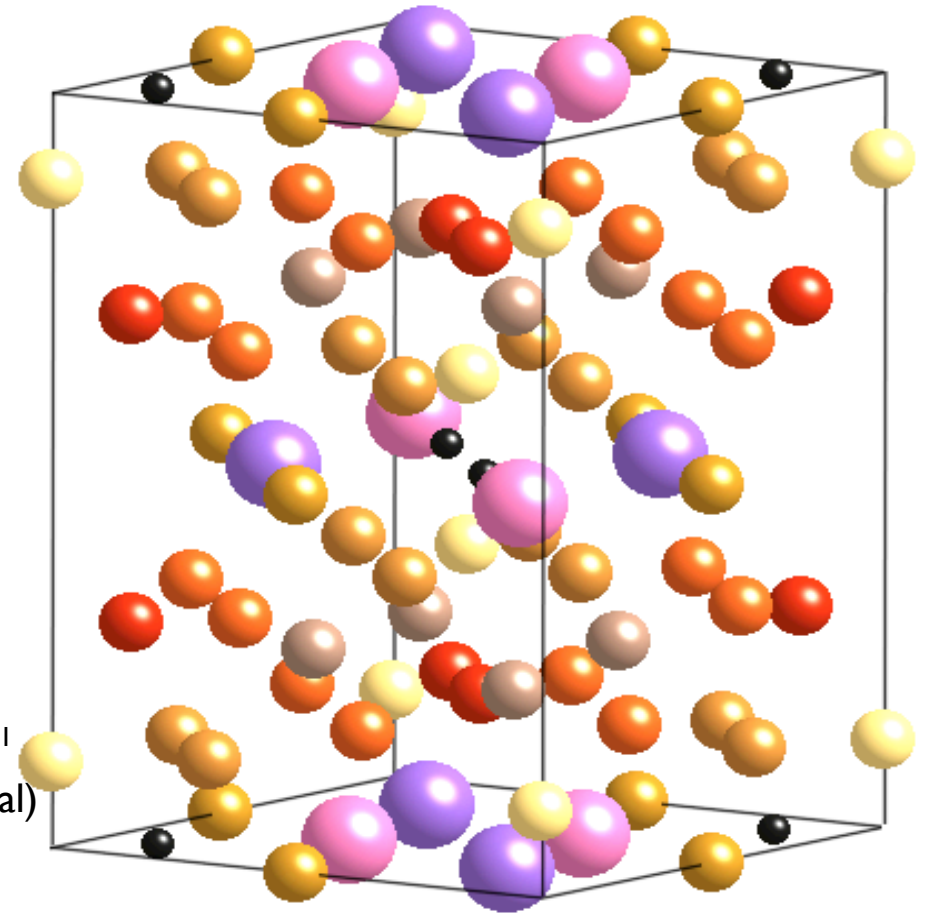
Good examples are  $\text{SmCo}_5$  and  $\text{Nd}_2\text{Fe}_{14}\text{B}$ .

$\text{SmCo}_5$

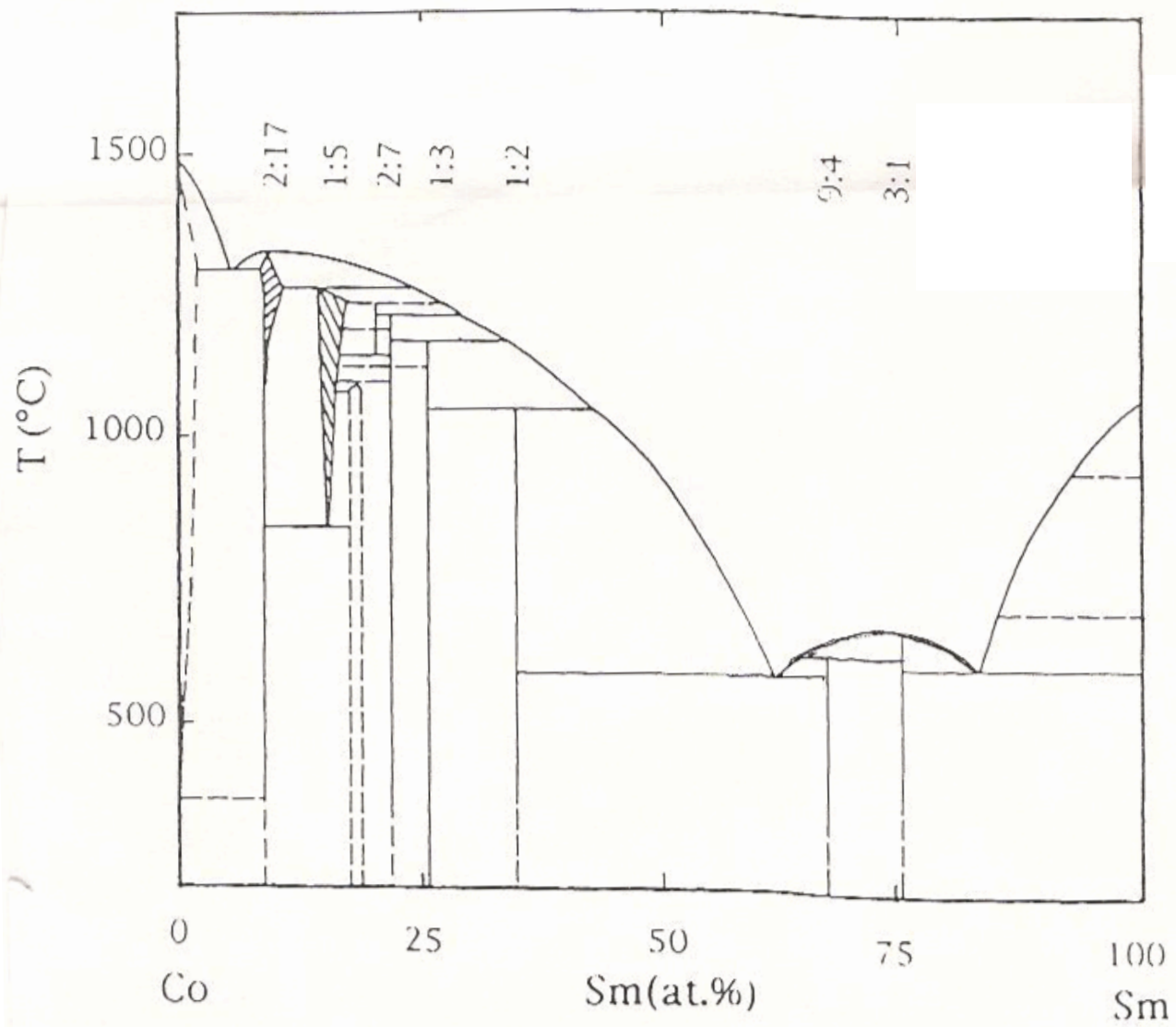


$J_r = 1.0 \text{ T}; M_s = 0.8 \text{ MA m}^{-1}$   
 $K_1 = 17 \text{ MJ m}^{-3}$  (hexagonal)  
 $T_C = 1020 \text{ K}$   
 $(BH)_{\text{max}} \approx 200 \text{ kJ/m}^3$

$\text{Nd}_2\text{Fe}_{14}\text{B}$



$J_r = 1.4 \text{ T}; M_s = 1.1 \text{ MA m}^{-1}$   
 $K_1 = 4.9 \text{ MJ m}^{-3}$  (tetragonal)  
 $T_C = 878 \text{ K}$   
 $(BH)_{\text{max}} \approx 400 \text{ kJ/m}^3$



The Sm-Co equilibrium phase diagram.



## BaFe<sub>12</sub>O<sub>19</sub>; Hexaferrite

*magnetoplumbite*;  $a = 589 \text{ pm}$   $c = 2319 \text{ pm}$

An hcp lattice of oxygen and Ba, with iron in octahedral (12k, 4f<sub>2</sub>, 2a) tetrahedral (4f<sub>1</sub>) and trigonal bipyramidal (2b) sites.

Brown ferrimagnetic insulator. All magnetic ions are Fe<sup>3+</sup>. Also SrFe<sub>12</sub>O<sub>19</sub> and La/Co substitution.

Structure is 12k↑2a↑2b↑4f<sub>1</sub>↓4f<sub>2</sub>↓

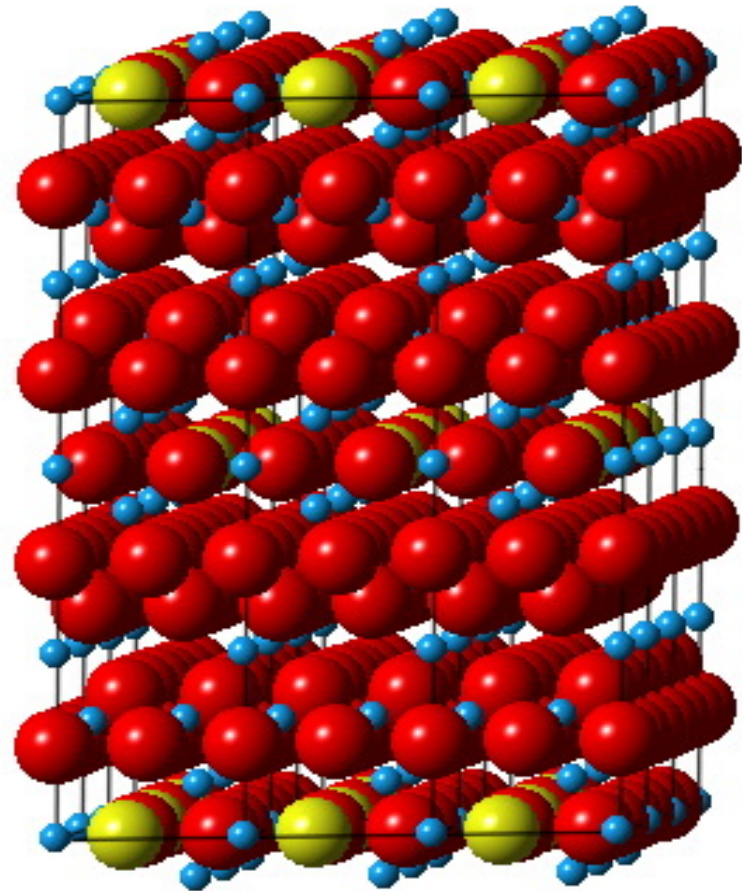
T<sub>C</sub> = 740 K.

$$m_0 = 20 \mu_B / \text{fu}$$

Low-cost permanent magnet, the first magnet to break the 'shape barrier'. 98% of all permanent magnets by mass are Ba or Sr ferrite. Found on every fridge door and in innumerable catches, dc motors, microwave magnetrons, ...

80g manufactured per year for everyone on earth

$$J_s = 0.48 \text{ T} \cdot \text{K}_1 = 450 \text{ kJ m}^{-3} \cdot B_a = 1.7 \text{ T}$$



*Polarization and energy product of different forms of  $\text{BaFe}_{12}\text{O}_{19}$*

(T)	$J_r$ (kJ/m <sup>3</sup> )	$(BH)_{\max}$
Intrinsic (crystal)	0.48	[46]
Oriented sintered	0.41	34
Isotropic sintered	0.23	9
Oriented bonded	0.30	16
Isotropic bonded	0.13	5



Sintered magnets

Ferrite magnets are made from powder platelets, with a particle size of about 2  $\mu\text{m}$ .

The powder may be sintered or bonded in plastic or rubber

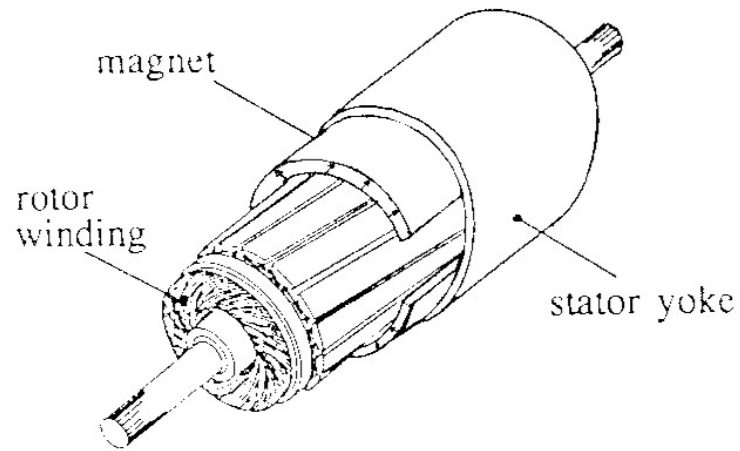


Bonded magnets

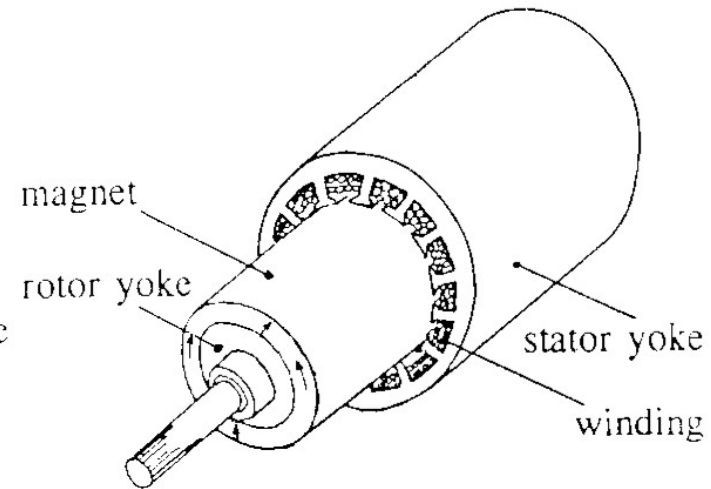
Examples of permanent magnet applications.

Field	Magnetic effect	Application
<i>Uniform</i>	Zeeman splitting Torque Hall effect, Magnetoresistance Force on conductor Induced emf	magnetic resonance imaging magnetic powder alignment sensors motors, actuators, loudspeakers generators, microphones
<i>Nonuniform</i>	Forces on charged particles Force on paramagnet Force on iron Force on magnet	beam control, radiation sources (microwave, uv, X-ray) mineral separation holding magnets bearings, couplings, maglev
<i>Time-varying</i>	Variable field Force on iron Eddy currents	magnetometry switchable clamps brakes, metal separation

## 8.1.1 Motors and Generators



(a)



(b)

DC motor designs: (a) brush motor with magnets on the stator and (b) brushless motor with magnets on the rotor.



Electric vehicles



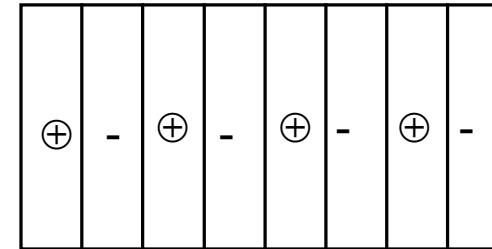
Direct drive turbines

### 8.1.2 Holding magnets

Magnets exert forces on each other, and on other ferromagnetic materials such as soft iron. The plastic-bonded ferrite magnets on the 'fridge are magnetized in a pattern of stripes about 3 mm wide magnetized alternately inwards and outwards from the sheet.

Check this by gently dragging two pieces of plastic magnet past each other !

Magnetization pattern of plastic magnet sheet.



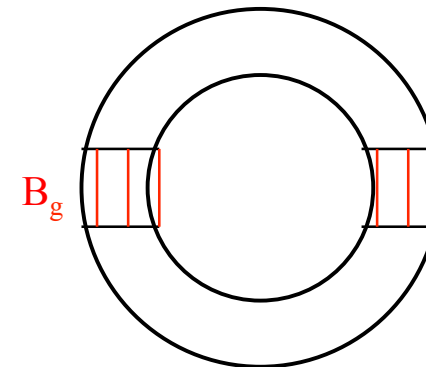
To work out the maximum force that can be generated at the face of a magnet, consider a toroid that is cut into two C-shaped segments and then separated slightly.

If the separation is  $d$  and the cross section area is  $A_g$ , the energy appearing in the air gaps is  $2 \times (1/2) \mu_0 H_g^2 A_g d = B_g^2 A_g d / \mu_0$ . The work done separating the segment is  $2Fd$ , hence the force per unit area is

$$F/A_g = B_g^2 / 2\mu_0$$

Forces of up to  $40 \text{ N cm}^{-2}$  can be achieved for  $B_g = 1 \text{ T}$ .

A magnetic toroid cut and separated to produce a field in the airgap.



The flux density at the surface of the plastic magnet is about 50 mT.

Estimate the force on a piece the size of a credit card

### 8.1.3 Generation of Uniform Magnetic Fields

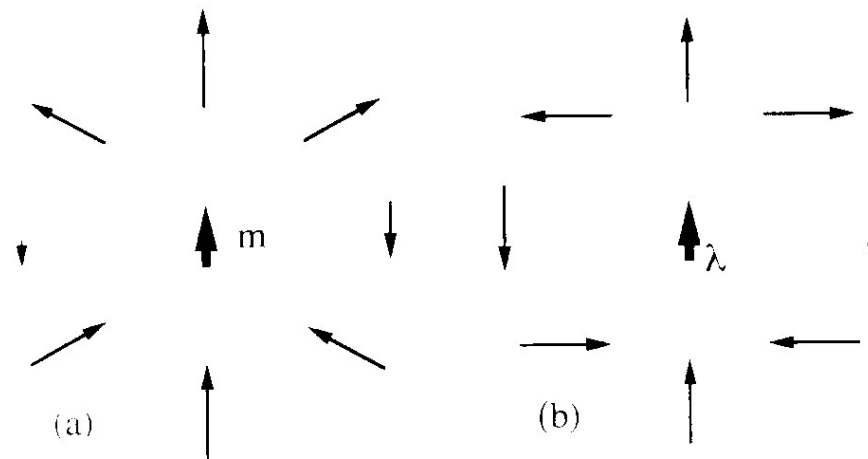
The magnetic field produced by a point dipole of moment  $m \text{ Am}^2$  is quite inhomogeneous. In polar coordinates, it is

$$H_r = 2m \cos \theta / 4\pi r^3, \quad H_\theta = m \sin \theta / 4\pi r^3, \quad H_\phi = 0$$

The field due to an extended line dipole of length  $L$  and dipole moment  $\lambda \text{ Am}$  per unit length is significantly different:

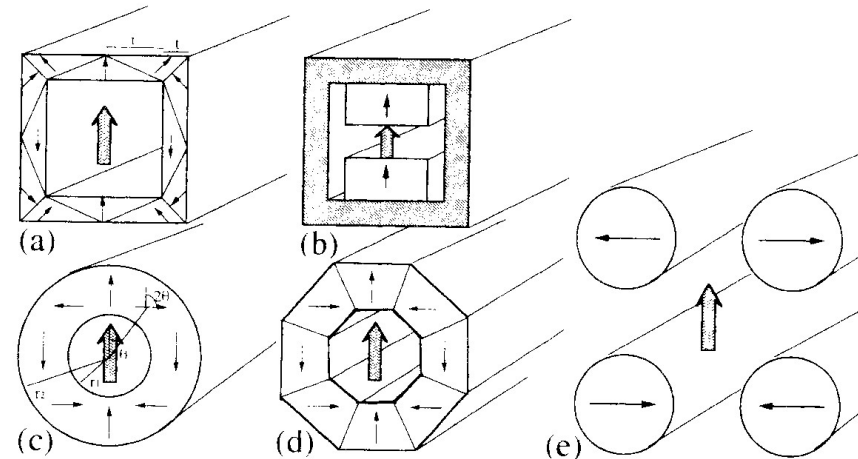
$$H_r = \lambda \cos \theta / 4\pi r^2, \quad H_\theta = \lambda \sin \theta / 4\pi r^2, \quad H_\phi = 0$$

The magnitude of  $\mathbf{H}$ ,  $\sqrt{H_r^2 + H_\theta^2 + H_\phi^2}$ , is now independent of  $\theta$  and its direction makes an angle  $2\theta$  with the orientation of the magnet.



Comparison of the magnetic field produced by a) a point dipole  $\mathbf{m}$  and b) a line dipole  $\lambda$ .

Magnetic circuits made of long cylindrical segments may be used to generate uniform fields. An open cylinder or a design with flat cuboid magnets and a soft iron return path is used to for nuclear magnetic resonance (NMR). Permanent magnet flux sources supply fields of order 0.3 T with homogeneity of 1 part in  $10^5$  in a whole-body scanners.



Designs for magnetic cylinders which produce a uniform transverse field.

Figure (c) shows a design where the direction of magnetization of any segment at angular position  $\vartheta$  in the cylinder is at  $2\vartheta$  from the vertical axis. According to the equations for the line dipole, all segments now contribute to create a uniform field across the airgap in a vertical direction. Unlike the structure of Fig (a), the radii  $r_1$  and  $r_2$  can take any values without creating a stray field outside the cylinder. This ingenious device is known as a *Halbach cylinder*. The field in the airgap is

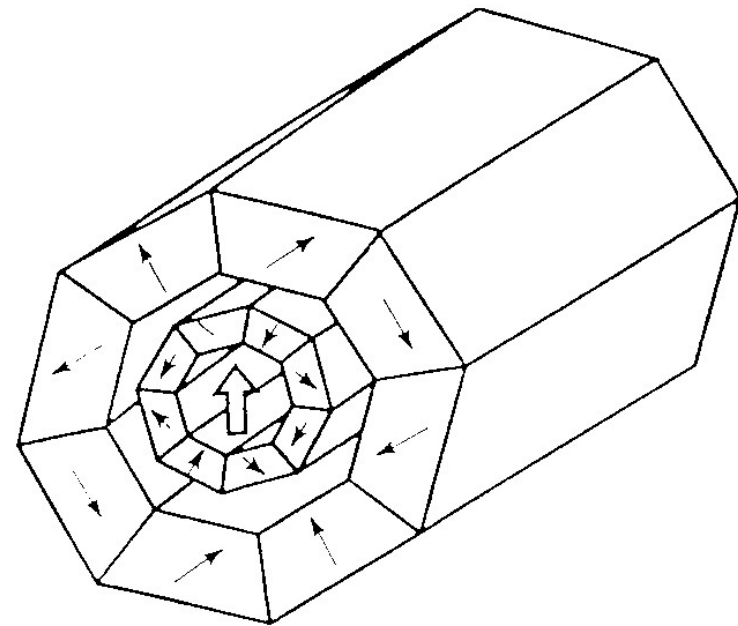
$$B_0 = B_r \ln(r_2/r_1)$$



There is no limit in principle to the magnitude of the field that can be produced in a Halbach cylinder, but in practice the coercivity and anisotropy field of the magnets limit the ultimate performance. Because of the logarithmic dependence in (8.5) and the high cost of rare earth magnets, it becomes uneconomic to use permanent magnets to generate magnetic fields that exceed twice the the remanence.

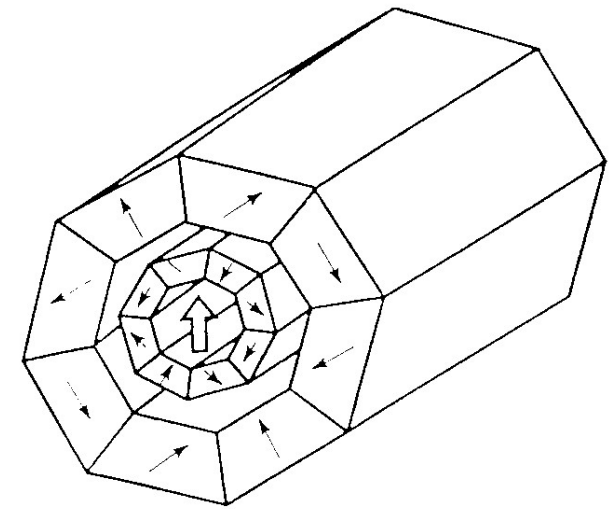
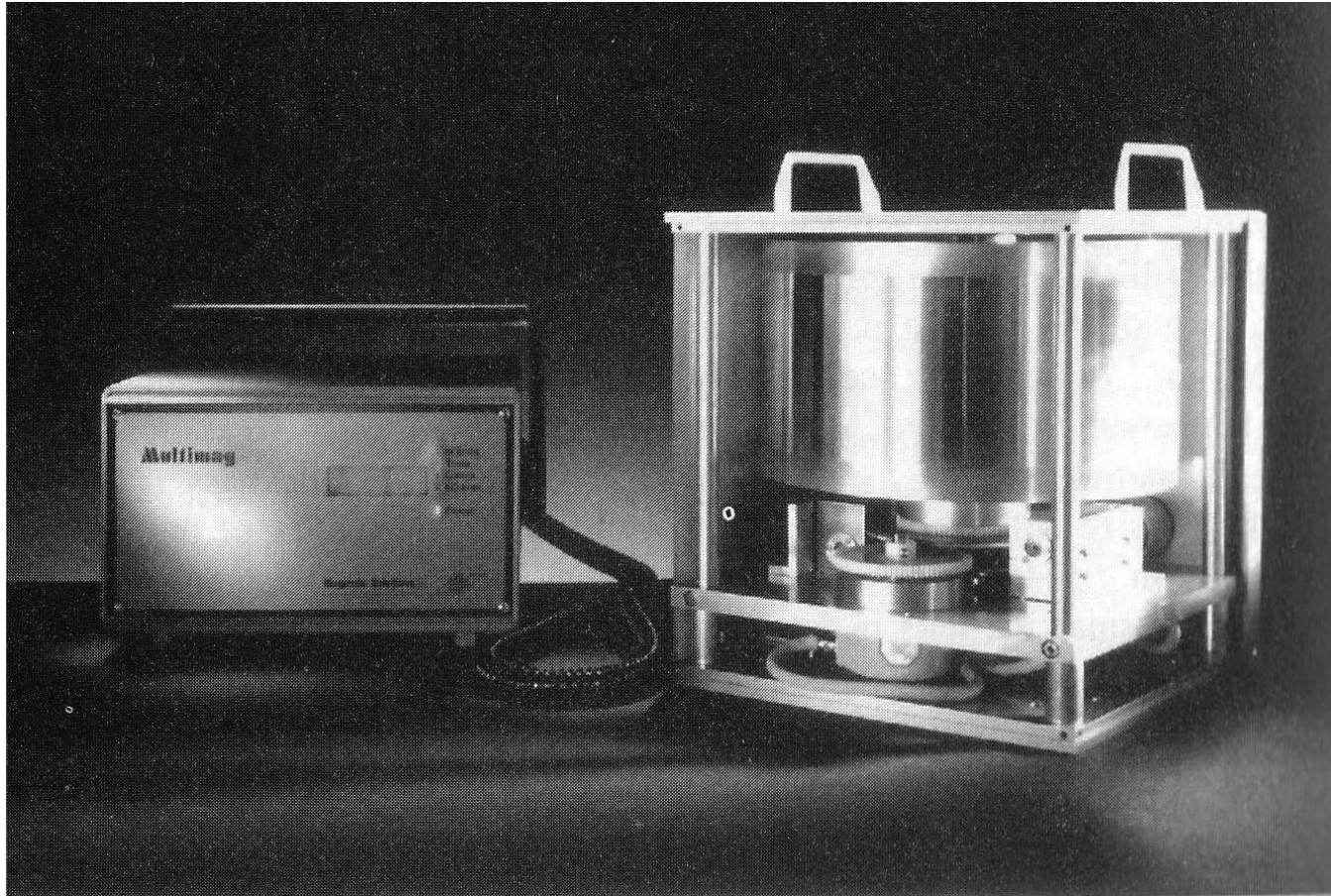
◆ *Variable fields* Two Halbach cylinders with the same radius ratio  $\rho = r_1/r_2$  can be nested inside each other. Rotating them both through an angle  $\pm \alpha$  about their common axis generates a variable field  $2B_r \ln \rho \cos \alpha$ . Permanent magnet variable flux sources are compact and particularly convenient to use since they have none of the high power and cooling requirements of a comparable electromagnet.

A commercial MULTIMAG system made by *Magnetic Solutions Ltd* uses a nested Halbach magnet made of 12 kg Nd-Fe-B magnet to generate  $\pm 1.8$  T in a 25 mm bore. These devices are ideal for compact instrumentation such as benchtop vibrating-sample magnetometer or a magnetoresistance measurement. Permanent magnet variable flux sources are expected to gradually displace resistive electromagnets to generate fields of up to about 2 T, but they cannot compete with superconducting solenoids in the higher field range. The conventional laboratory electromagnet is a *dinosaur*.



Permanent magnet variable flux source based on a rotatable double Halbach cylinder.





A MULTIMAG permanent-magnet variable flux source and controller. The magnet is composed of two concentric Halbach cylinders with the same radius ratio, which can be rotated about their common axis.

## 8.2 Soft magnets

A soft magnetic material should have minimal hysteresis and high permeability. In some range of field, the  $B(H')$  characteristic is linear

$$\mathbf{B} = \mu \mathbf{H}' \quad \text{or} \quad \mathbf{B} = \mu_0 \mu_r \mathbf{H}'$$

where the relative permeability  $\mu_r$  is a pure number. The value depends on sample shape, due to the demagnetizing field.

Values of  $\mu_{\max}$  can exceed  $10^6$  in toroids of the softest materials. Hence  $B$  is greatly enhanced compared to the free space value  $\mu_0 H$ . The permeability and loop shape can be modified by annealing, especially in a weak magnetic field.

The relation between relative permeability and susceptibility follows from  $\mathbf{B} = \mu_0(\mathbf{H}' + \mathbf{M})$ ; dividing by  $\mathbf{H}'$ , it follows that

$$\mu_r = 1 + \chi_r.$$

Soft materials are used for *static* and *ac* applications. Static and low-frequency applications are such as flux guidance and concentration in magnetic circuits.

Major ac applications include cores for transformers and inductors.

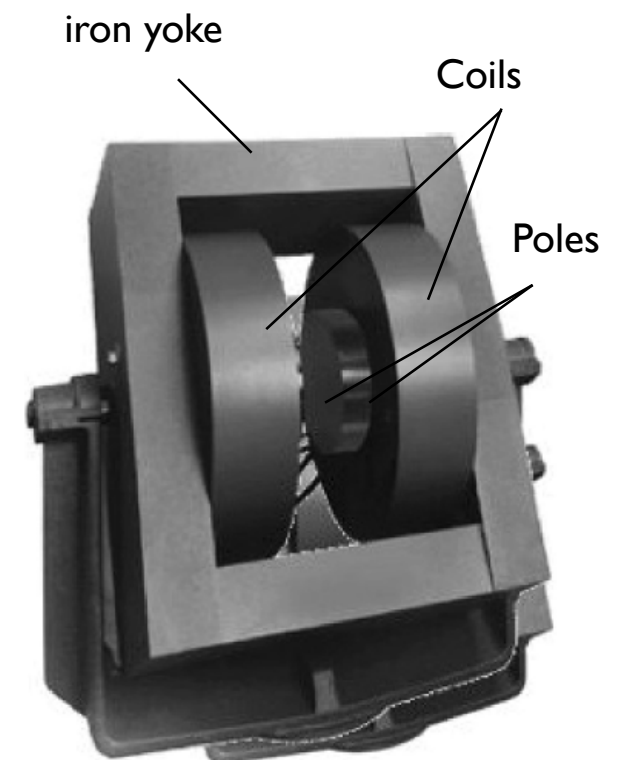
## 8.2.1 Magnetic circuits

*Transformers, motors and generators* include soft iron cores to generate and guide flux. Eddy-current losses are reduced by using thin laminations of material with a high resistivity. Transformer efficiencies are  $> 99\%$ .

Eddy-current losses at high frequencies ( $> 100$  kHz) are eliminated by using insulating ferrimagnetic oxides, the *ferrites*, to guide and concentrate the flux.

*Electromagnets* consist of field coils to generate the field, an iron yoke to guide the flux and pole pieces to concentrate the flux in the airgap. Flux guidance and concentration in electromagnets requires material with the highest polarization and very little remanence. Usually pure soft iron or  $\text{Fe}_{65}\text{Co}_{35}$  is used. For best results, tapered pole pieces with an angle of  $55^\circ$  are used.

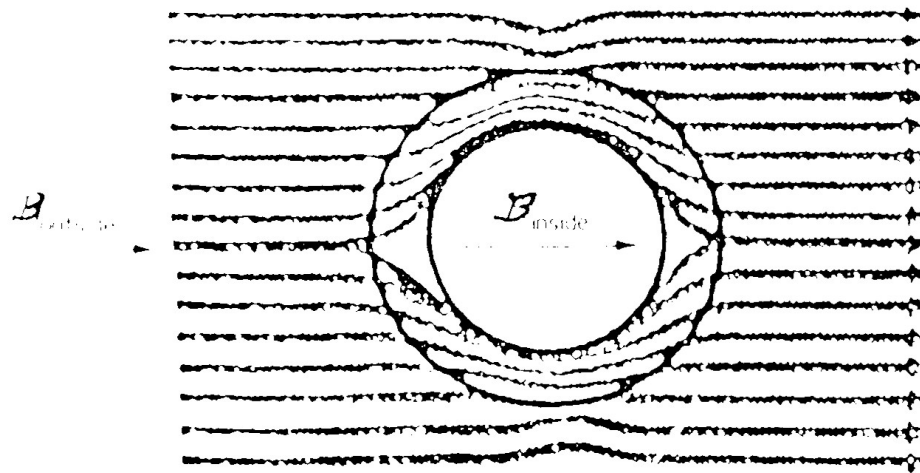
Electromagnetic *relays* and *solenoid valves* are miniature electromagnets where an iron core is magnetized and exerts a force on another iron member. The force per unit area if the gap flux is  $B_g$  is  $B_g^2/2\mu_0$



An electromagnet

## 8.2.2 Magnetic shielding

Shielding of weak dc or low-frequency ac fields (e.g. the Earth's field) requires material to provide an easy flux path around the shielded volume. The shielding ratio  $R$  is the ratio of the field outside to the field inside. Values of  $R \approx 100$  are achieved in low fields. The shielding material is chosen so that its polarization is unsaturated by the collected flux. dc shields are often made of *permalloy*  $\text{Ni}_{80}\text{Fe}_{20}$ , which has high permeability and no anisotropy or magnetostriction, and is therefore immune to shock and strain.



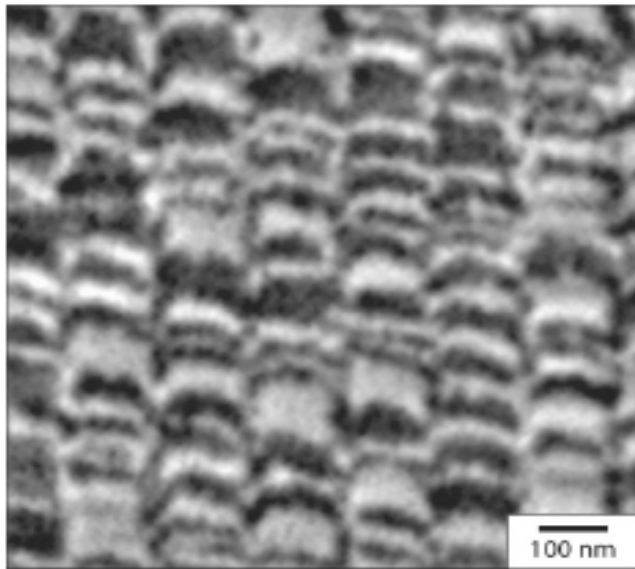
Magnetic shielding.



## 8.3 Magnetic recording

Digital and analog recording is a huge industry, consuming large quantities of ferrite and other semi-hard magnetic materials for recording media, and using sophisticated miniature magnetic circuits in the read and write heads.

The magnetic record is now generally perpendicular to the plane of the medium. The data are recorded on tracks whose width is determined by the width of the write head.



Perpendicular tracks on a hard-disc imaged by high-resolution magnetic force microscopy. The width of the tracks is determined by the width of the write head. The density is 300 bits/ $\mu\text{m}$  or 250 Gbit/square inch.

Miniaturization



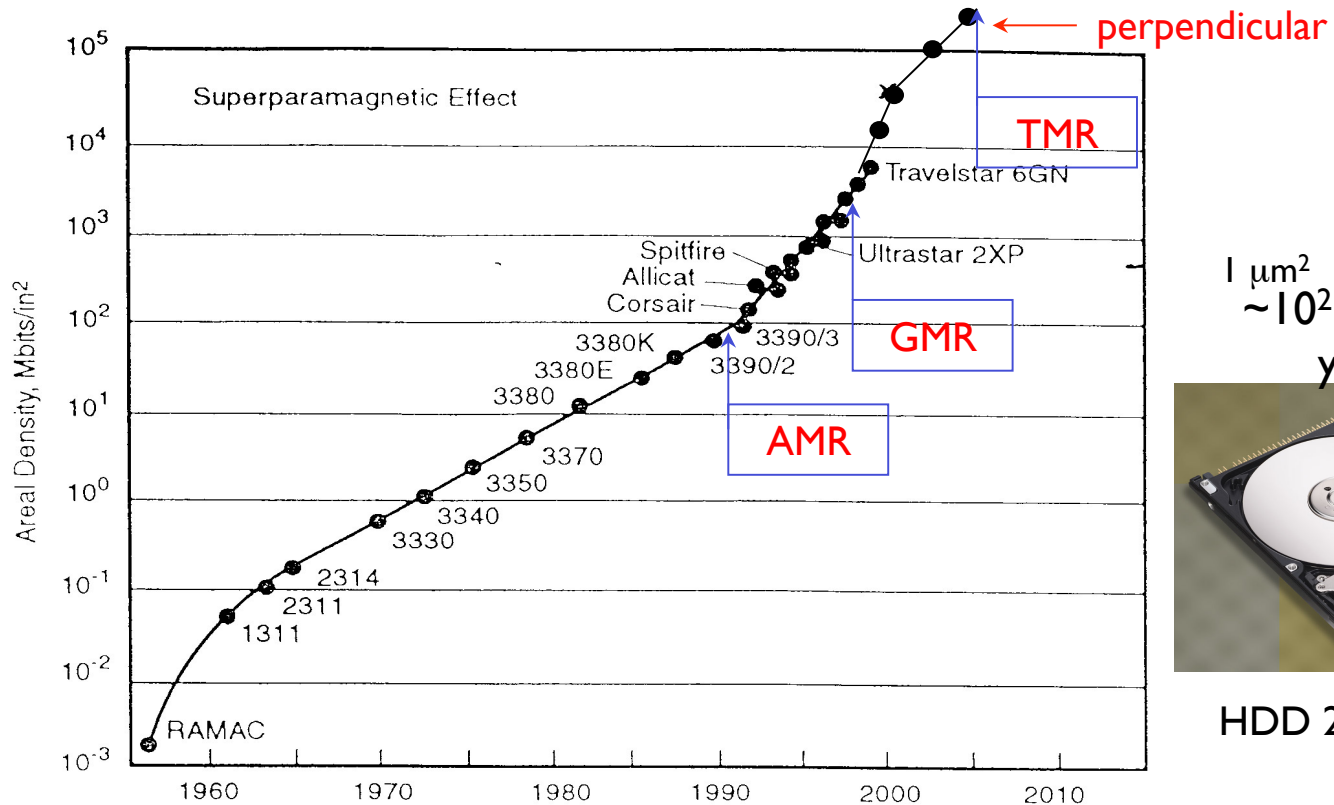
**A personal stereo, ca 1935.  
(Courtesy Orphée Cugat.)**

$\sim 10^{10}$  bytes/year



RAMAC 1955 40 Mb

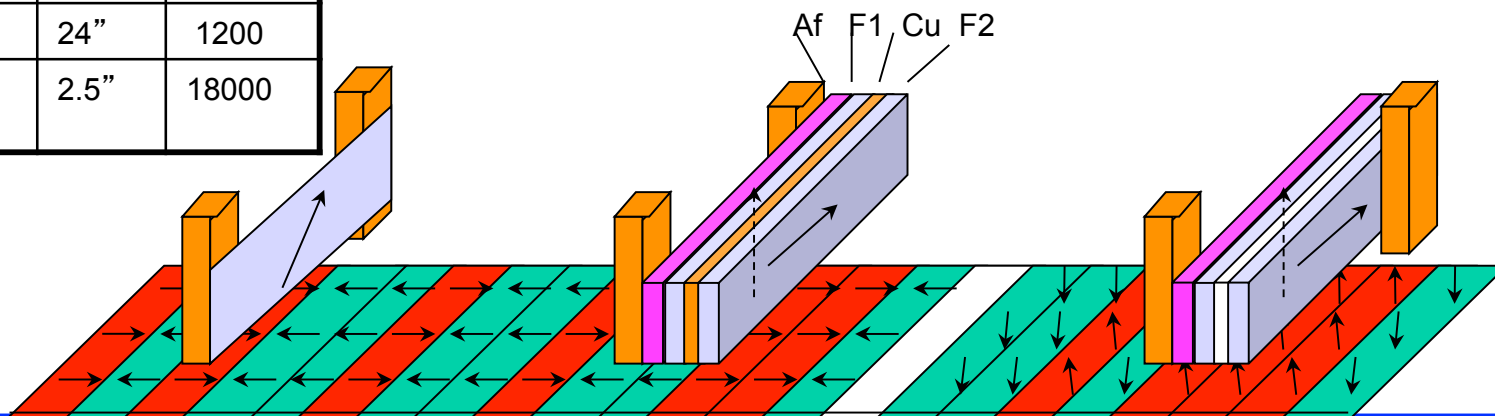
year	capacity	platters	size	rpm
1955	40 Mb	50x2	24"	1200
2005	160 Gb	1	2.5"	18000



$1 \mu\text{m}^2$   
 $\sim 10^{21}$  bytes/  
year



HDD 2005 160 Gb

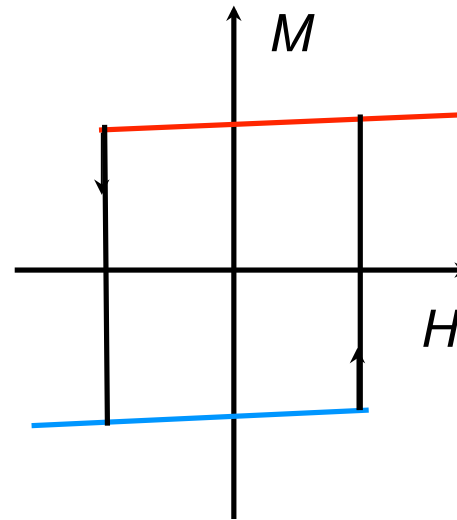
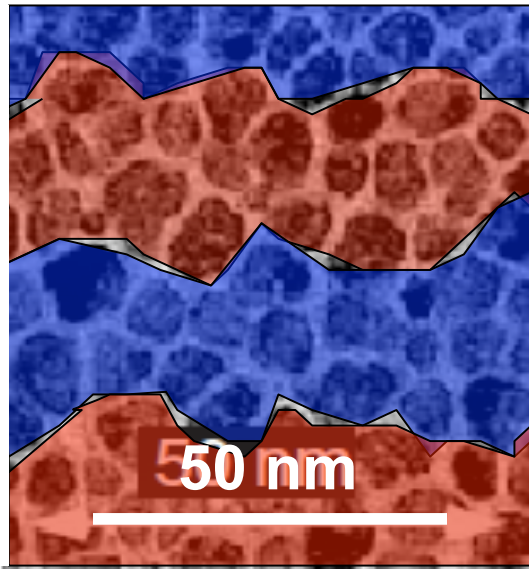


AMR

GMR

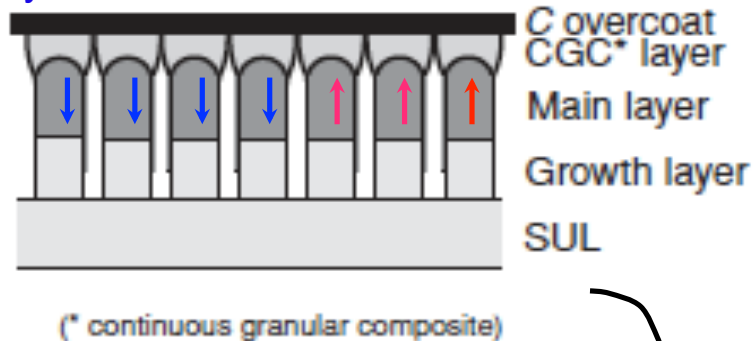
TMR

### 8.3.1 Magnetic media

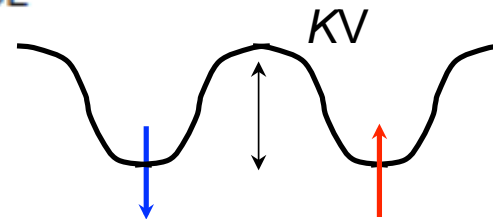


Magnetic recording medium consisting of sub-10-nm metallic grains with oxide-rich grain boundaries. The bit is recorded on a patch of grains along the track. The cross section shows the layer structure of the recording layer.

CoPtCr alloy

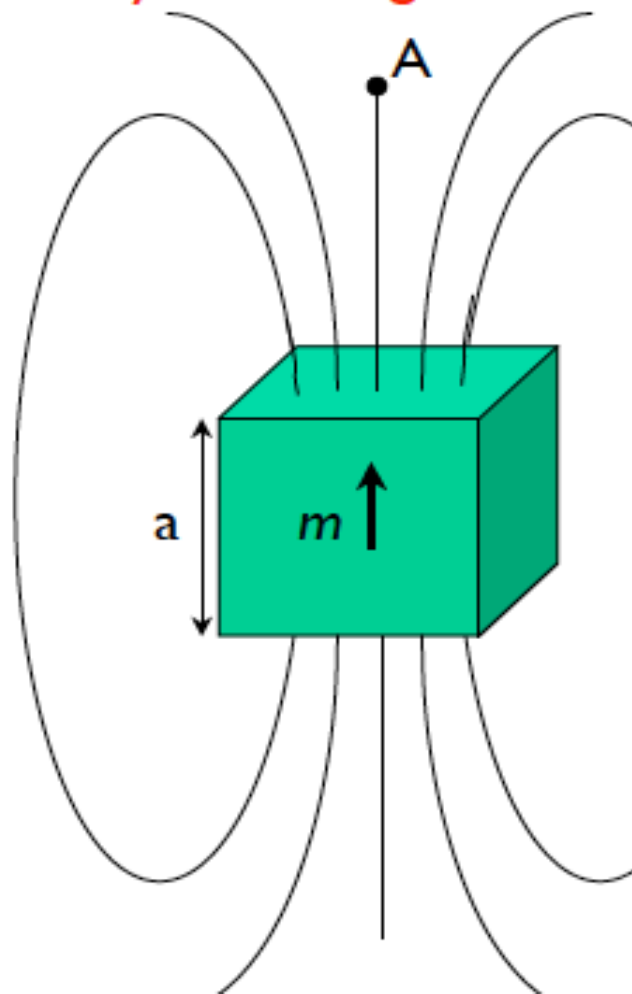


$$KV/kT > 50$$



## 8.3.2 Scaling

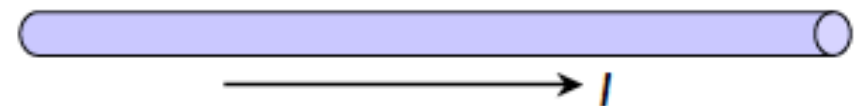
Why does magnetism lend itself to miniaturization ?



$$\mathbf{H} = (m/4\pi r^3)[2\cos\theta\mathbf{e}_r + \sin\theta\mathbf{e}_\theta] \quad H_A = 2Ma^3/4\pi r^3;$$

$$\text{If } a = 0.1\text{ m, } r = 2a, M = 1 \text{ MA m}^{-1} \quad H_A = M/16\pi = 20 \text{ kA m}^{-1} (\sim 25 \text{ mT})$$

Magnet-generated fields are limited by  $M$ . *Scale-independent*



$$H = I/2\pi r = 8jr \quad H \sim r$$

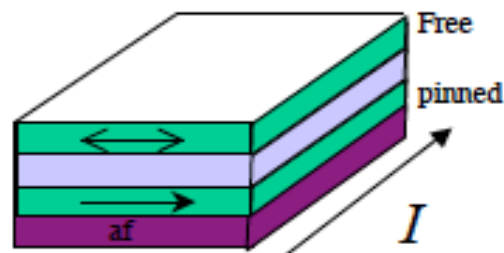
Current-generated fields are limited by  $j$ . *Scaling is poor*



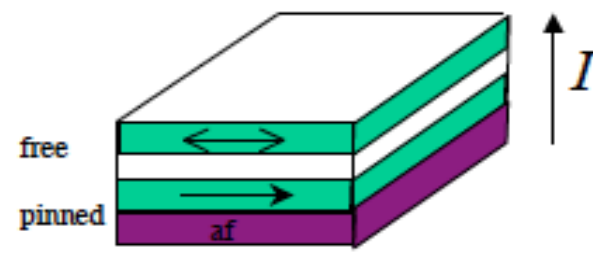
## 8.4 Spin Electronics

First-generation spin electronics has been built on *spin-valves* – sandwich structures using GMR or TMR with a pinned layer and a free layer.

These can serve as very sensitive field sensors, or as bistable memory elements



GMR spin valve



planar magnetic tunnel junction

One layer in the sandwich has its magnetization direction pinned by exchange coupling with an antiferromagnet – *exchange bias*.

## 8.4.1 Spin currents.

➤ Pure charge currents;

charge flow



➤ Spin-polarized charge currents

charge and  
angular momentum flow



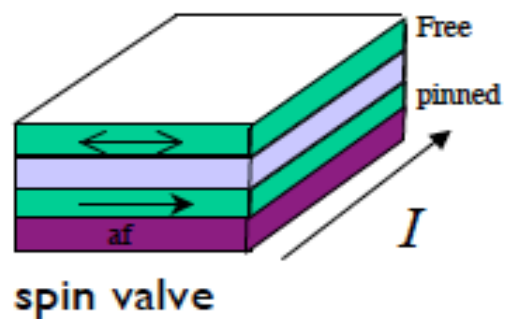
➤ Pure spin currents

angular momentum flow

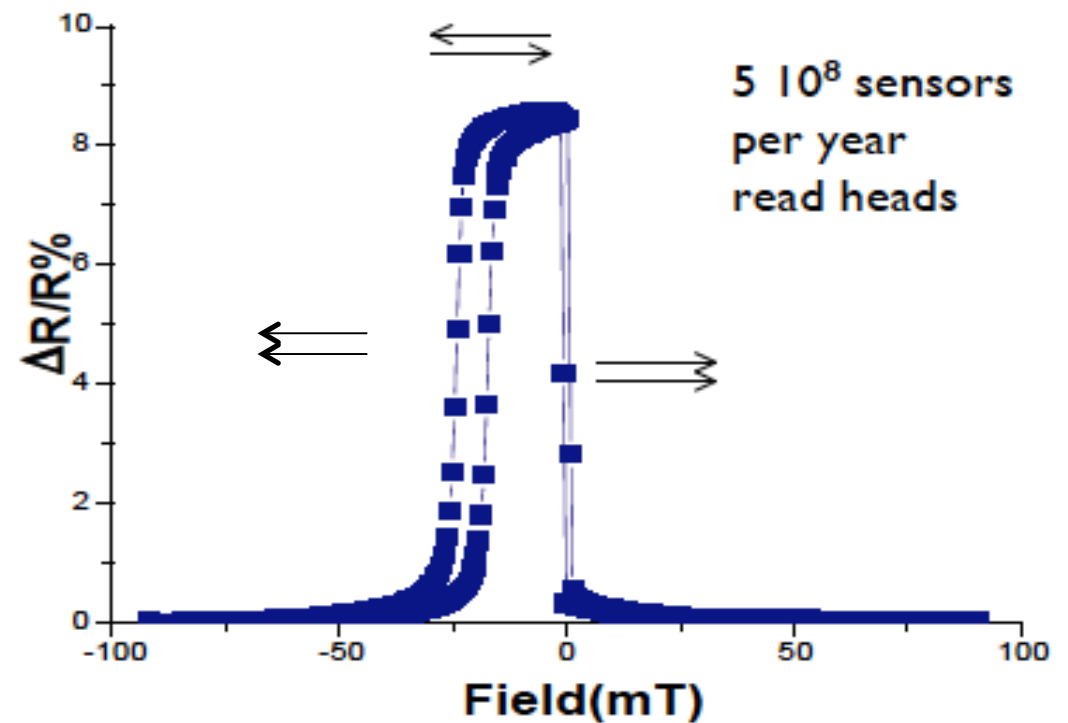


Charge is conserved; Spin is not

## 8.4.2 Giant magnetoresistance spin valve

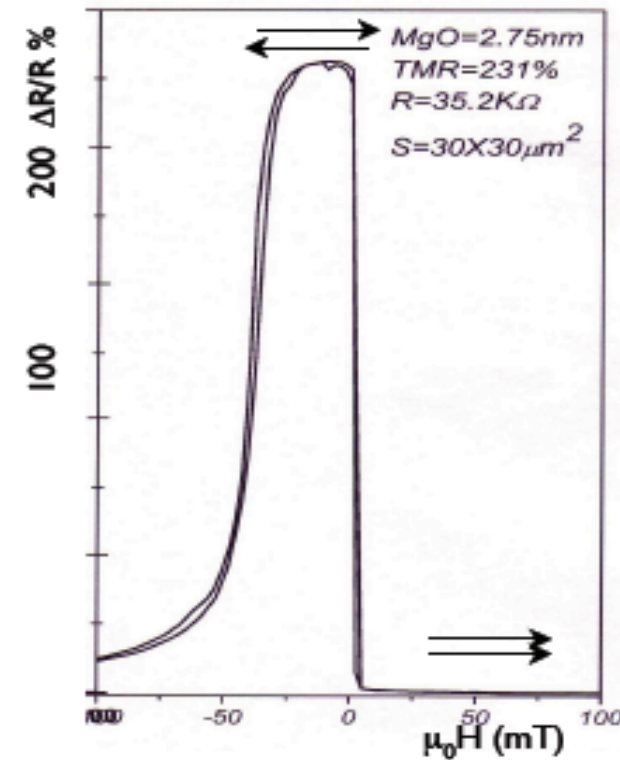
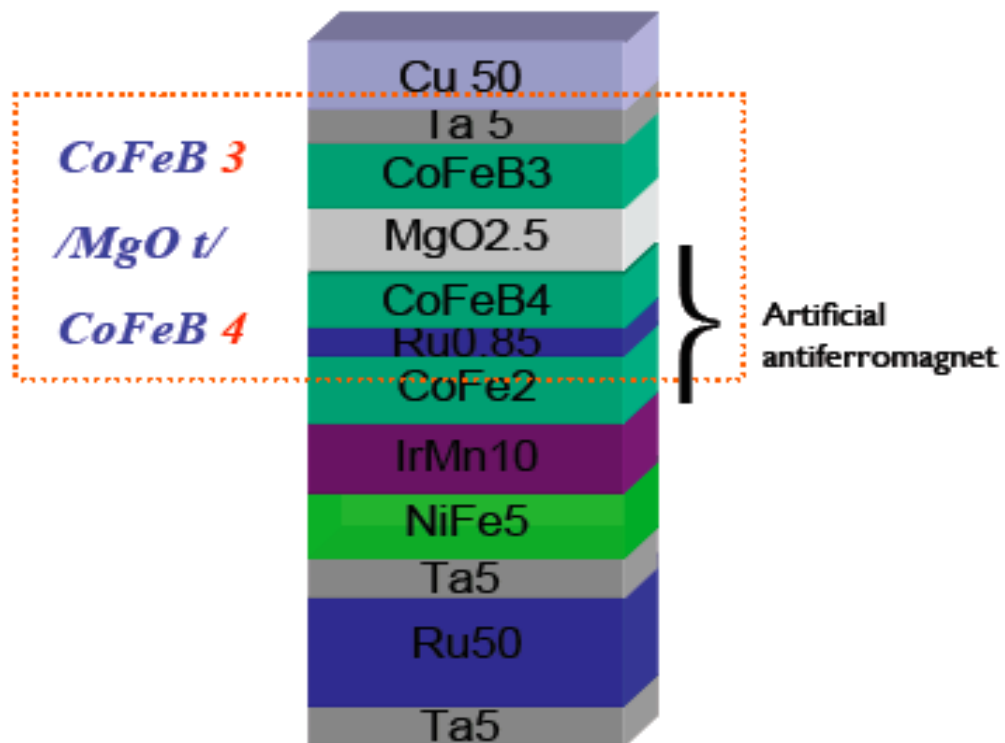


Perter Grunberg, Albert Fert;  
Nobel Prize 2007

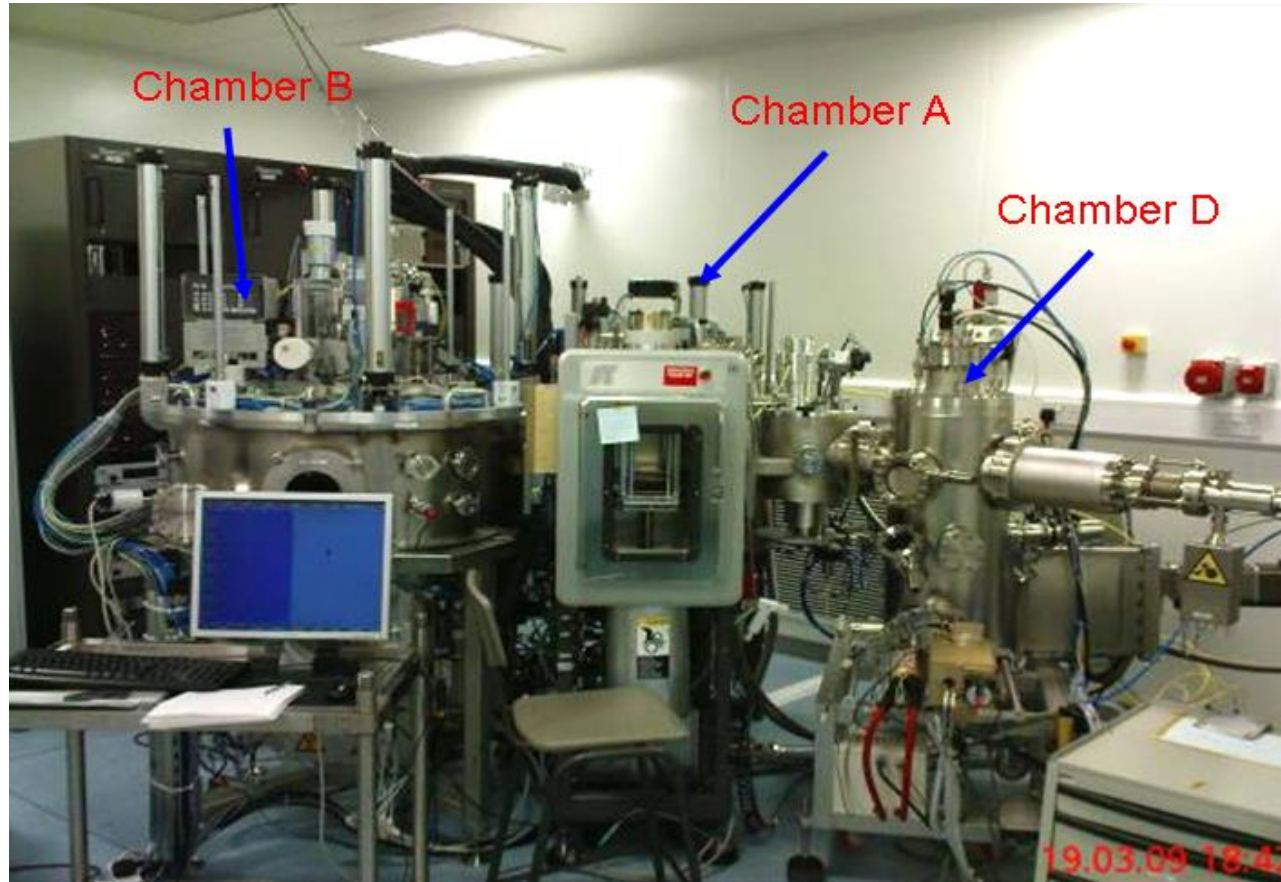


Magnitude of the effect  $\approx 10\%$

### 8.4.3 MgO-barrier magnetic tunnel junctions



## Shamrock sputtering tool



***Chamber A: Metal Sputtering (6 guns + 1 ion gun)***

***Chamber B: Oxide Sputtering (8 guns + 1 ion gun)***

***Chamber C: Wafer flip***

***Chamber D: UHV E-beam (4 pockets) + Sputtering (1 gun)***

**The End**