PYU44P13 Magnetism and Superconductivity

J. M. D. Coey

1. Introduction
2. Magnetic fields and forces
3. Magnetism of electrons
4. Magnetism of atoms
5. Magnetism in solids.
6. Simple models of metals
7. Superconductivity
8. Theory
9. Tunnelling
10. Applications

Comments and corrections please email: jcoey@tcd.ie

Magnetism and Superconductivity

PYU44P03 J.M. D. Coey 24 (lectures + tutorials)
Moday 11, Wednesday, 10 Thursday 10 Weeks 22 - 31

➢ Inntroductory lecture/discussions	4 x 1 hr
➢ MOOC Short lectures on Magnetism Look at one before lectures 2, 3, 4, 11	4 x 15’
> Magnetism lectures	9 x ~1hr
➢ Simple Metal Physics lectures	2 x ~1h
➢ Superconductivity recorded lectures	9 x ~1h
> Some recommended U-tube videos	3 x 10’

Magnetic Properties of Solids
Books

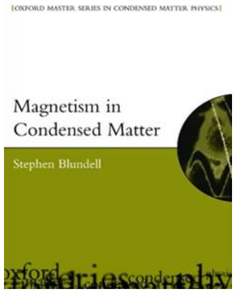
PYU44P13 J.M. D. Coey 12 (lectures + tutorials)

- J M D Coey: *Magnetism and Magnetic Materials*, Cambridge 2010
  A detailed advanced text..Sections 1.1-.4; 2.1-4; 3.1-2; 1,4.1-3; 5.1-2; 6.1-2; .7.1-.3; 11.1

- Stephen Blundell *Magnetism in Condensed Matter*, Oxford 2001
  A readable treatment of the basics.

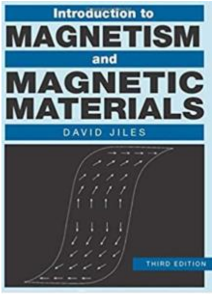
- J. Crangle; *The Magnetic Properties of Solids*, Arnold 1977: 1990
  A short book which treats the material at an appropriate level.

- David Jiles *Introduction to Magnetism and Magnetic Materials,* Hall 1991; 1997; 2015
  A more detailed introduction, written in a question and answer format.


[OXFORD MASTER SERIES IN CONDENSED MATTER PHYSICS]

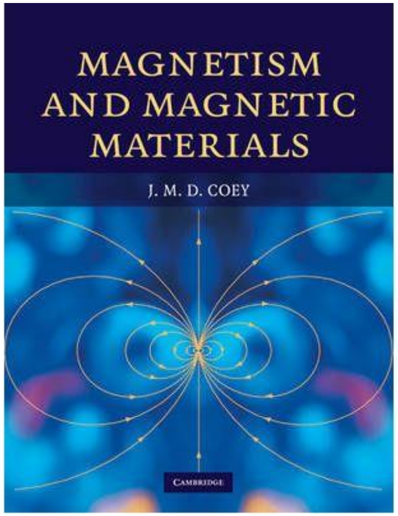
Magnetism in Condensed Matter

Stephen Blundell


Introduction to MAGNETISM and MAGNETIC MATERIALS

DAVID JILES

THIRD EDITION


MAGNETISM AND MAGNETIC MATERIALS

J. M. D. COEY

CAMBRIDGE

638 pages. Published March 2010

From Amazon.de for ~ €52

Magnetism module overview

1. **Introduction** Lecture 1
1.1 Historical background.
1.2 Magnetization and hysteresis; Overview

2. **Basic concepts** [1] Lectures 2,3
2.1 Moments and Magnetization MOOC1.1
2.2 Two fields *B* and *H* MOOC1.2
2.3 Energy and Force
2.4 Units and Dimensions

3. **Magnetism of the electron** [2] Lectures 4,5
3.1 Spin and Orbital moment MOOC2.1
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

4. **Magnetism of localized electrons on the atom** Lectures 6,7
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

5. **Paramagnetism** Lecture 8
5.1 Classical Theory
5.2 Quantum theory
5.3 Paramagnetism of metals

6. **Ferromagnetism** [3] Lecture 9,10
6.1 Mean field theory
6.2 Exchange Interactions.
6.3 Ferromagnetic domains
6.4 Magnetic measurements
6.5 Hard and soft ferromagnets

7. **Miscellaneous Topics** Lecture 11
7.1 Antiferromagnetism
7.2 Ferrimagnets.
7.4 Spin waves
7.5 Spin electronics MOOC2.2

See also some YouTube videos

[1] **Richard Feynman Magnets**
[2] **How Special Relativity Makes Magnets Work**
[3] **Magnets: How Do They Work?**

Video Material.

Since the detailed Magnetism and Spin Electronics Website has been taken rendered inaccessible by IT services, it will take some time to reinstate it properly.

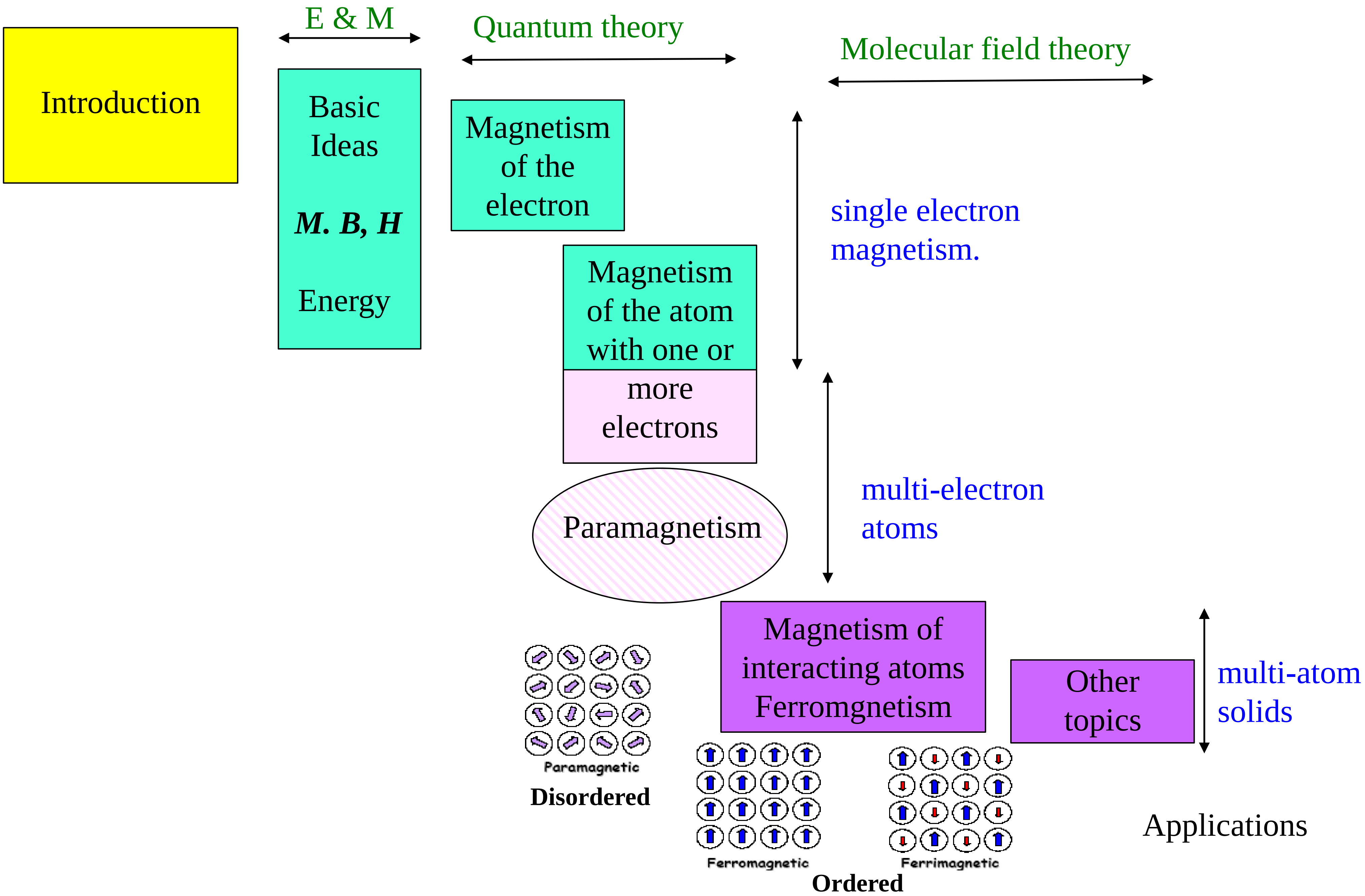
For this course, the video material you need to, or the appropriate links to it can be found on **Blackboard.**

— Four short MOOCs (15’ each) constituting an introduction to magnetism and spintronics have been recorded professionally at the University of Mainz

MOOC 1.1 Introduction — Basic Ideas 1
MOOC 1.2 Introduction — Basic ideas 2
MOOC 2.1 Electron spin
MOOC 2.2 The way into spintronics

U-tube videos:

Richard Feynman Magnets https://www.youtube.com/watch?v=Dp4dpeJVDxs
How Special Relativity Makes Magnets Work https://www.google.com/search?client=firefox-b-d&q=https%3A%2F%2Fwww.youtube.com%2Fwatch%3Fv%3D1TKSfAkWWN0#fpstate=ive&vld=cid:2aca1753,vid:1TKSfAkWWN0
Magnets: How Do They Work?
https://www.google.com/search?client=firefox-d&q=Magnets%3A+How+Do+They+Work%3F+#fpstate=ive&vld=cid:5f988f88,vid:hFAOXdXZ5TM



Introduction

E & M

Basic Ideas

M. B, H

Energy

Quantum theory

Magnetism of the electron

Magnetism of the atom with one or more electrons

Molecular field theory

single electron magnetism.

multi-electron atoms

Paramagnetism

Magnetism of interacting atoms Ferromgnetism

Other topics

multi-atom solids

Applications

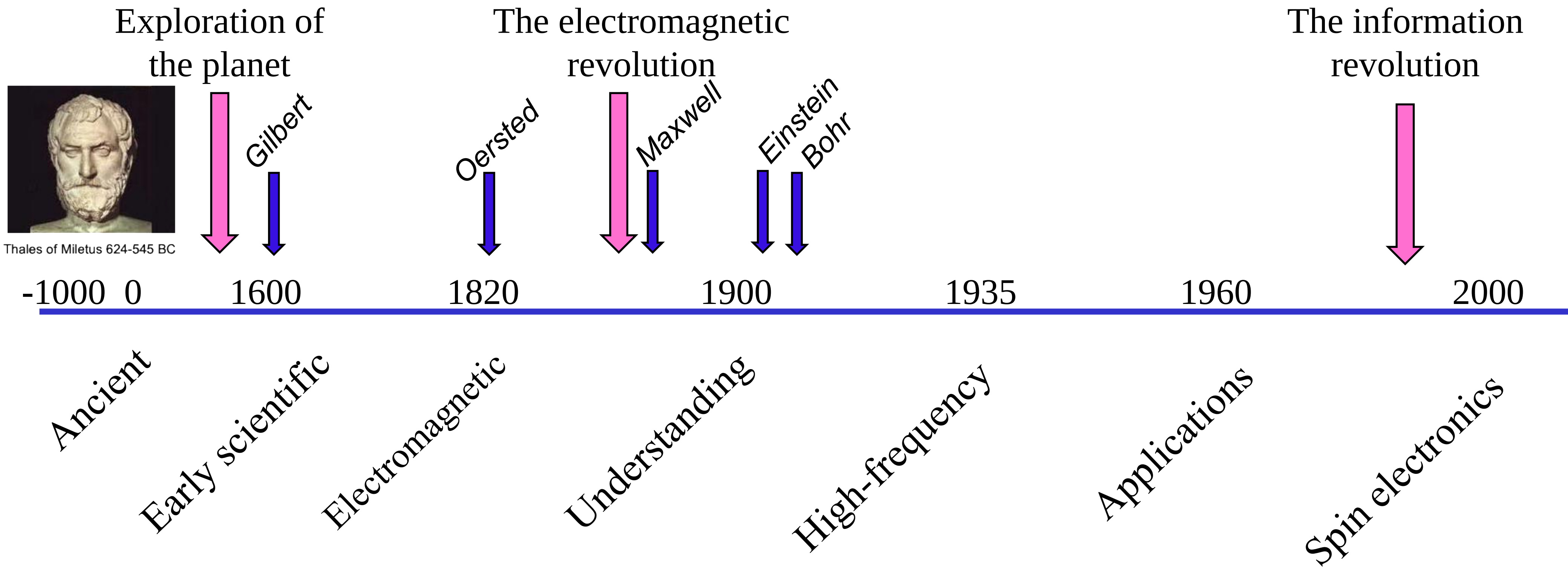
Disordered

Ordered

1. Introduction

1.1 A little history; Magnetism

Magnetism has changed the world three times



Exploration of the planet

The electromagnetic revolution

The information revolution

Thales of Miletus 624-545 BC

Seven ages of Magnetism

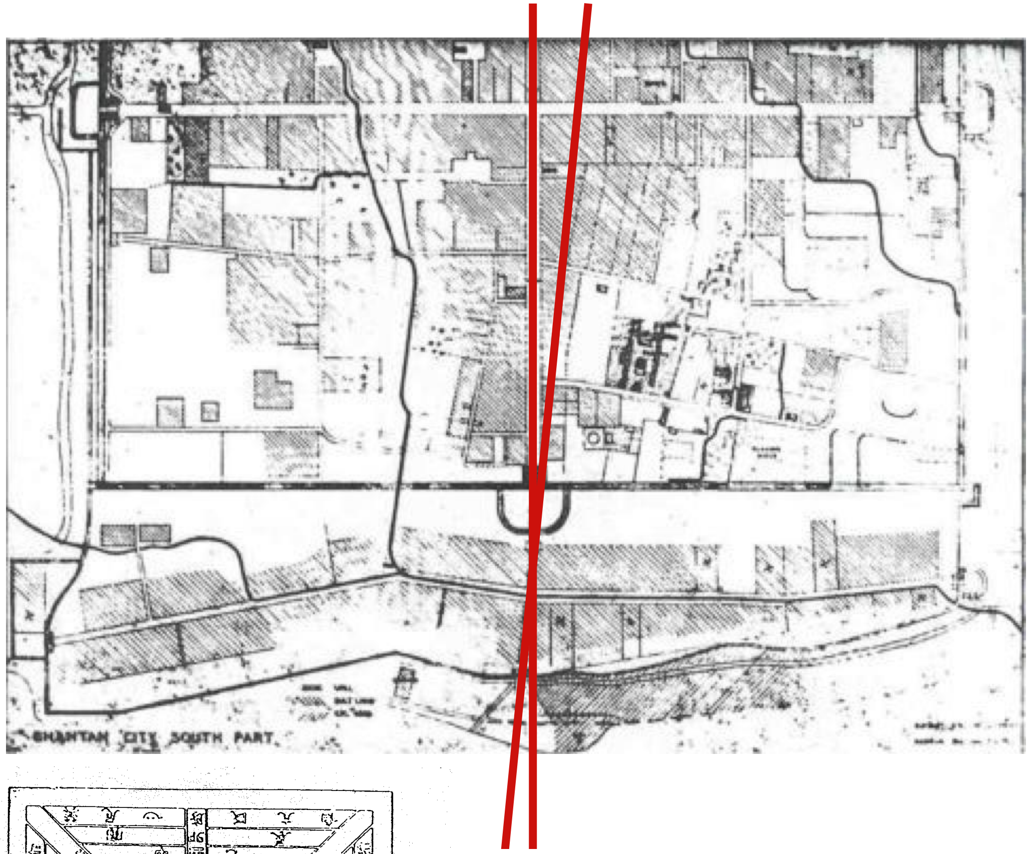
www.tcd.ie/Physics/Magnetism/Guide/magmoments/php

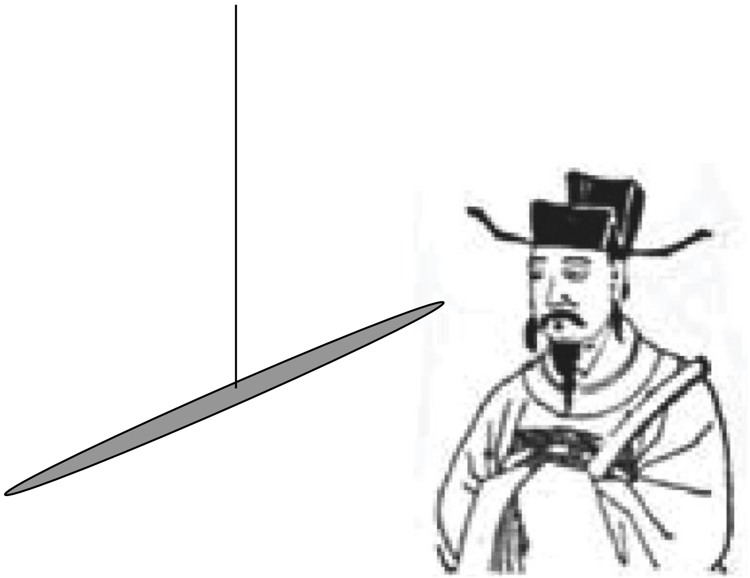
1.2 The Three Magnetic Revolutions

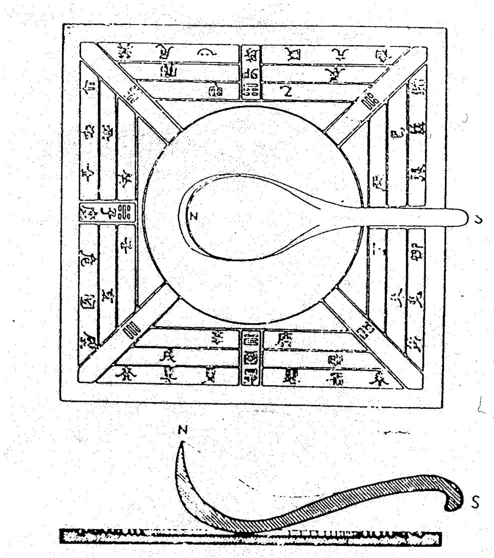
1 - The Compass

“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.”

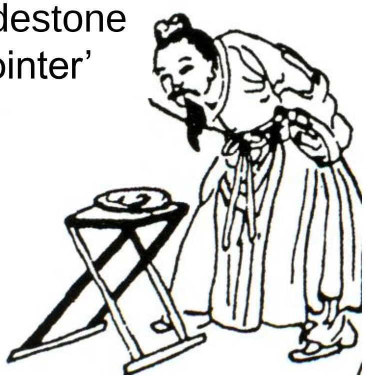
Francis Bacon *Novum Organum* 1620





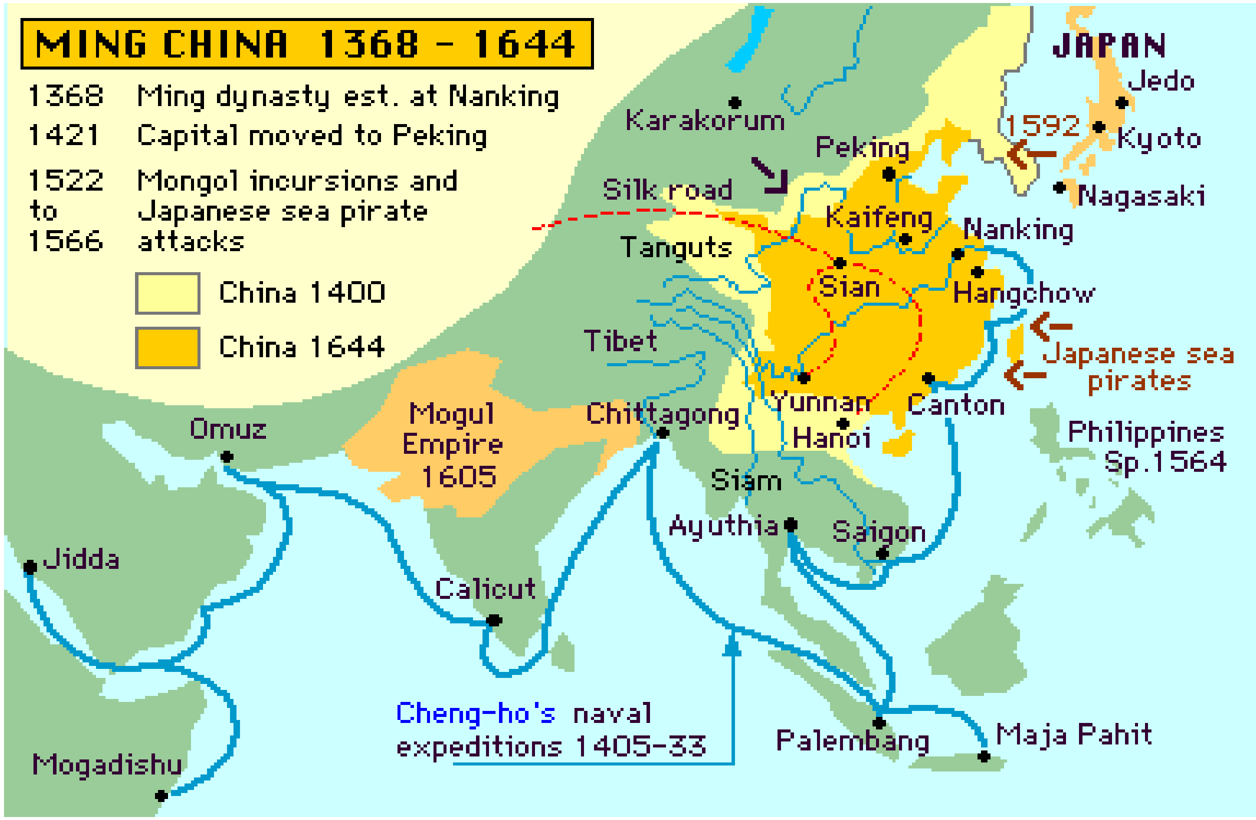


Carved Lodestone
‘South pointer’



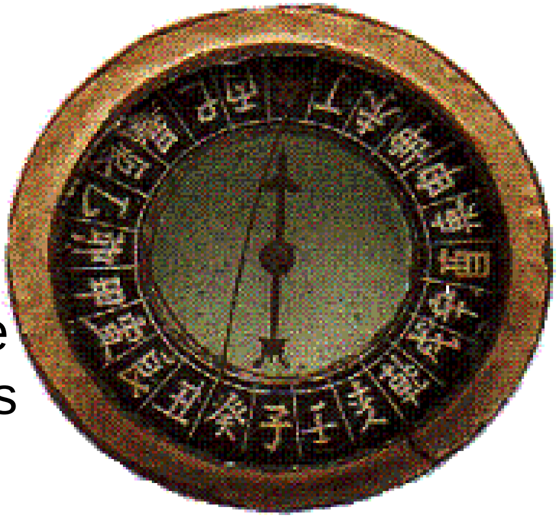
Shen Kua (沈括) reported how to make magnetized iron needles in 1060, and he described the suspended needle compass in 1088. *Thermoremanence* and *induced magnetization* were discovered in China. The English monk Alexander Neckham, working at the University of Paris, gives the first European account of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

Zheng He 郑和 1371-1432



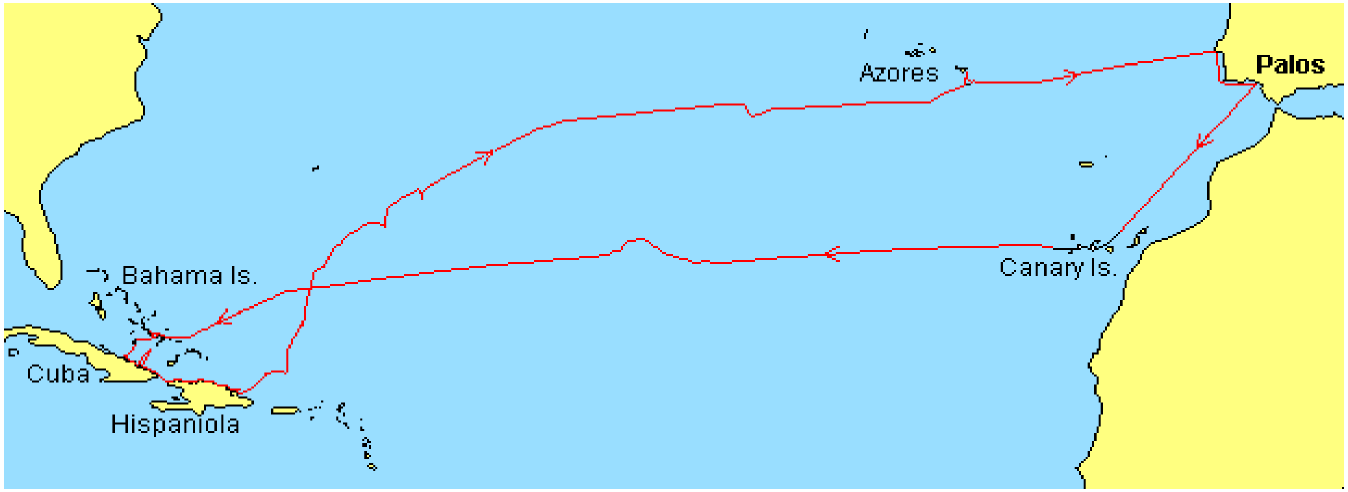
120m Treasure ship

Yongle Emperor
1402 1424



Chinese compass

Christopher Columbus
1452 - 1506



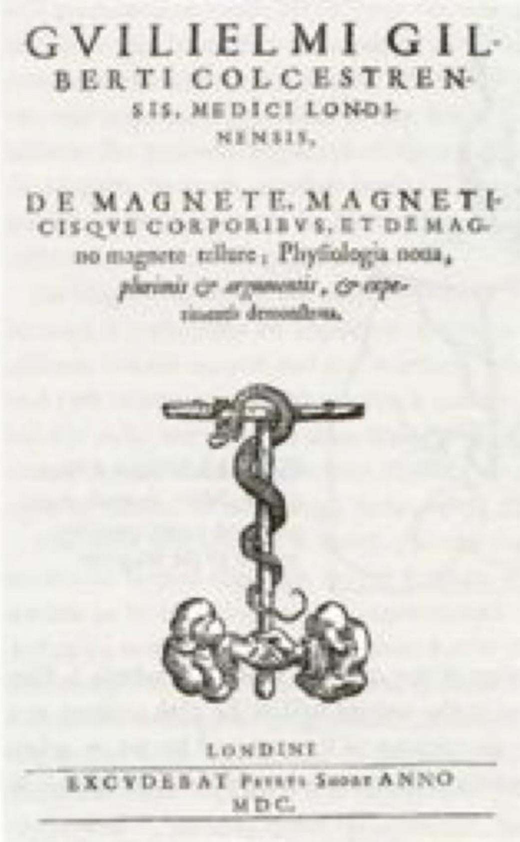
1492

Portuguese compass 18th century.

20 m Santa Maria, La Pinta, La Niña1

The beginnings of modern Science

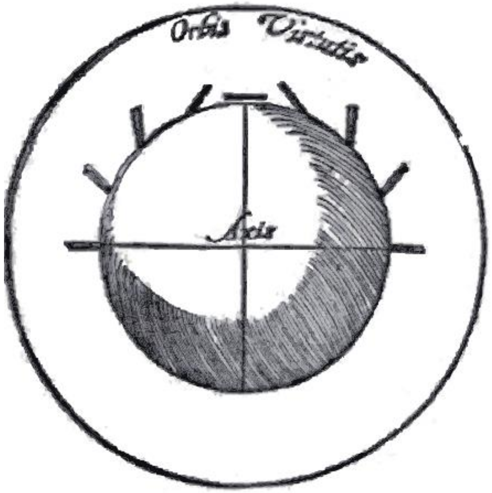
William Gilbert wrote *DeMagnete* in 1600, denouncing speculation and folklore. He insisted on experiments as the way to get to the truth

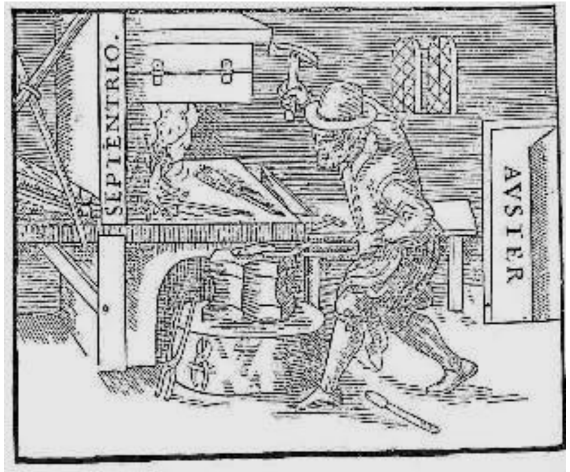


GVILIELMI GIL-
BERTI COLCESTREN-
SIS, MEDICI LONDI-
NENSIS,

DE MAGNETE, MAGNETI-
CISQVE CORPORIBVS, ET DE MAG-
no magnete tellure; Phyſiologia noua,
plurimis & argumentis, & expe-
rimentis demonſtrata.

LONDINI
EXCVDEBAT PETRVS SHORT ANNO
MDC.

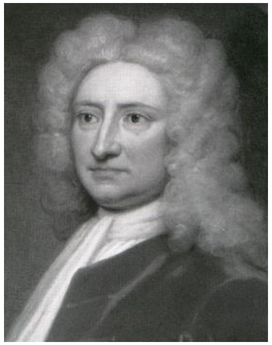




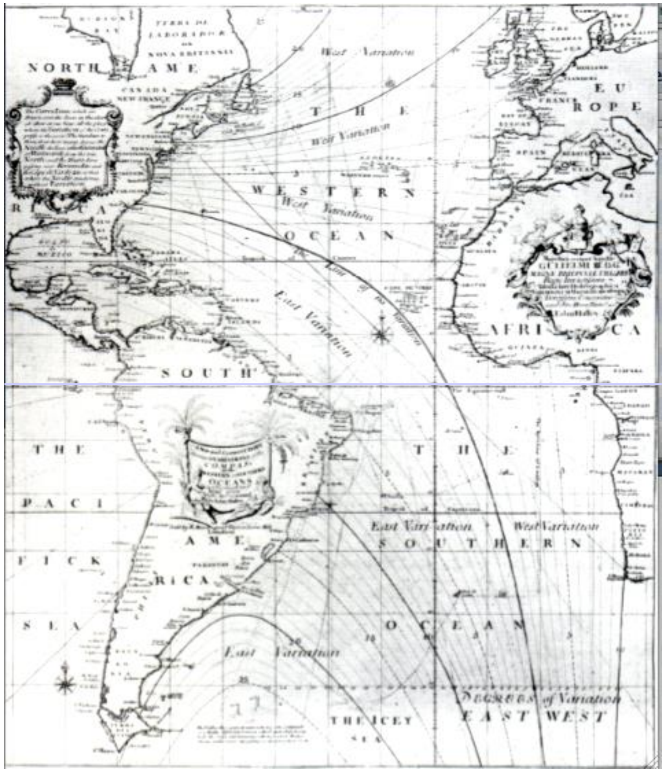
Experiments on lodestone terellae led William Gilbert to conclude in 1600 that Magnus magnes ipse est globus terrestris

Magnetic exploration of the Earth for much of the 18th century was motivated by the desire to solve the longitude problem

Edmond Halley led three research voyages from 1698 - 1701 to map the Earth’s magnetic field.



A large lodestone presented to TCD in 1724 for experiments in natural philosophy



The horseshoe magnet popularized by Daniel Bernouilli in 1743 was a clever solution to the problem of self-demagnetization

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.”

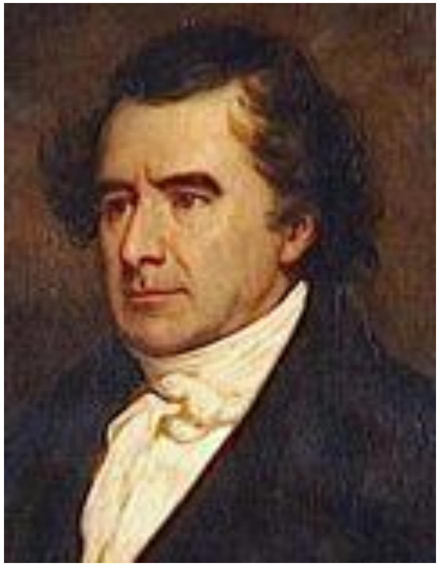
Richard Feynman 1970

The electromagnetic revolution; 1820 to 1905

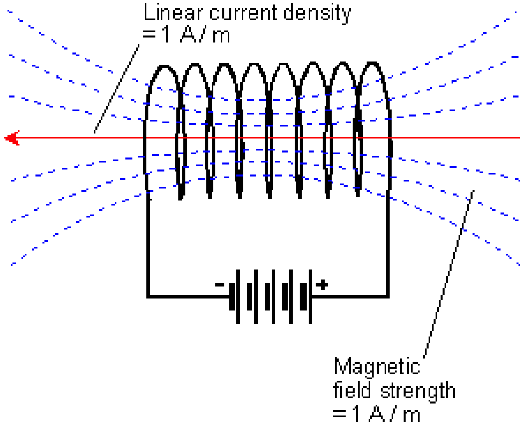
Hans Christian Oersted
1777 - 1851

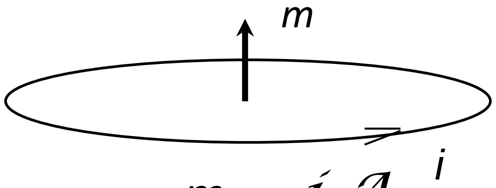
Oersted's famous 1820 experiment showed that a current-carrying conductor created a field everywhere *perpendicular* to the wire

Within a week of the news reaching Paris in August 1820, **Andre-Marie Ampère** and **Francois Arago** showed that a current-carrying coil acts as a magnet, especially when wound into a solenoid. Ampère measured the force between conductors, and proposed that huge internal electric currents (‘amperian currents’) were responsible for the magnetism of iron.



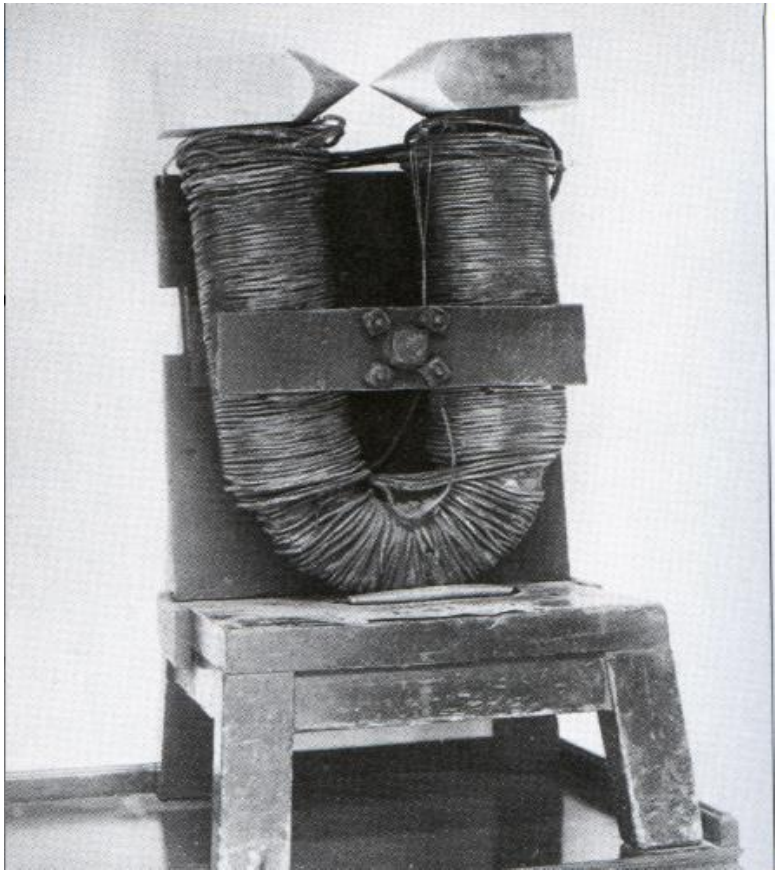
Laplace
Poisson
Fresnel
Fourier
Biot
Savart





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

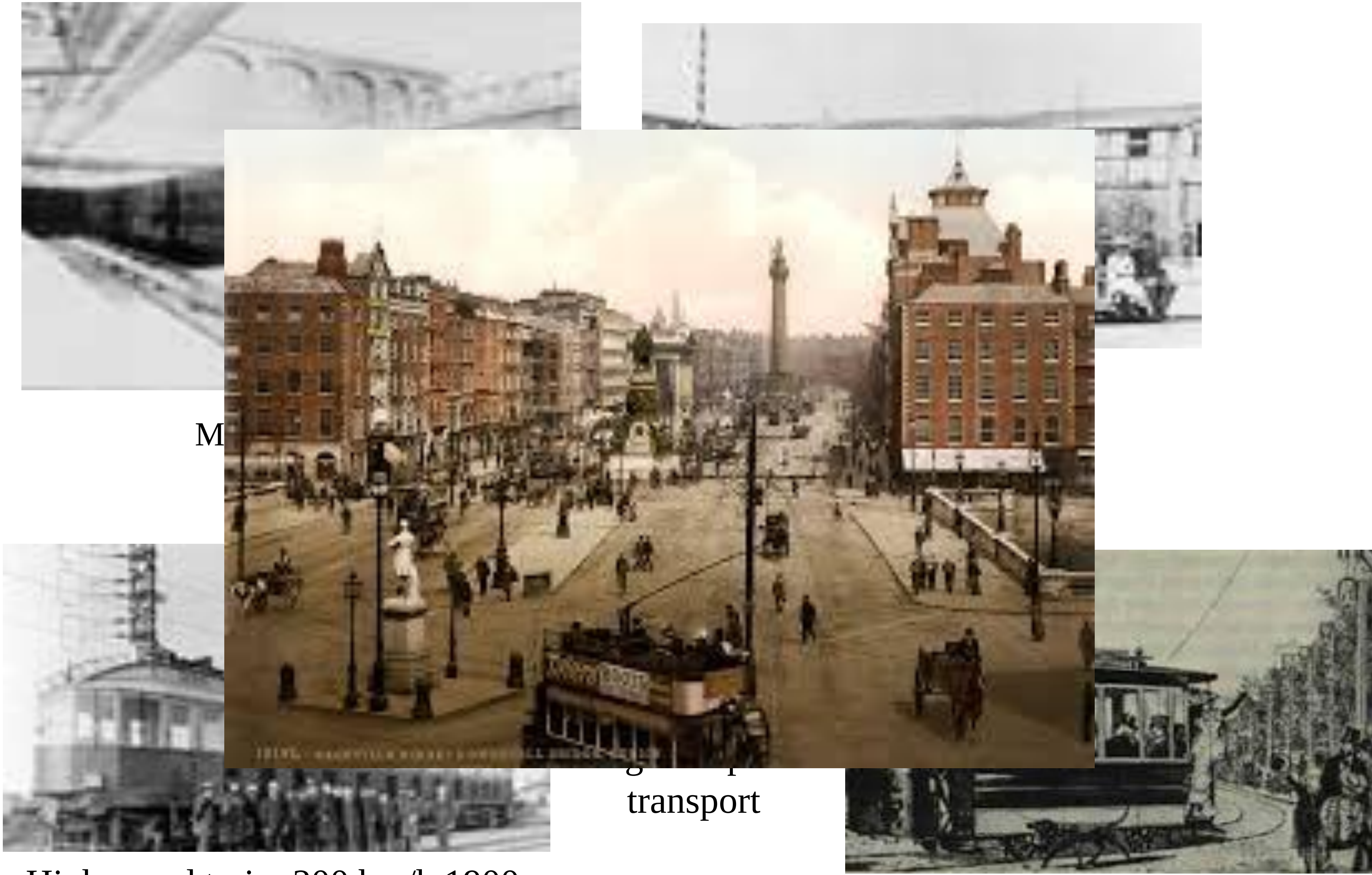
It was a field day for experimentalists. The most intuitive and talented of all was **Michael Faraday**, who made a simple motor, discovered electromagnetic induction in 1831 and found a connection between magnetism and light (magneto-optic Faraday effect).



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 pracical 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 Morely 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 Poulson invents magnetic recording



M

transport

High speed train; 200 km/h 1900

Trams

Maxwell's equations…

$$\boxed{\begin{gathered}\nabla . \boldsymbol{B} = \boldsymbol{0} \\ \varepsilon_0 \nabla . \boldsymbol{E} = \rho \\ \nabla \times \boldsymbol{B} = \boldsymbol{\mu_0}(\boldsymbol{j} \ + \varepsilon_0 \frac{\partial \boldsymbol{E}}{\partial t}) \\ \nabla \times \boldsymbol{E} = -\frac{\partial \boldsymbol{B}}{\partial t}\end{gathered}}$$

…in free space

$$\boxed{\begin{gathered}\nabla . \boldsymbol{B} = \boldsymbol{0} \\ \nabla . \boldsymbol{D} = \rho \\ \nabla \times \boldsymbol{H} = \boldsymbol{j} \ + \varepsilon_0 \frac{\partial \boldsymbol{E}}{\partial t} \\ \nabla \times \boldsymbol{E} = -\frac{\partial \boldsymbol{B}}{\partial t}\end{gathered}}$$

…in matter

In *free space* two fields, ***E*** (N/C) and ***B*** (T) are needed, *in matter* there are four.
The two magnetic fields ***B*** (T) and ***H*** (A/m) are related: $\boxed{\boldsymbol{B} = \mu_0 (\boldsymbol{H} + \boldsymbol{M})}$

Magnetization
M* = *m*/*V

The fields are related to the charge density ρ (C/m^3),and the current density ***j*** (A/m^2) at a point and two constants.

$\boxed{c = 1/\sqrt{(\varepsilon_0 \mu_0)}}$ $c = 2.998 \times 10^8$ m/s (velocity of light)

Also, the Lorenz force on a moving charge q, velocity **v**

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

$\mu_0 = 4\pi\ 10^{-7}$ T m/A
$\varepsilon_0 = 8.85\ 10^{-12}$ C V/m

3. The Information Revolution

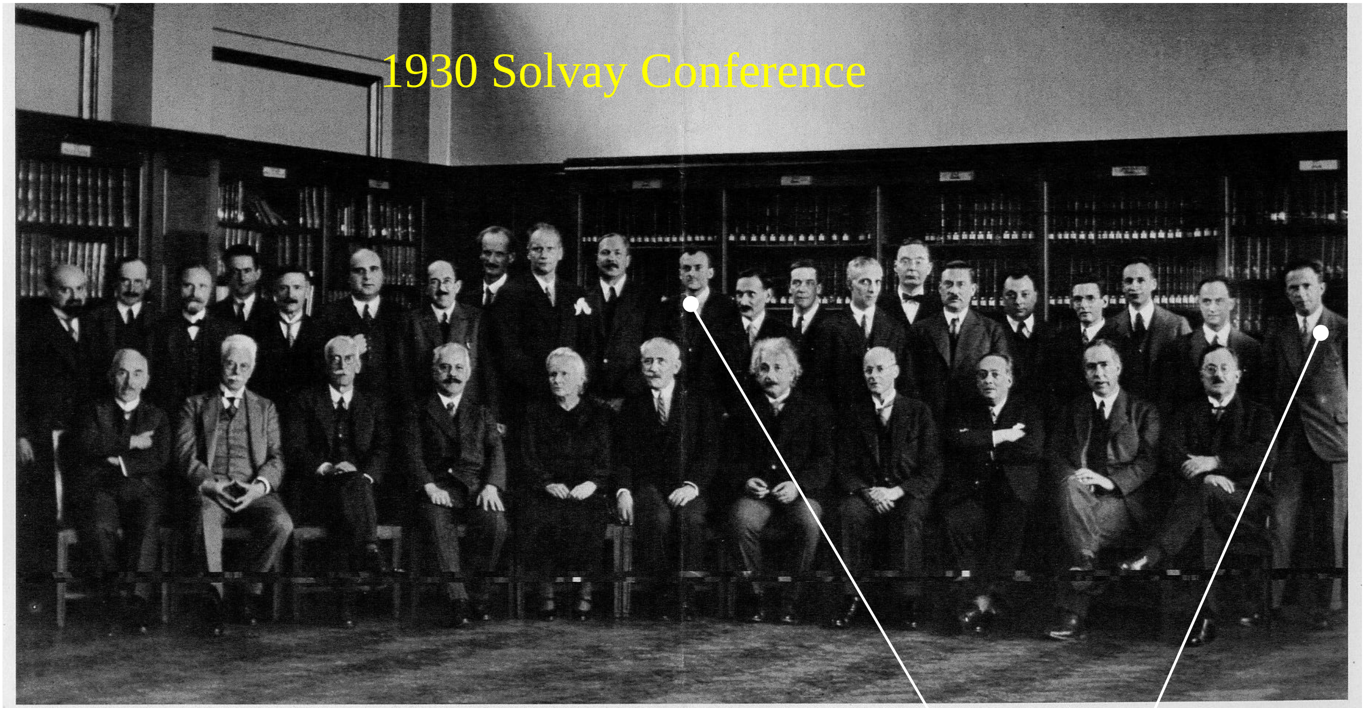
Magnetism Understood 1905 - 1930

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

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

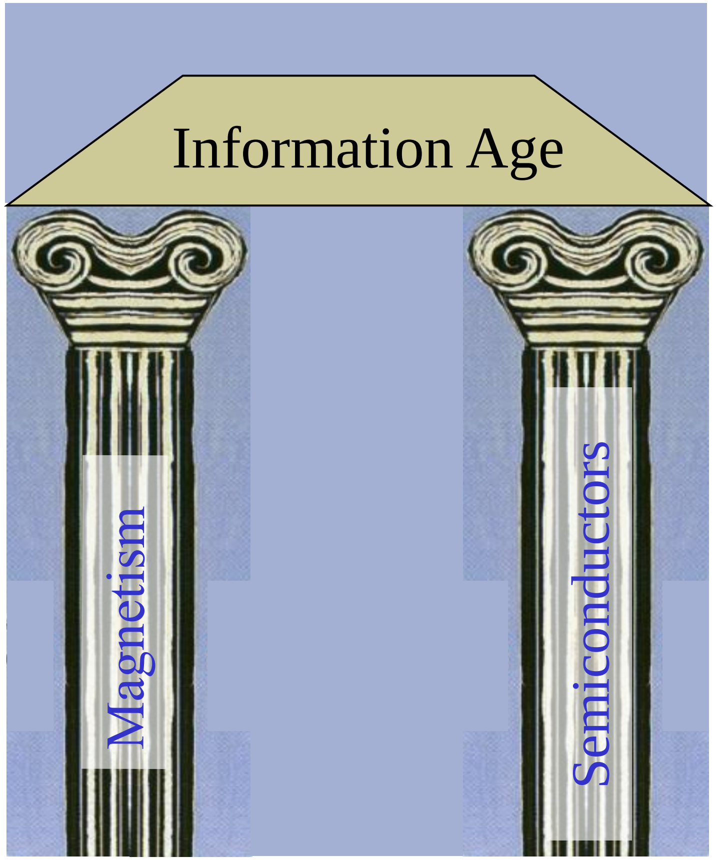
m represents the magnetic moment, mainly localized on the *atoms*

J represents the exchange coupling of electron *spins*.



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 to difficult to solve... P.A.M. Dirac

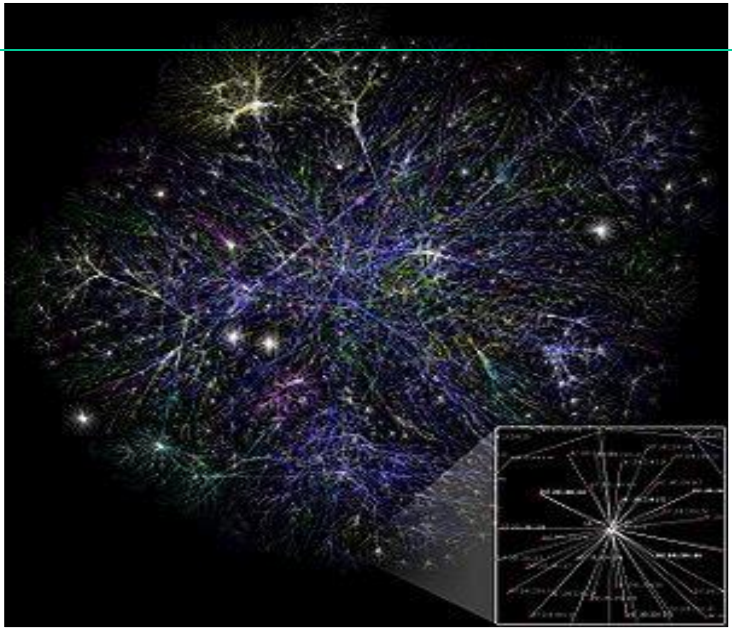
Magnetism and semiconductor physics are the two pillars supporting information technology.



Magnets store information

Semiconductors process information

10 x **10^{21} bytes** of new information are generated every year, most is stored … *Magnetically*

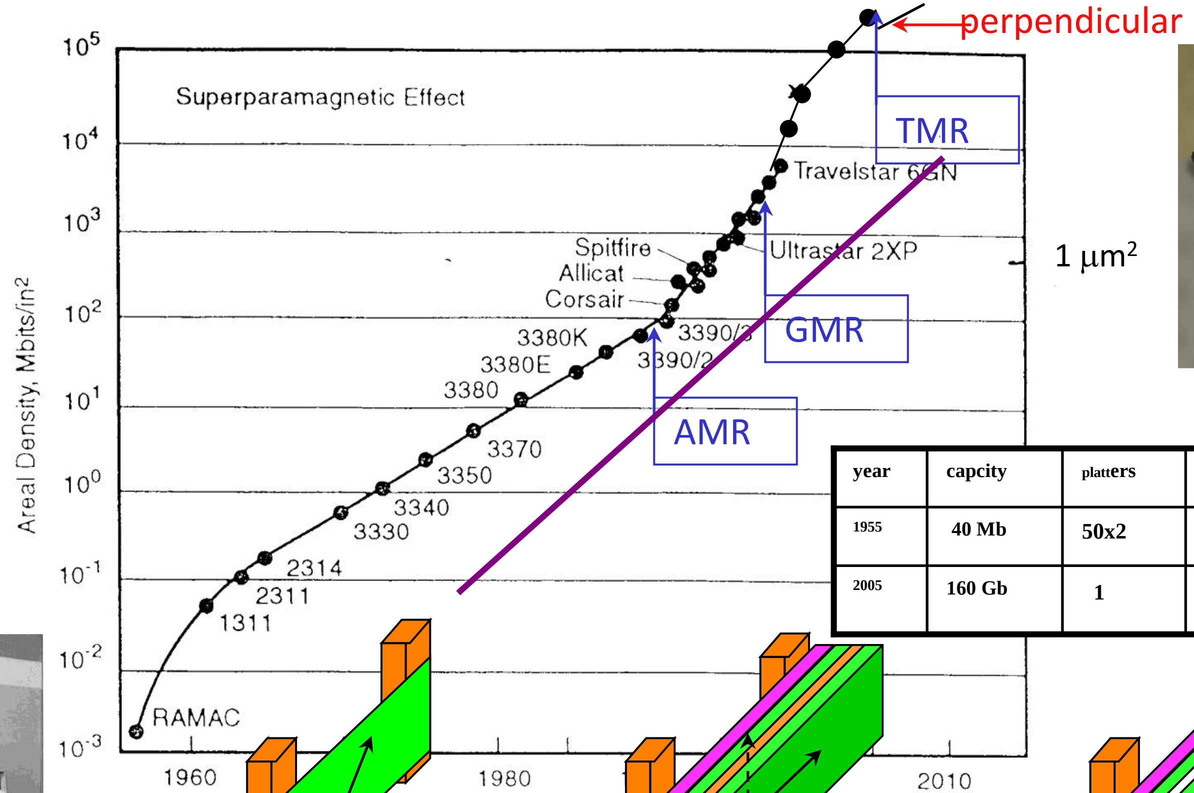


Giga	9
Tera	12
Peta	15
Exa	18
Zetta	21
Yotta	24

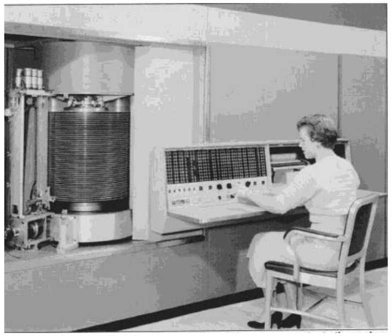
Every year we make more transistors and magnets in our fabs than we grow grains of wheat and rice in our fields.

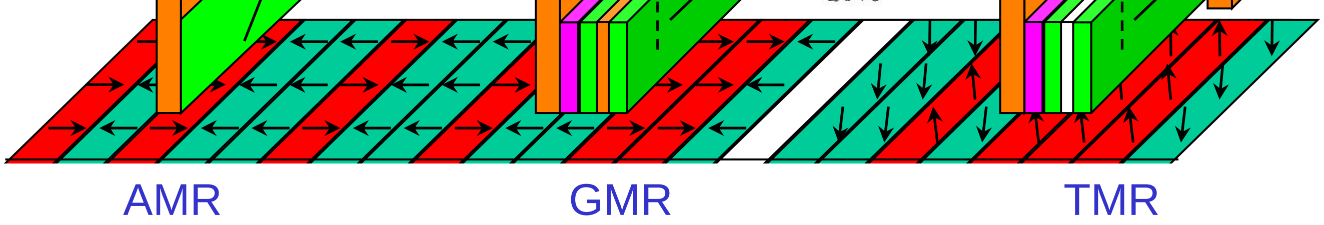
INTEL make 5 10^9 transistors per second. (20 10^{16} p/a)

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 exobit (10^{21}bits) of data is stored



year	capcity	platters	size	rpm
1955	40 Mb	50x2	24”	1200
2005	160 Gb	1	2.5”	18000





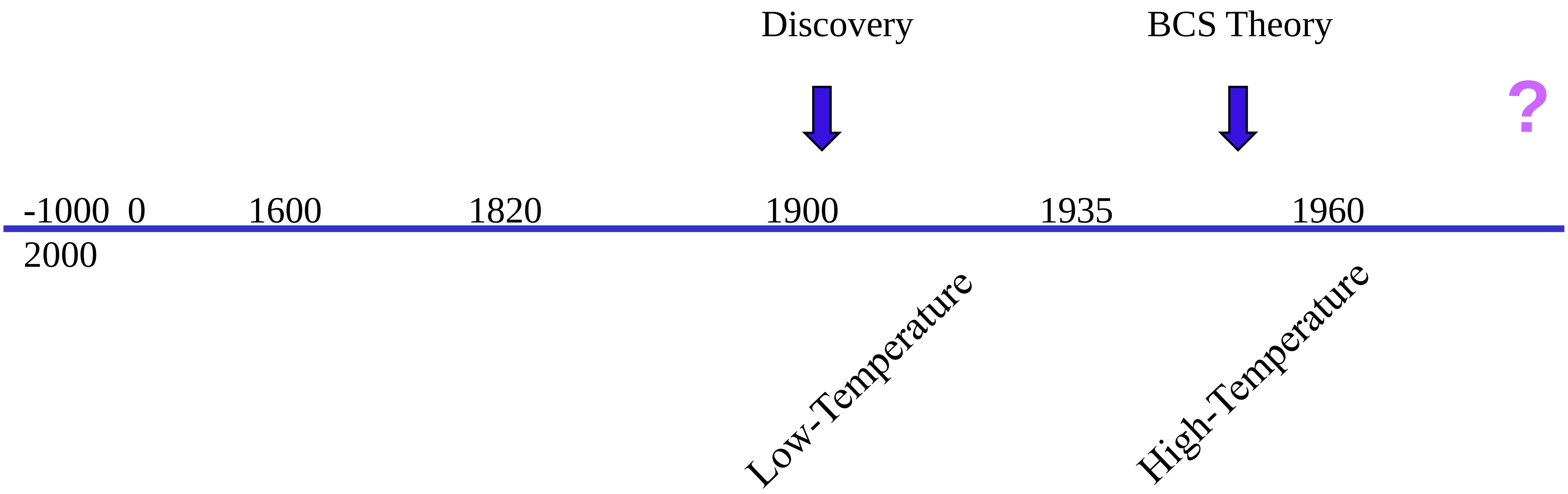
A Server - Facebook have 30,000 of them

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

This is what the “cloud” *looks* like

1.4 A little history: Superconductivity

Superconductivity has not yet changed the world



Discovery

BCS Theory

?

-1000 0

2000

1600

1820

1900

1935

1960

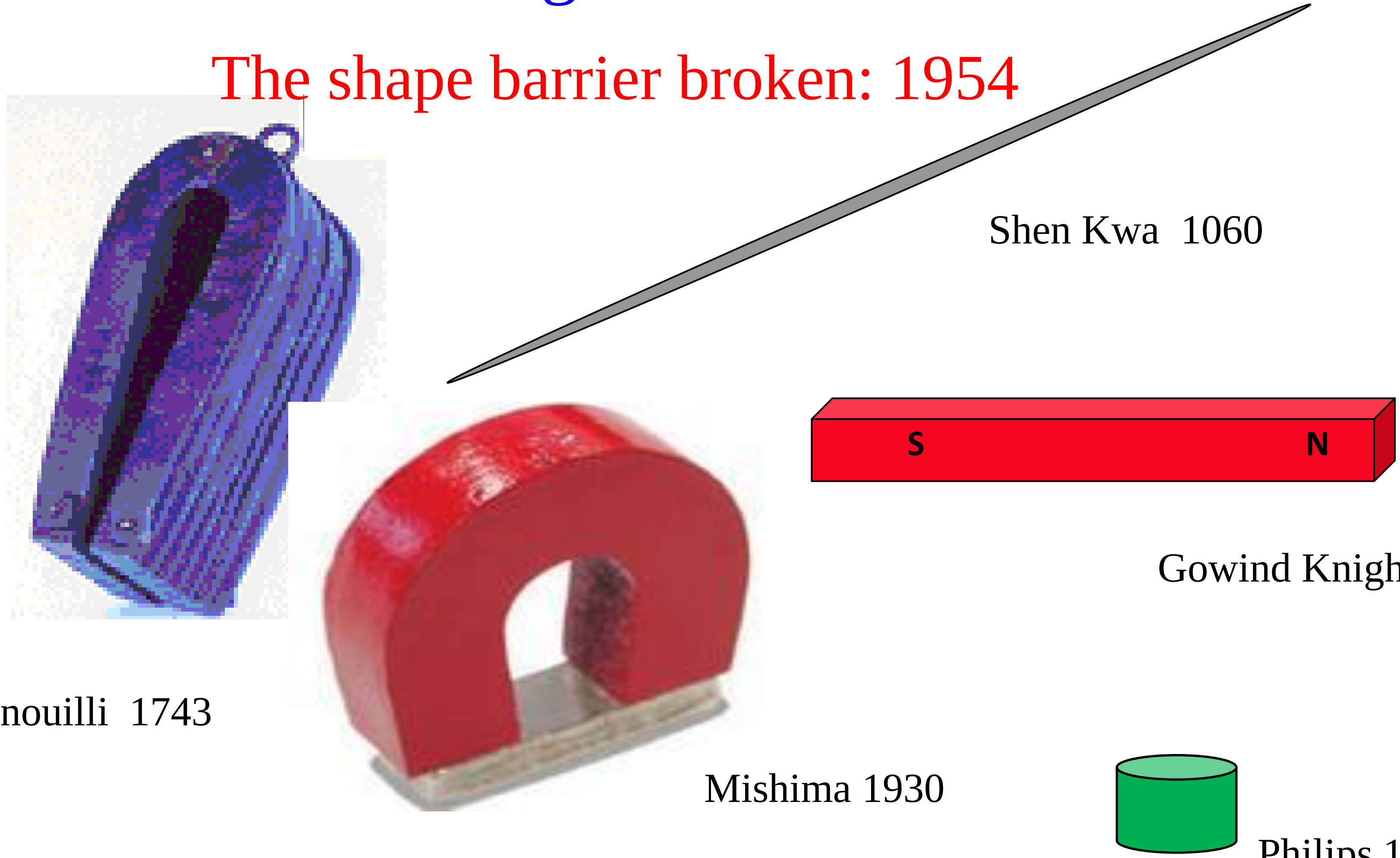
Low-Temperature

High-Temperature

Two eras of Superconductivity

1.5 Modern Breakthroughs

The shape barrier broken: 1954



Shen Kwa 1060

Gowind Knight 1760

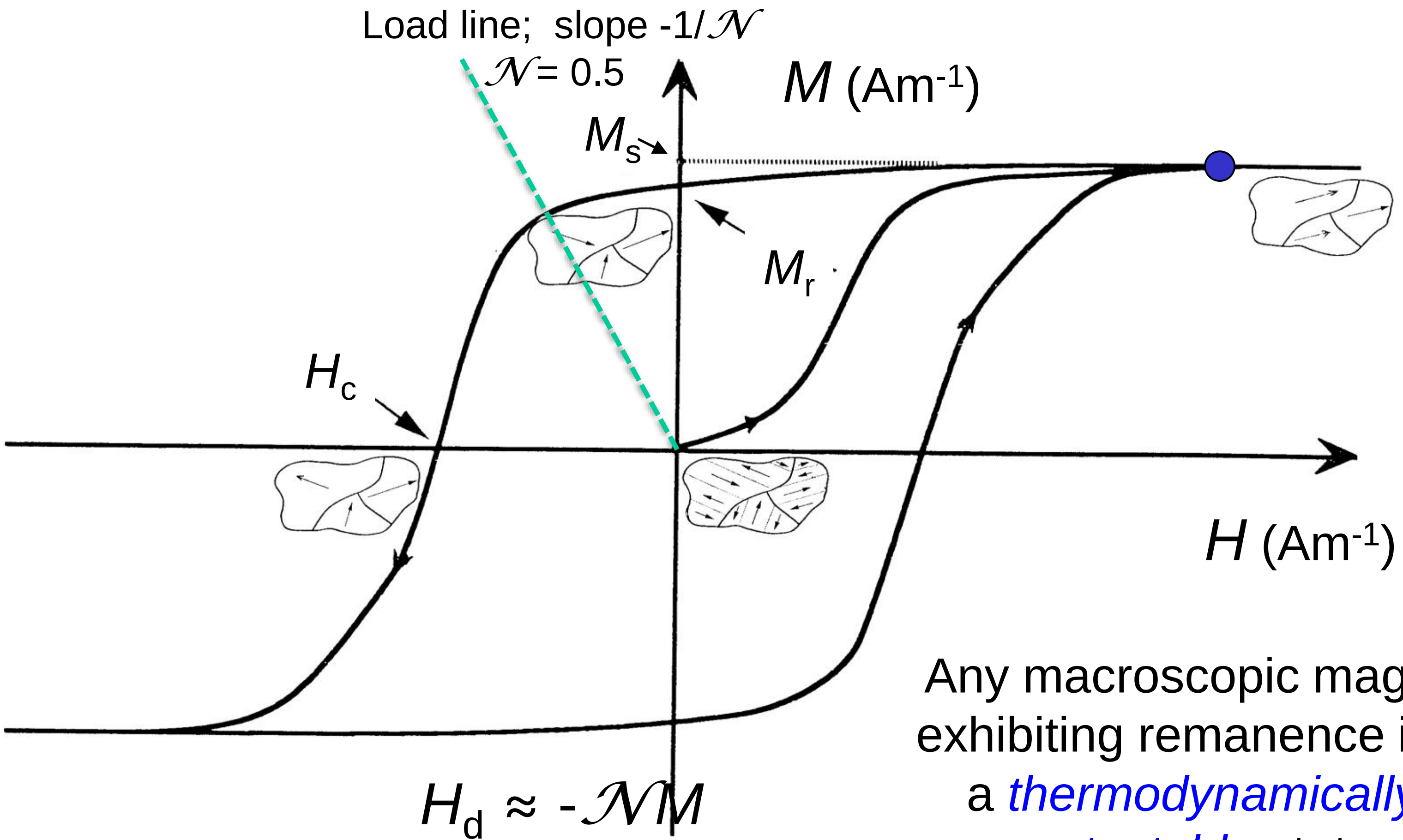
Daniel Bernouilli 1743

Mishima 1930

Philips 1952

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

The hysteresis loop (hard magnet)

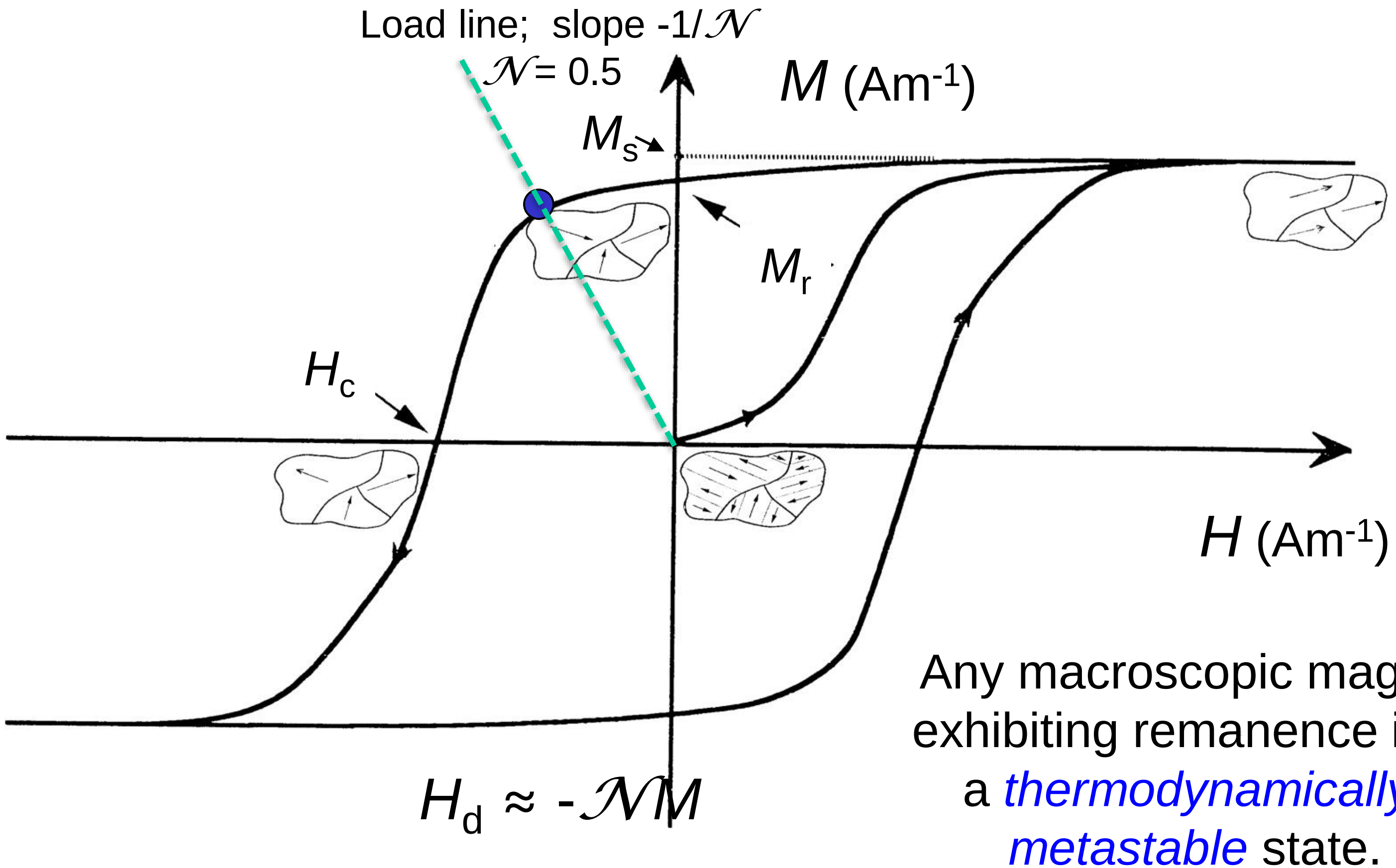


$H_d \approx -\mathcal{N}M$

Any macroscopic magnet exhibiting remanence is in a *thermodynamically-metastable* state.

Magnetostatic energy $E_{ms} = ½\mathcal{N}\mu_0 M^2$

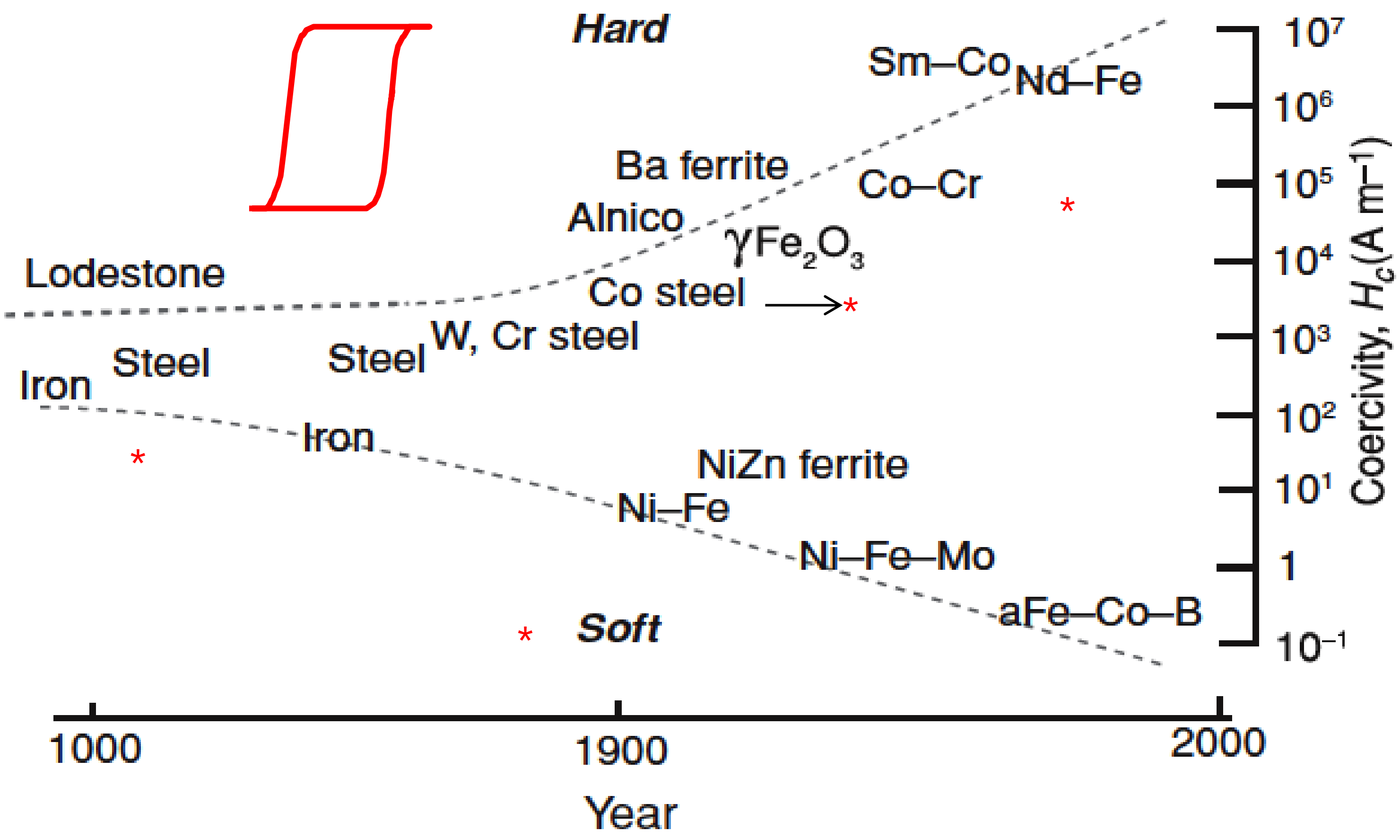
The hysteresis loop (hard magnet)



Magnetostatic energy $E_{ms} = \frac{1}{2}\mathcal{N}\mu_0 M^2$

Any macroscopic magnet exhibiting remanence is in a *thermodynamically-metastable* state.

Coercivity



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

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

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

2. Basic ideas

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

It is assumed that there is no time-dependence, i.e. we are in the magnetostatic regime

Units and dimensions in magnetism are discussed.

View the **MOOC 1.1** *before* the lecture. We begin with *magnets*.

See Richard Feynman Magnets 7'
https://www.youtube.com/watch?v=Q1lL-hXO27Q

Introduction

E & M

Basic Ideas

M. B, H

Energy

Quantum theory

Magnetism of the electron

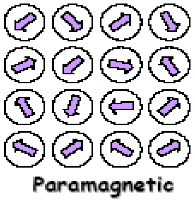
Magnetism of the atom with one or more electrons

Molecular field theory

single electron magnetism.

Paramagnetism

multi-electron atoms

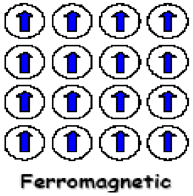


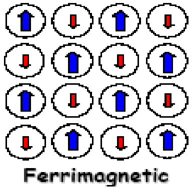
Disordered

Magnetism of interacting atoms Ferromgnetism

Other topics

multi-atom solids



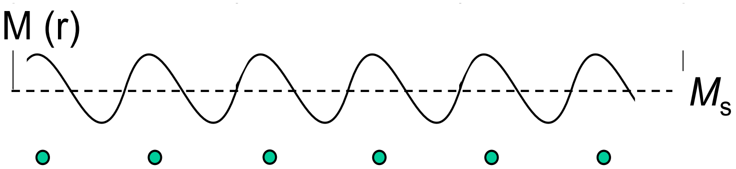


Ordered

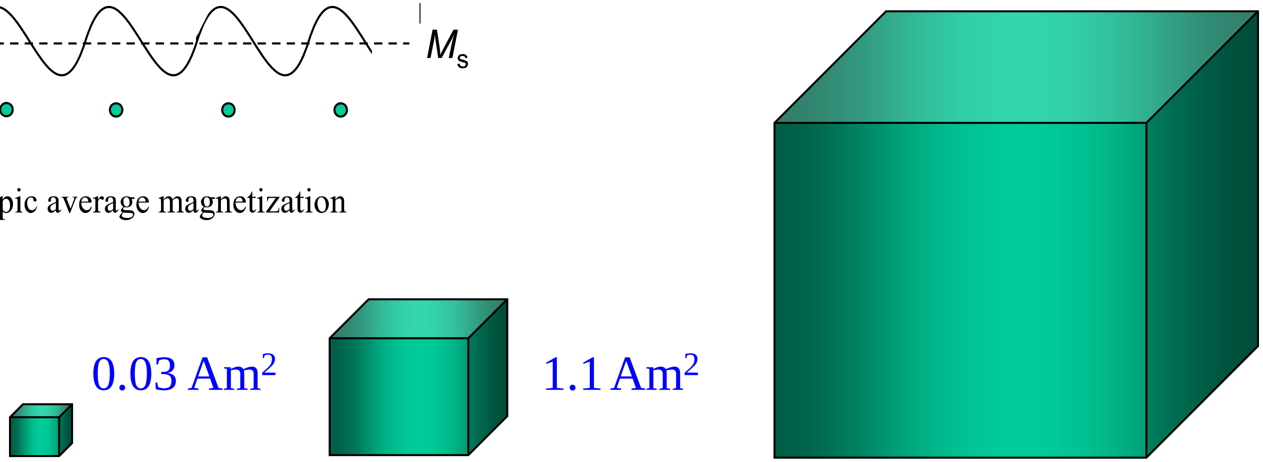
Applications

2.1 Magnets and magnetization

MOOC 1.1 13'



The mesoscopic average magnetization



m is the magnetic (dipole) moment of the magnet & it is proportional to volume

$$\boxed{\boldsymbol{m} = \boldsymbol{M}V}$$

magnetic moment

magnetization

volume

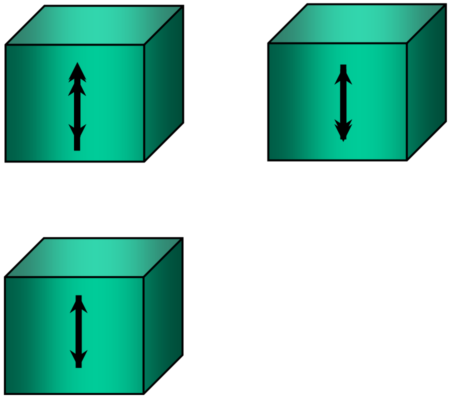
If they are made of $Nd_2Fe_{14}B$
($M \approx$ 1.1 MAm^{-1})

What are the moments?

Magnetic moment is a property of a particular magnet. [Am^2]
Magnetization is the property of the material. [Am^{-1}].

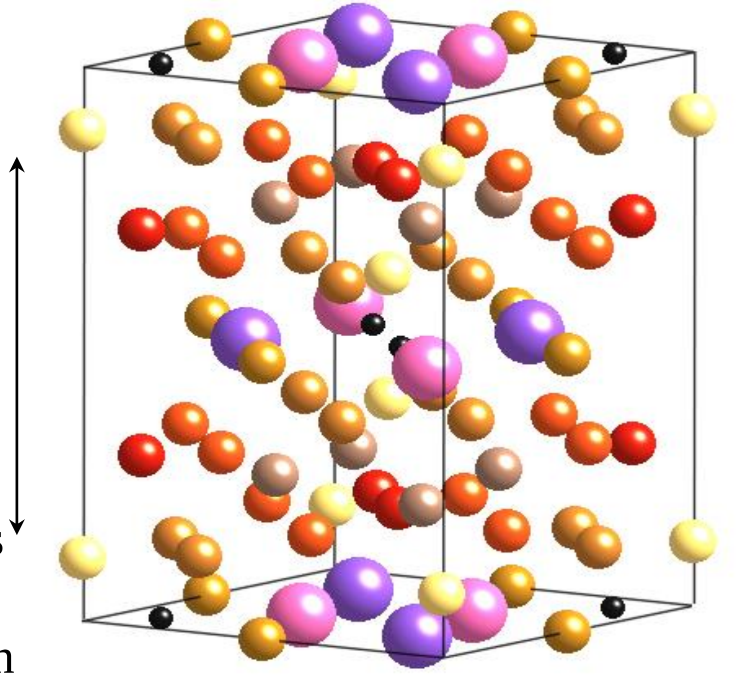
Magnetic moment – a polar vector

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.



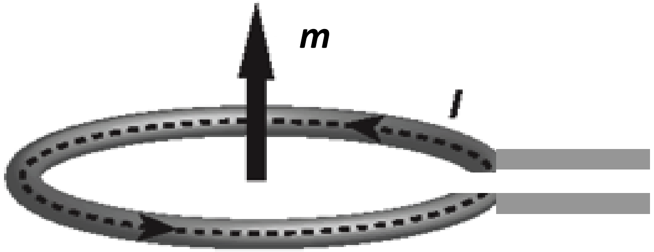
↑↑	Weak repulsion
↑↓	Weak attraction
←←	Strong attraction
←→	Strong repulsion

$Nd_2Fe_{14}B$



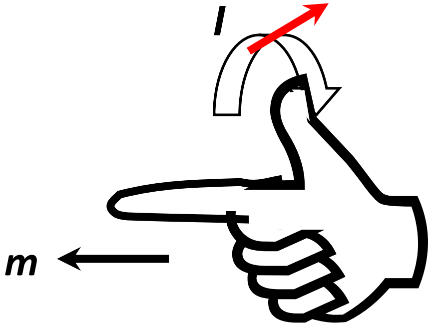
Tetragonal crystal axis is the axis of magnetization

Units



Ampère (1821) - A current loop or coil is equivalent to a magnet.

What do the units mean?
m – A m^2
M – A m^{-1}



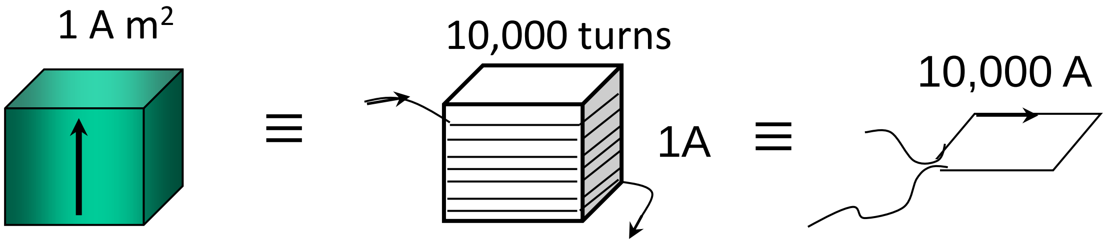
Right-hand corkscrew

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

area of the loop

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

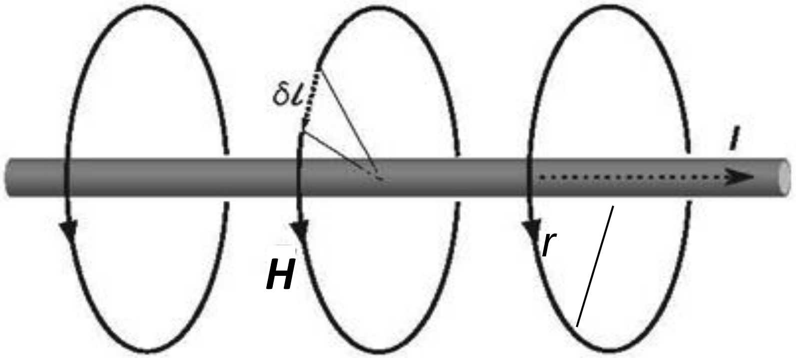
number of turns

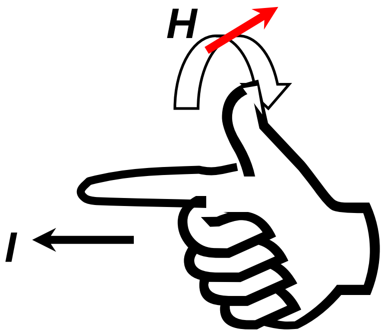


Permanent magnets win over electro-magnets at small sizes

Magnetic field $\boldsymbol{H}$ due to a current I

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





Right-hand corkscrew

The relation between electric current and magnetic field was discovered by **Hans-Christian Øersted** (1820).

Earth's field ≈ 40 A m^{-1}

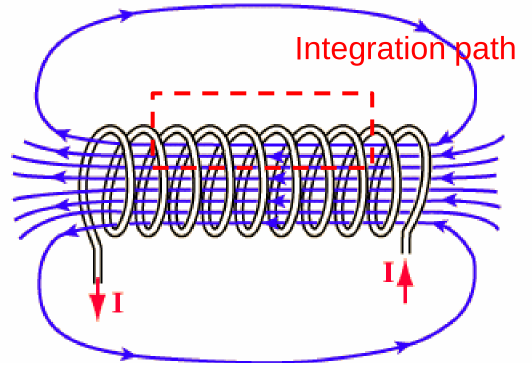
$$\boxed{\oint \boldsymbol{H}.d\boldsymbol{l} = I}$$

Ampère's law

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

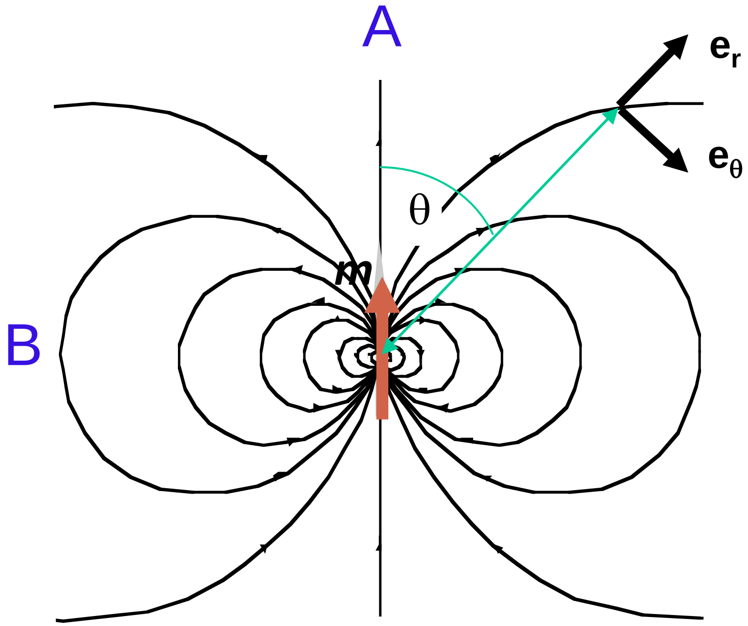
Derive from M3
(slide 21)
$\nabla \times \boldsymbol{B} = \mu_0 \boldsymbol{j}$
+
Stoke's Theorem

If $I = 1$ A, $r = 1$ mm
$H = 159$ A m^{-1}



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

Magnetic field due to a moment *m*



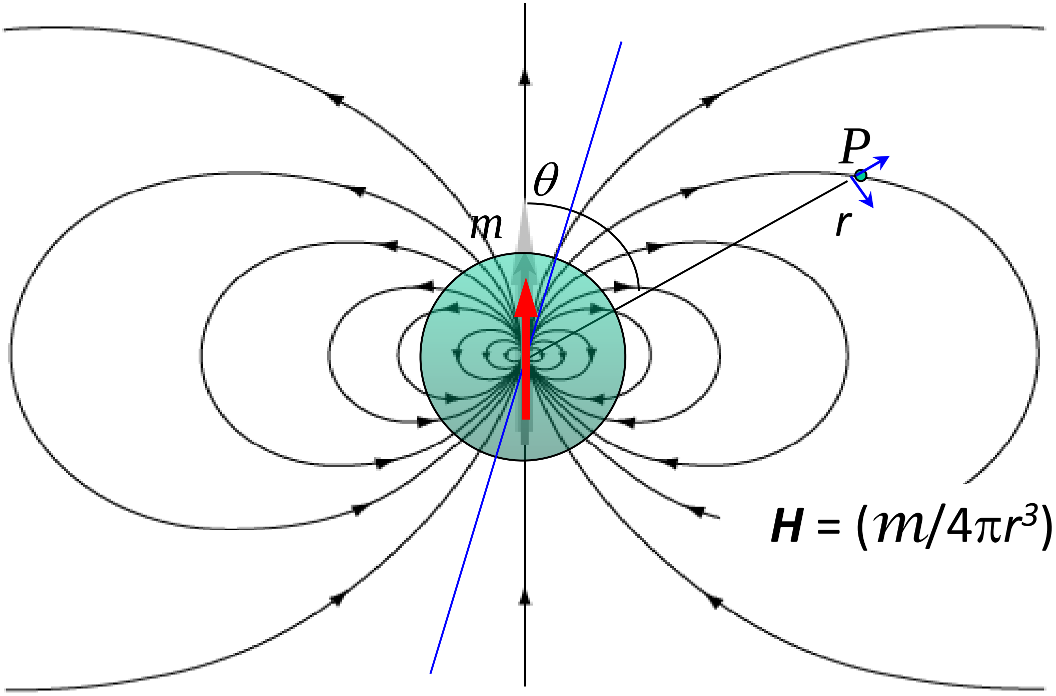
Dipole field

$$\boxed{\boldsymbol{H} = \frac{m}{4\pi r^3}\left(2\cos\theta\,\boldsymbol{e_r} - \sin\theta\,\boldsymbol{e_\theta}\right)}$$

It is independent of ϕ

Note: The field is *anisotropic*: At ‘A’, a point ***r*** on the axis, it is twice as big as at ‘B’ a point ***r*** perpendicular to the axis, and oppositely directed.

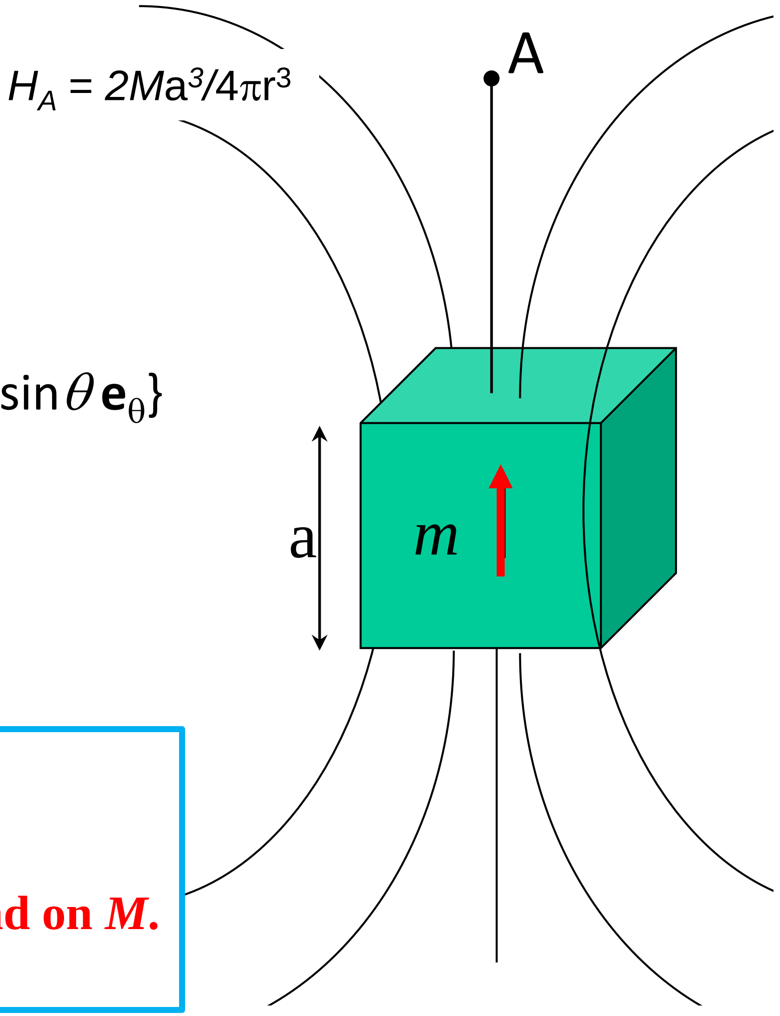
Magnetic field due to a moment *m*; Scaling



$$\boldsymbol{H} = (m/4\pi r^3)\{2\cos\theta\,\mathbf{e}_r - \sin\theta\,\mathbf{e}_\theta\}$$

Just like the field of an electric dipole

Why does magnetism lend itself to miniaturization ?

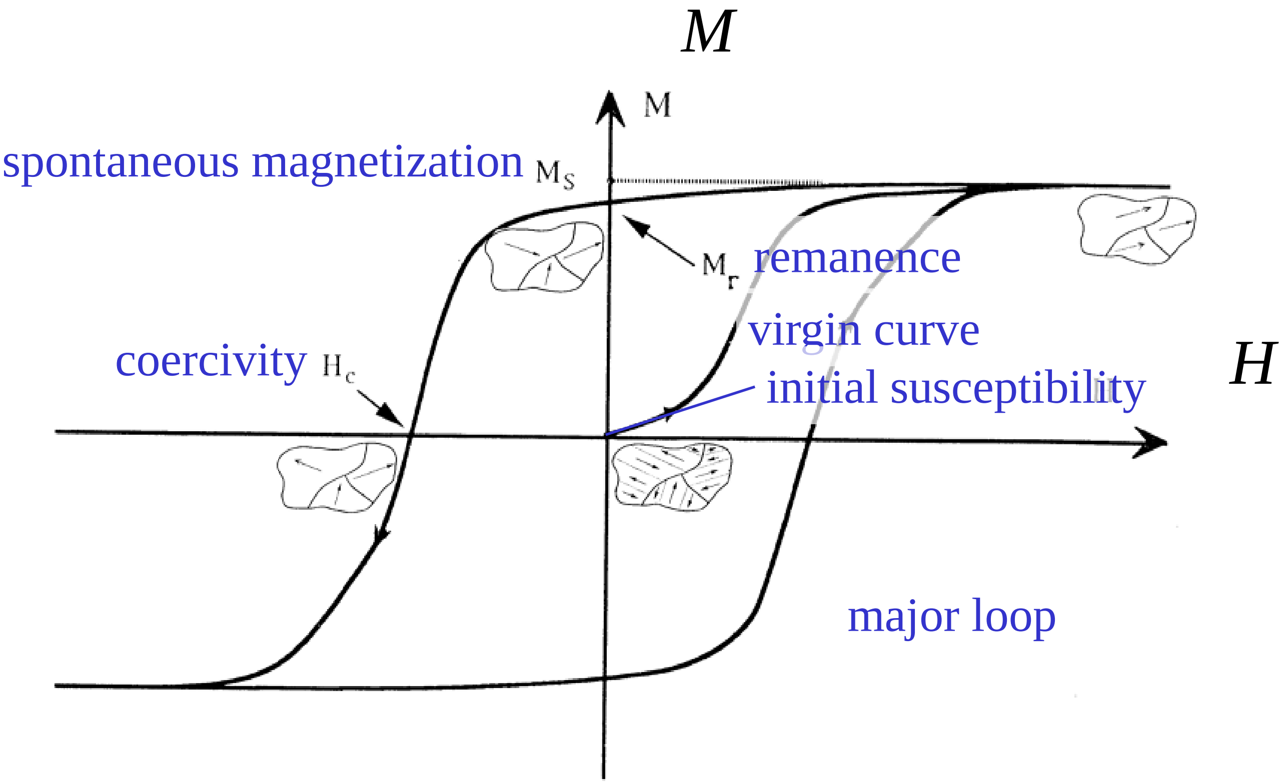


Estimate the average magnetization of the Earth. (r_e = 6400 km)

If a = 0.01m, $r = 2a$, M = 1 MA m^{-1}
$H_A = M/16\pi \approx$ 20 kA m^{-1}

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

2.2 Magnetization curves - Hysteresis loop



spontaneous magnetization

remanence

virgin curve

coercivity

initial susceptibility

major loop

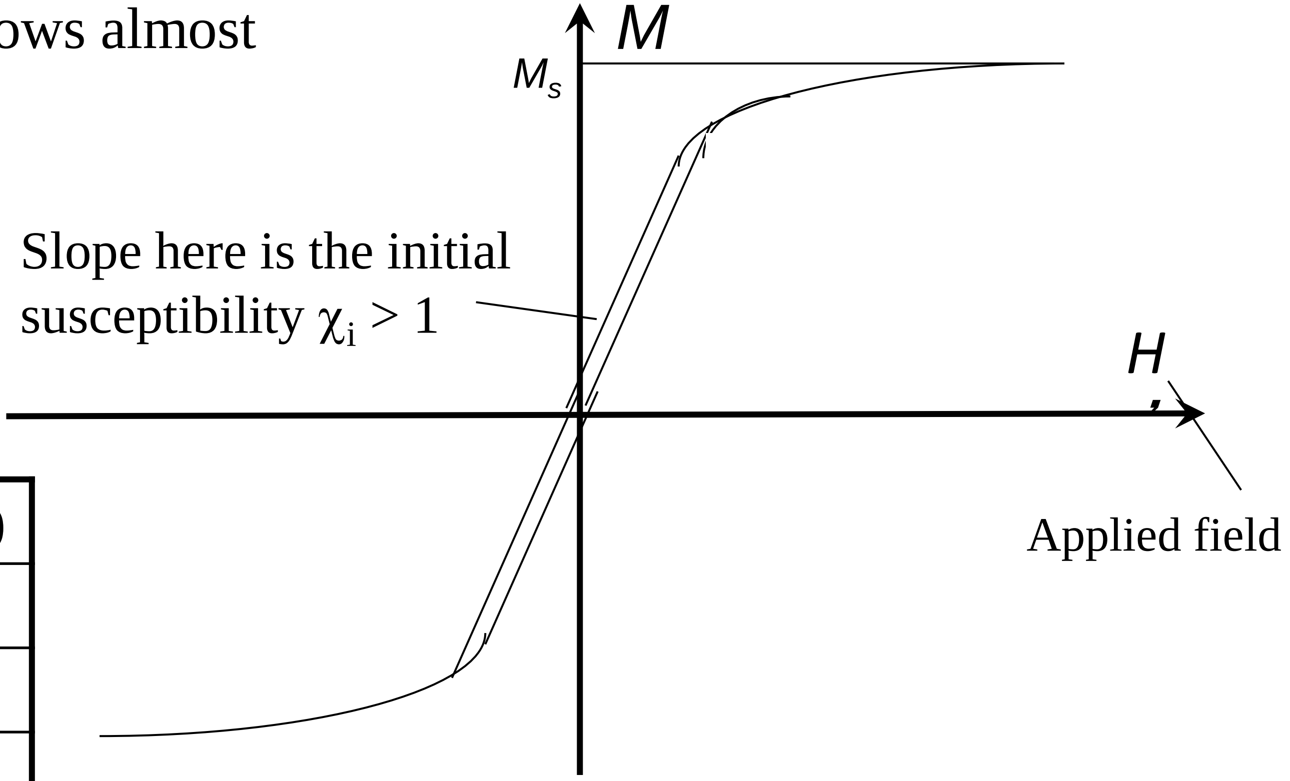
The hysteresis loop shows the irreversible, nonlinear response of a ferromagnet to a magnetic field. It reflects the arrangement of the magnetization in ferromagnetic *domains*. A broad loop like this is typical of a *hard* or *permanent* magnet.

Soft magnets

A *soft* or *temporary* magnet shows almost no hysteresis.

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

	M_s (MAm^{-1})	T_C (°C)
Fe	1.71	771
Ni	0.49	355
$Fe_{20}Ni_{80}$	0.83	570

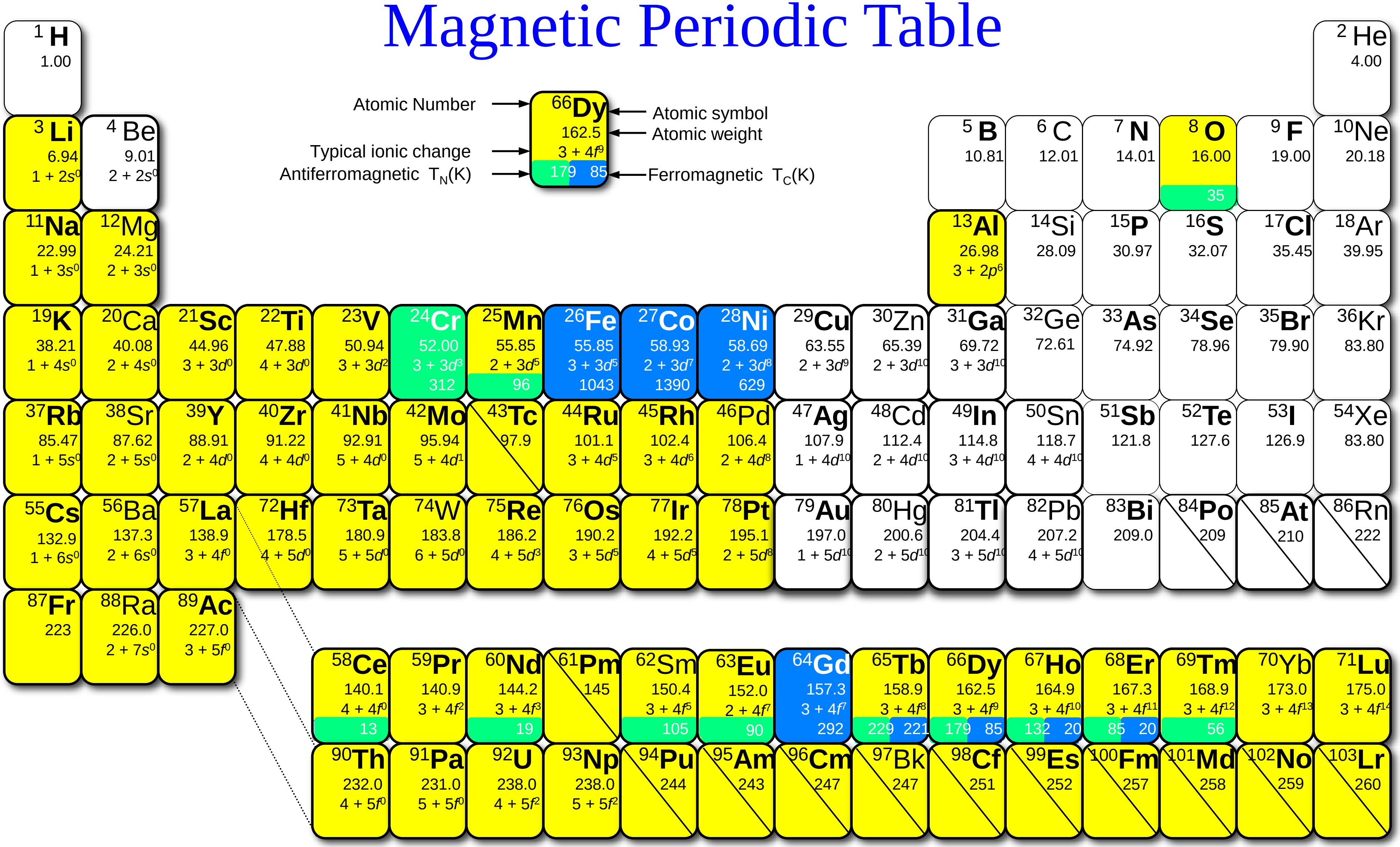


Slope here is the initial susceptibility $\chi_i > 1$

Applied field

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 .

Magnetic Periodic Table



Atomic Number → 66 **Dy** ← Atomic symbol

162.5 ← Atomic weight

Typical ionic change → 3 + 4f^9

Antiferromagnetic T_N(K) → 179 85 ← Ferromagnetic T_C(K)

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

▭ Nonmetal

▭ Metal

⧄ Radioactive

⬜ Diamagnet

🟨 Paramagnet

BOLD Magnetic atom

🟦 Ferromagnet T_C > 290K

🟩 Antiferromagnet with T_N > 290K

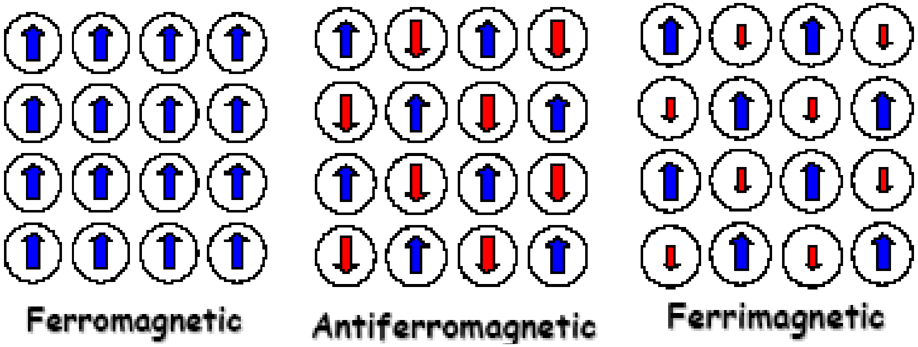
🟩🟦 Antiferromagnet/Ferromagnet with T_N/T_C < 290 K

Paramagnets, diamagnets & antiferromagnets.

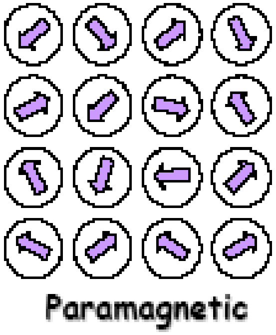
Only a few elements and alloys are **ferromagnetic**. (See the Magnetic Periodic Table). The atomic moments in a ferromagnet order spontaneously parallel to each other.

Most have no spontaneous magnetization, and they show only a **very weak response** to a magnetic field. $\boldsymbol{M} = \chi \boldsymbol{H}$

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



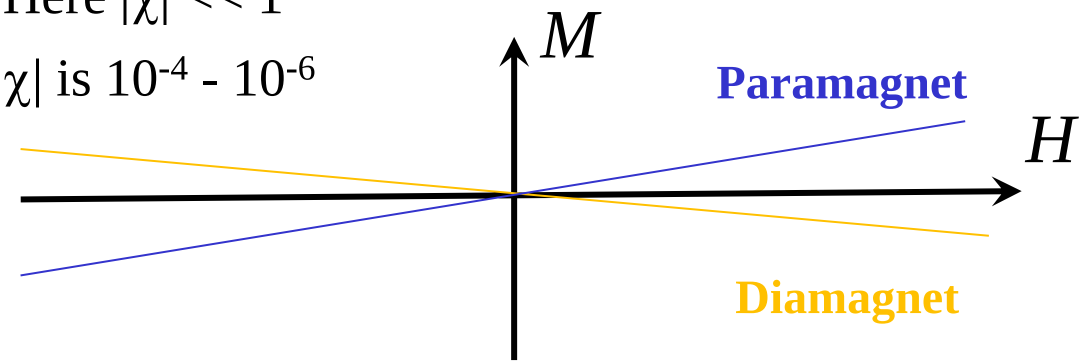
Ordered $T < T_c$



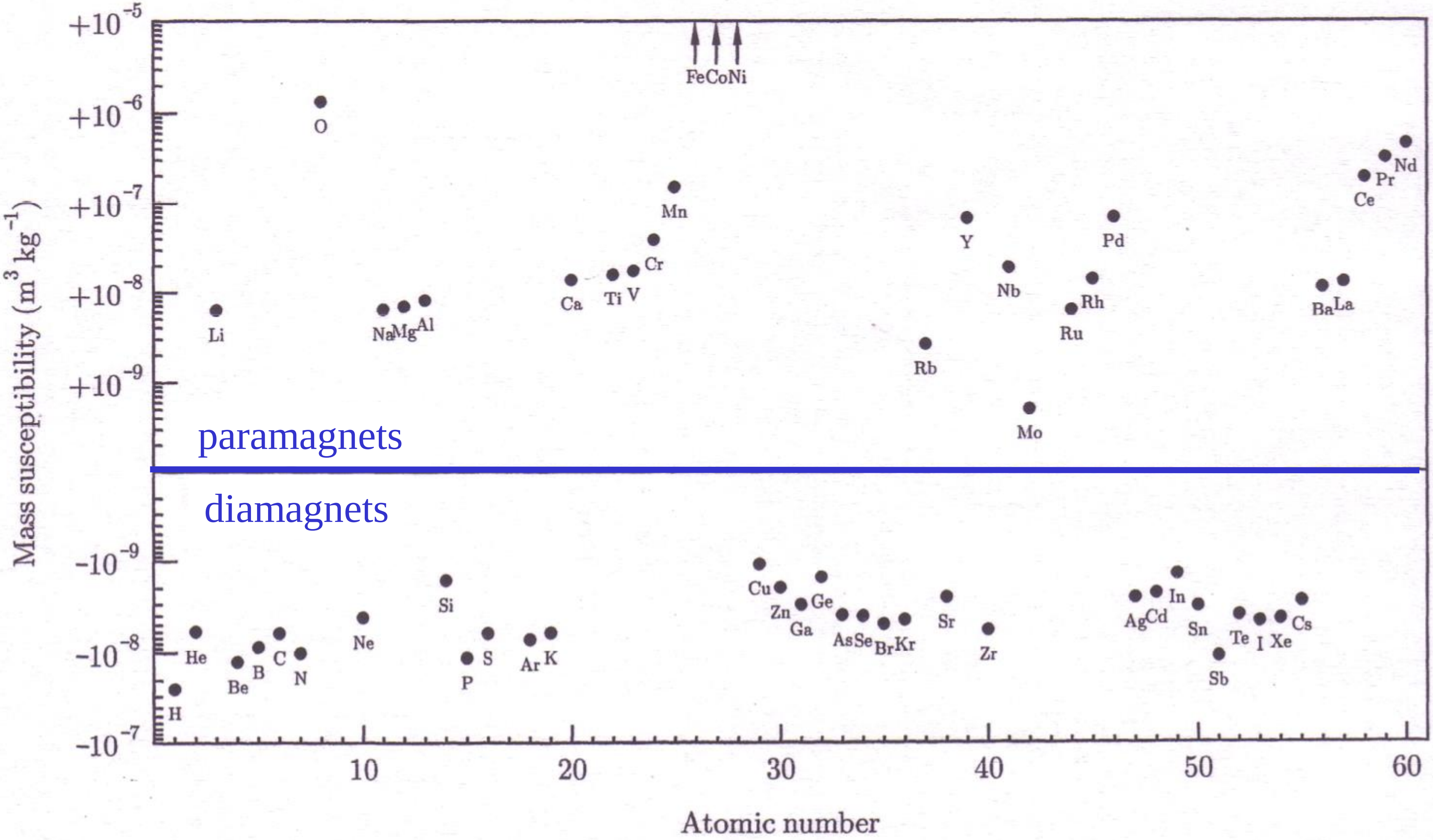
Disordered $T > T_c$

Here $|\chi| \ll 1$

$|\chi|$ is 10^{-4} - 10^{-6}



Susceptibility of the elements



Introduction

E & M

Basic Ideas

M. B, H

Energy

Quantum theory

Magnetism of the electron

Molecular field theory

single electron magnetism.

Magnetism of the atom with one or more electrons

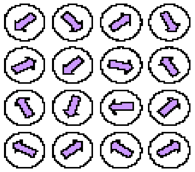
multi-electron atoms

Paramagnetism

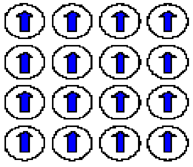
Magnetism of interacting atoms Ferromgnetism

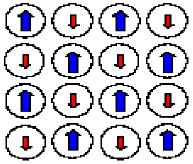
Other topics

multi-atom solids


Paramagnetic

Disordered


Ferromagnetic


Ferrimagnetic

Ordered

Applications

2.3 The magnetic fields fields ***B*** and ***H*:** MOOC1.2 16'

The ***B***-field

B is the primary magnetic field. It satisfies Maxwell's equation. (slide 21) M1

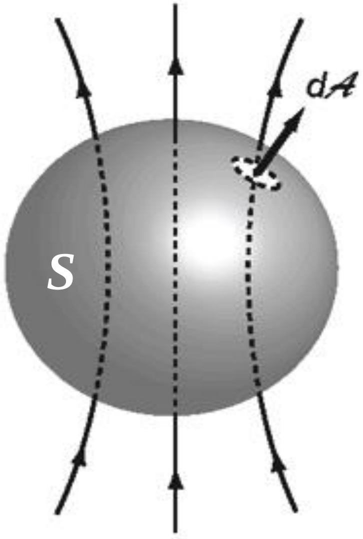
$$\boxed{\nabla . \boldsymbol{B} = 0}$$

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

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

$$\boxed{\int_S \boldsymbol{B} . dA = 0}$$

Gauss's law



In other words the flux Φ (= *B*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

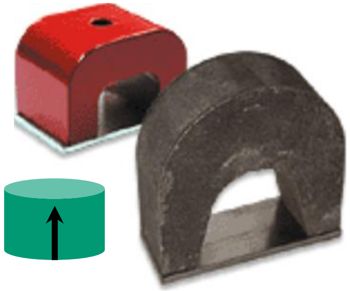
(for ***H*** in A m^{-1} multiply by 800,000)

Earth 50 μT

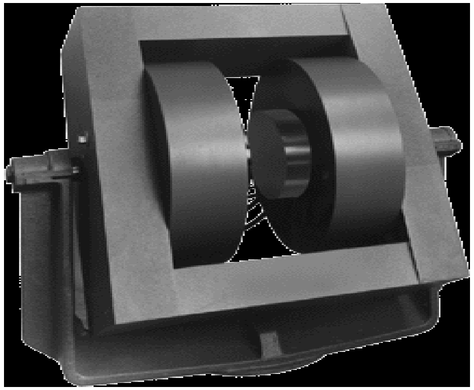
Helmholtz coils 10 mT

Human brain 1 fT

Magnetar 10^{12} T



Permanent magnets 0.5 T



Electromagnet 1 T

Superconducting magnet 10 T

2.3 The magnetic fields fields *B* and *H*:

The *H*-field

The other Maxwell equation for ***B*** is M3

$$\nabla \times \boldsymbol{B} = \mu_0(\boldsymbol{j} + \varepsilon_0 \partial \boldsymbol{E}/\partial t).$$

'$\nabla \times$' is the rotation (curl) of a vector,

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

In a static situation

$$\boxed{\nabla \times \boldsymbol{H} = \mu_0 \boldsymbol{j}}$$

The equivalent integral formulation is **Ampere's law**

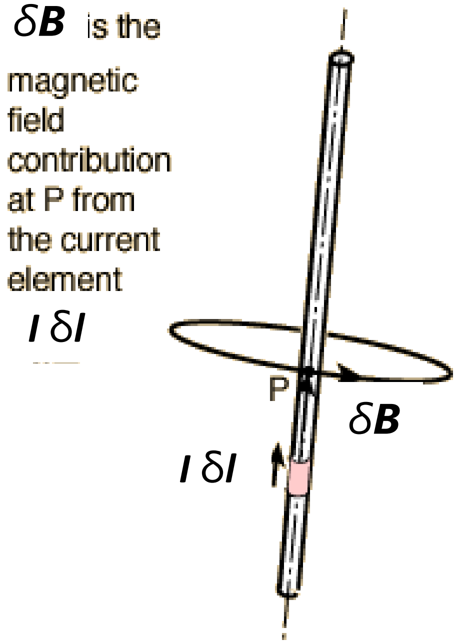
$$\boxed{\oint \boldsymbol{B}.\mathrm{d}\boldsymbol{l} = \mu_0 I}$$

A different formulation is the **Biot-Savart Law**, which gives the field due to a current element $I\,\delta\boldsymbol{l}$

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

M1 and M3 follow

Field at the centre of a current loop $B = \mu_0 I/2r.$



The current density $\boldsymbol{j} = \boldsymbol{j}_c + \boldsymbol{j}_M$, where $\boldsymbol{j}_c$ is the **conduction** current density, and

$$\boldsymbol{j}_M = \nabla \times \boldsymbol{M}$$

is the current density associated with the **magnetization**.

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

Since

$$\nabla \times \boldsymbol{B} = \mu_0(\boldsymbol{j}_c + \boldsymbol{j}_M)$$

it follows that

$$\nabla \times (\boldsymbol{B}/\mu_0 - \boldsymbol{M}) = \boldsymbol{j}_c.$$

We just define

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

or

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

H has the same units as ***M***

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

In point form,

$$\nabla \times \boldsymbol{H} = \boldsymbol{j}_{\mathrm{c}}$$

or in integral form

$$\boxed{\oint \boldsymbol{H}.\mathrm{d}\boldsymbol{l} = I_{\mathrm{c}}}$$

The $\boldsymbol{H}$-field is not solenoidal, because $\nabla . \boldsymbol{H} = 0$ does not always hold. In fact $\nabla . \boldsymbol{H} \neq 0$ wherever $\nabla . \boldsymbol{M} \neq 0$, which means that the $\boldsymbol{H}$-field will have sources (or sinks), e.g. at the surface of a magnet (these are the famous North and South ‘poles’ of a magnet).

In free space, $\boldsymbol{M} = 0$ and the *H*-field is simply proportional to the *B*-field.

There is no significant difference between them.

Permeability μ is the ratio *B*/*H*.   Susceptibility χ is *M*/*H*   μ = μ0(1 +χ)

μ_0 is the permeability of free space.

In free space $\boldsymbol{B} = \mu_0\boldsymbol{H}$ $\mu_0 = 4\pi \times 10^{-7}$ TmA^{-1} 1 T ≈ 800,000 A m^{-1}

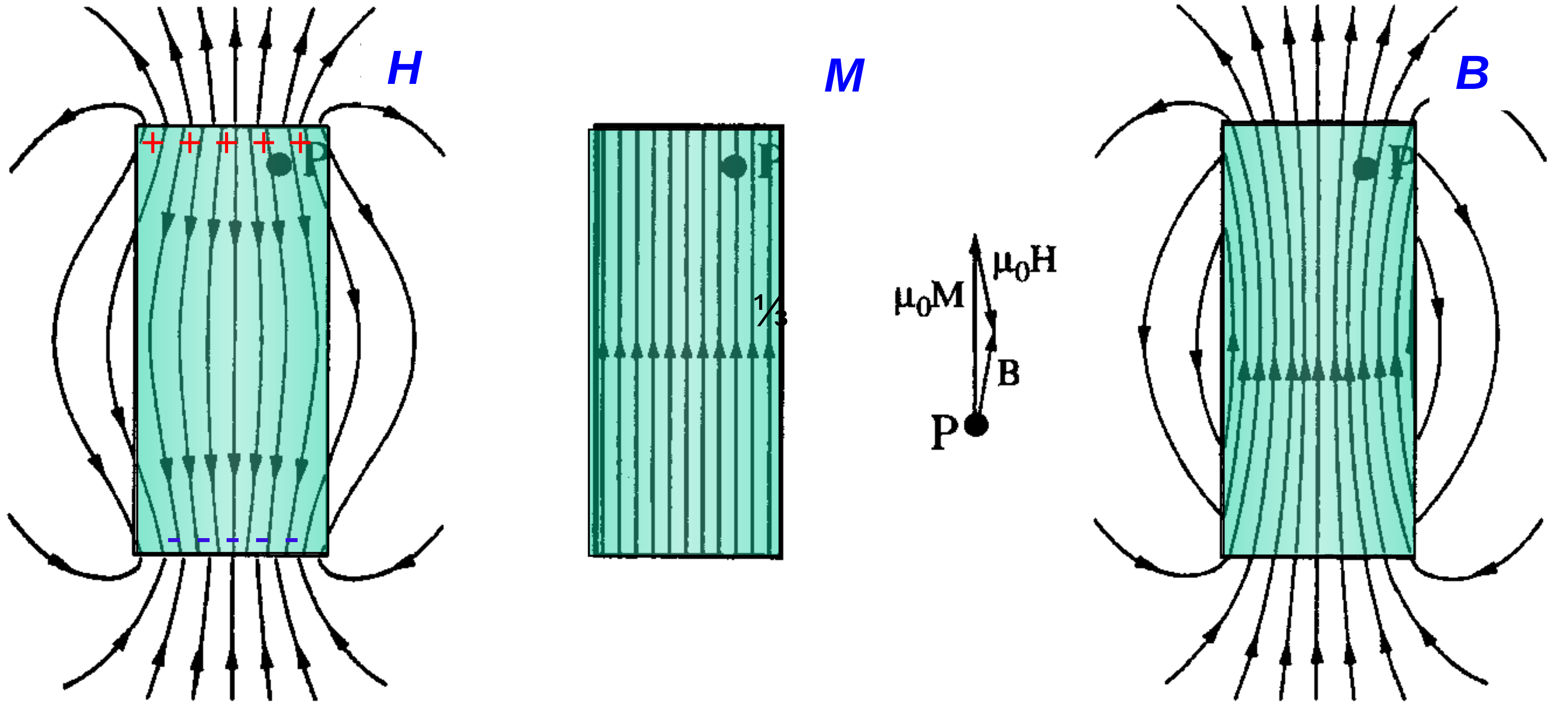
Note that the *H*-field is created *not only* by conduction currents. Any piece of magnetized material creates an *H*-field both in the space around it and *within its own volume*.

Generally the field at a point is $\boldsymbol{H} = \boldsymbol{H}_0 + \boldsymbol{H}_d$, where $\boldsymbol{H}_0$ is the external field, and $\boldsymbol{H}_d$ 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.

$\boldsymbol{B}$, $\boldsymbol{H}$ and $\boldsymbol{M}$ in and around a permanent magnet

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

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



We call the *H*-field due to a magnet - *stray field* outside the magnet

- *demagnetizing field* (H_d) inside the magnet

Potentials for *B* and *H*

Vector potential for **B**

It is convenient to derive a field from a potential, by taking a spatial derivative, for example

$$\boldsymbol{E}(\boldsymbol{r}) = -\nabla\varphi_e(\boldsymbol{r})$$

where $\varphi_e(\boldsymbol{r})$ is the electric potential. Any constant φ_0 can be added to $\varphi_e(\boldsymbol{r})$.

For ***B***, we know from Maxwell's equation that MI

$$\nabla . \boldsymbol{B}(\boldsymbol{r}) = 0.$$

Using the vector identity

$$\nabla.\nabla \times \boldsymbol{A}(\boldsymbol{r}) = 0,$$

we can derive $\boldsymbol{B}(\boldsymbol{r})$ from a *vector potential* $\boldsymbol{A}(\boldsymbol{r})$,

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

The gradient of any scalar f can be added to ***A*** (*a gauge transformation*) , because

$$\nabla \times \nabla f = 0.$$

Scalar potential for *H*

Generally, $\boldsymbol{H}(\boldsymbol{r})$ *cannot* be derived from a potential.
In a static situation it satisfies

$$\nabla \times \boldsymbol{H} = \boldsymbol{j}_{\mathrm{c}}$$

When *no conduction currents* are present,

$$\nabla \times \boldsymbol{H} = 0,$$

we can use

$$\nabla \times \nabla f = 0.$$

to get

$$\boxed{\boldsymbol{H}(\boldsymbol{r}) = - \nabla \varphi_{\mathrm{m}}(\boldsymbol{r})}$$

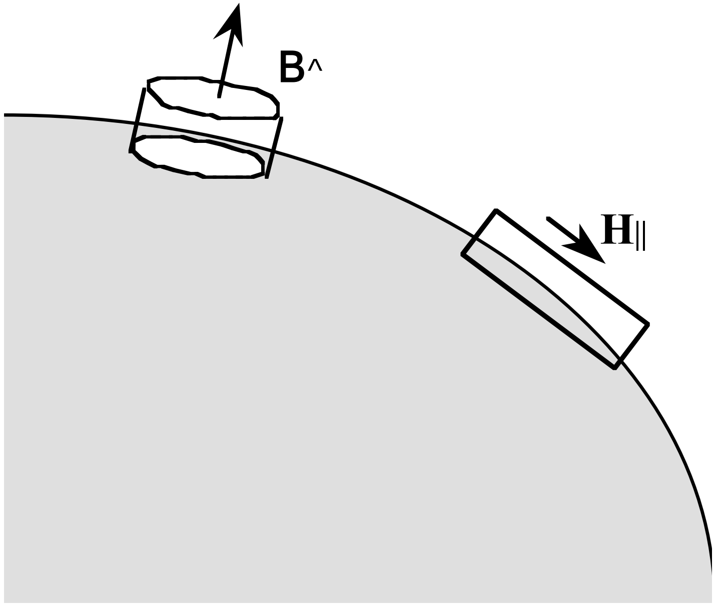
In these special conditions, it is possible to derive $\boldsymbol{H}(\boldsymbol{r})$ from a magnetic scalar potential $\varphi_{\mathrm{m}}(\boldsymbol{r})$.
We can imagine that $\boldsymbol{H}$ is produced by the distribution of magnetic '± charge', i.e. North and South poles.

Boundary conditions for ***B*** and ***H***

At any interface, it follows from Gauss' s law

$$\int_S \boldsymbol{B}.\mathrm{d}\mathbf{A} = 0$$

that the *perpendicular component of **B** is continuous*.



It follows from Ampère's law

$$\oint \boldsymbol{H}.\mathrm{dl} = I = 0$$

that the *parallel component of **H** is continuous*,
i.e. there are no conduction currents on the surface.

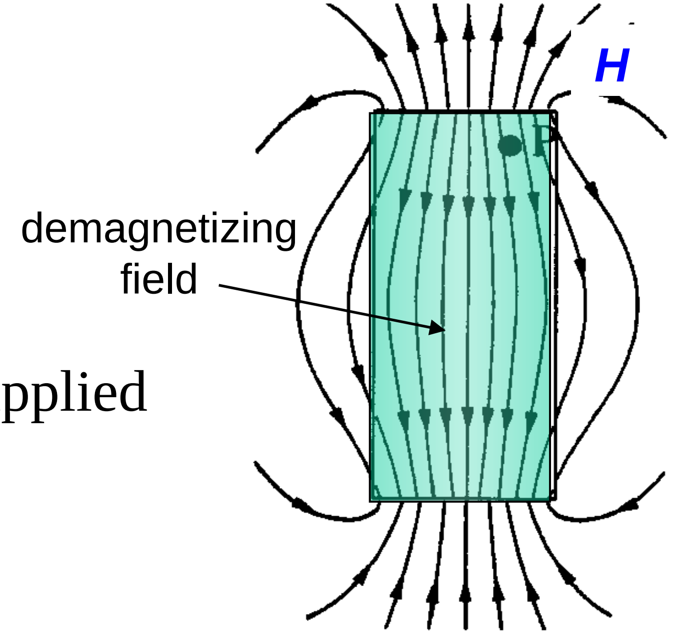
Demagnetizing field in a material - $\boldsymbol{H}_\mathrm{d}$

The demagnetizing field is the field produced by the magnet in its own volume. It 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.

$$\boxed{\boldsymbol{H}_\mathrm{d} = -\,\mathcal{N}\boldsymbol{M}}$$

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

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



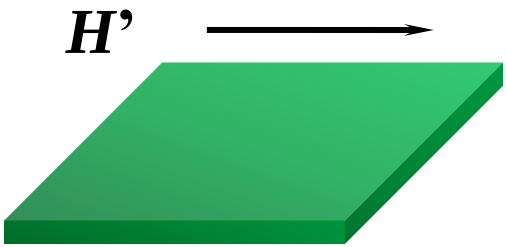
Note that the internal field $\boldsymbol{H}$ is always less than the applied field $\boldsymbol{H'}$ since

$$\boxed{\boldsymbol{H} = \boldsymbol{H'} - \mathcal{N}\boldsymbol{M}}$$

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

$\mathcal{N} = 0$

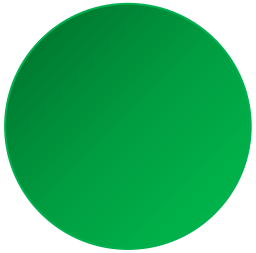
Long needle, ***M*** parallel to the long axis



Thin film, **M** parallel to plane

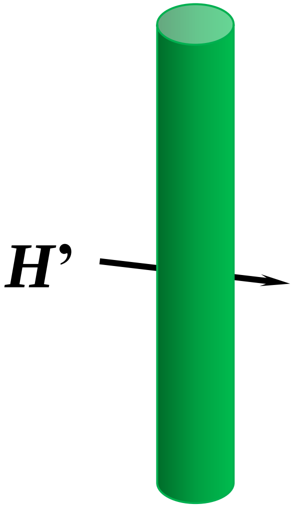
Toroid, **M** perpendicular to **r**

$\mathcal{N} = 1/3$

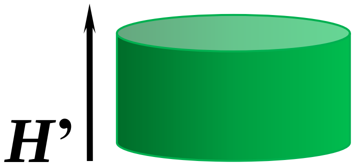


Sphere

$\mathcal{N} = 1/2$



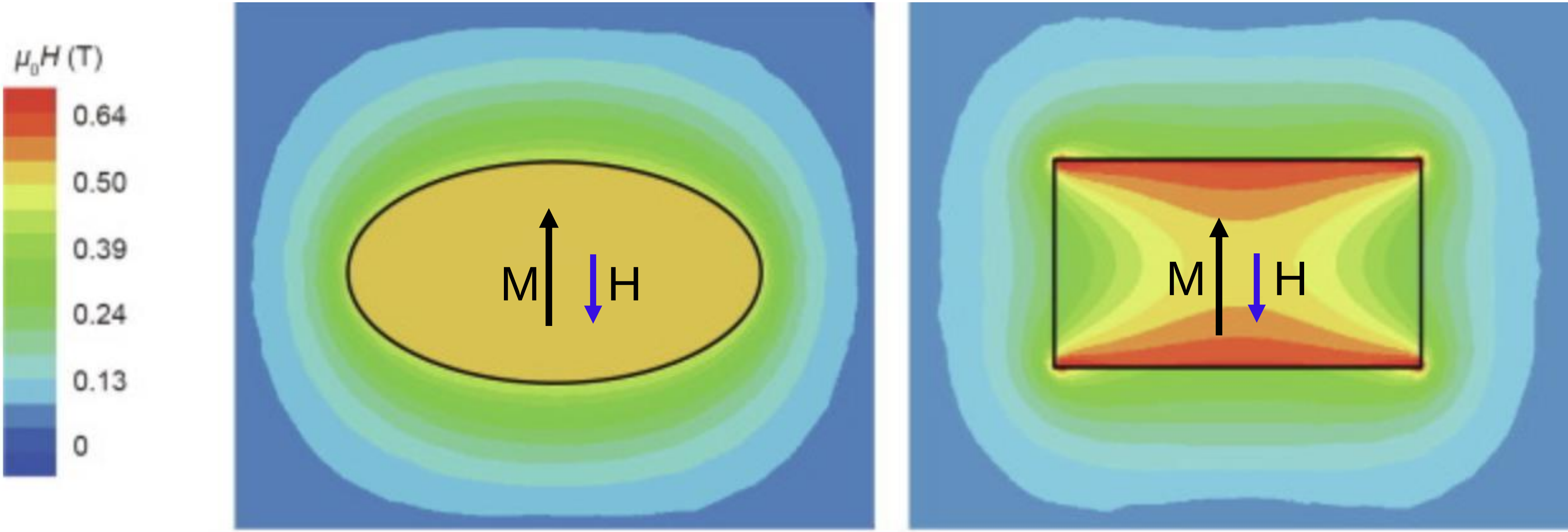
Long needle,
M perpendicular to the long axis



$\mathcal{N} = 1$

Thin film,
M perpendicular to plane

When is the demagnetizing factor $\mathcal{N}$ approximation exact ?



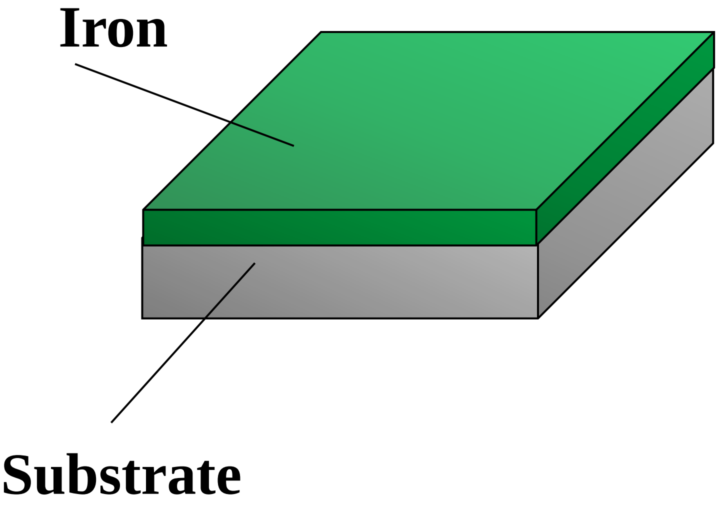
Two uniformly magnetized shapes with $\mu_0 M$ = 1 T and $\mathcal{N}$ = ½, an ellipsoid of revolution (left) and a cylinder (right).

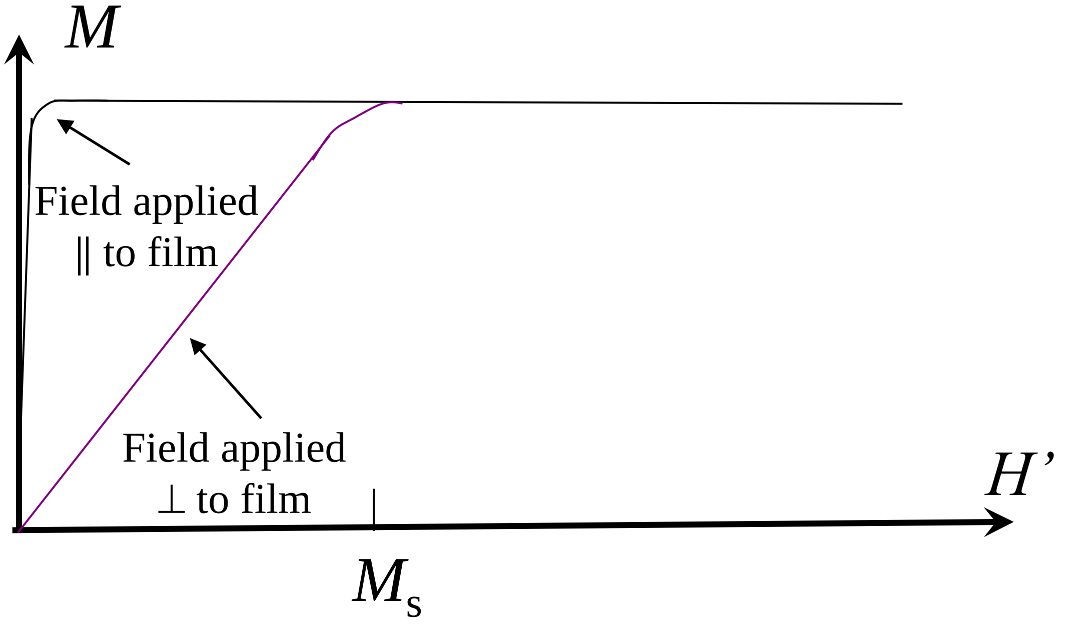
The approximation is exact only for the *ellipsoid of revolution*. H_d = -0.5 T

2.4 Magnetic fields - Internal and applied fields

The internal and applied fields are *not* the same. If they were, any applied field would instantly saturate the magnetization.

Consider a thin film of iron.





$$\boldsymbol{H} = \boldsymbol{H}' + \boldsymbol{H}_d$$

Internal field

Applied field

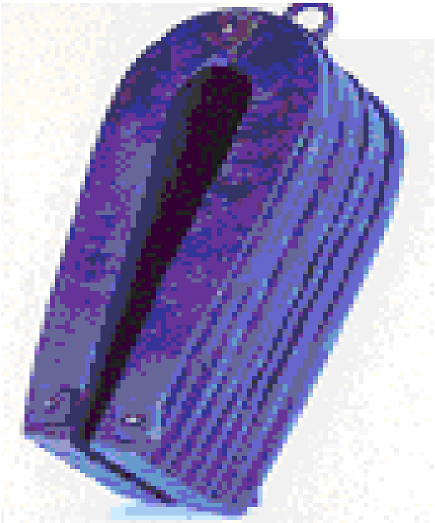
Demagnetizing field

The magnetization is a response to the *internal field.*

Hence $H_i = 0$ during the magnetization process

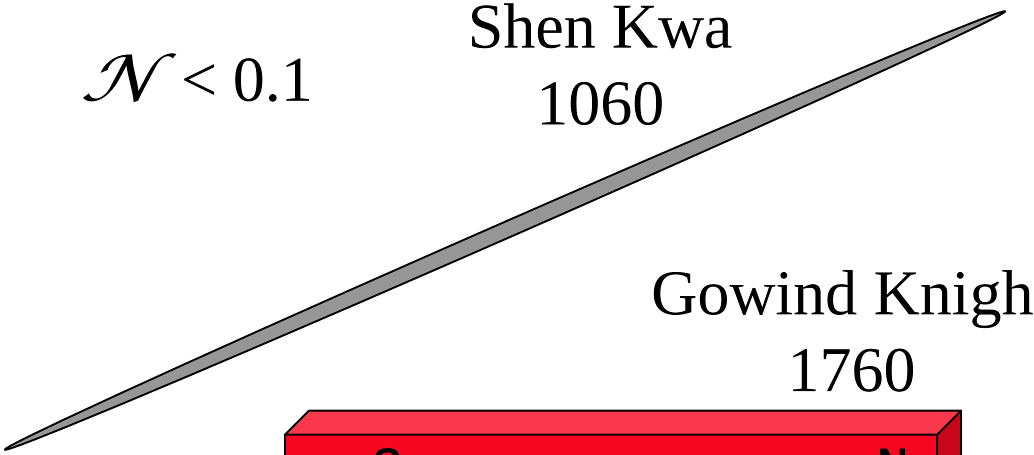
The shape barrier

Daniel Bernouilli
1743



$\mathcal{N} < 0.1$

Shen Kwa
1060

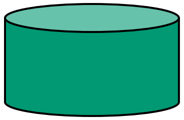


Gowind Knight
1760

T. Mishima
1931

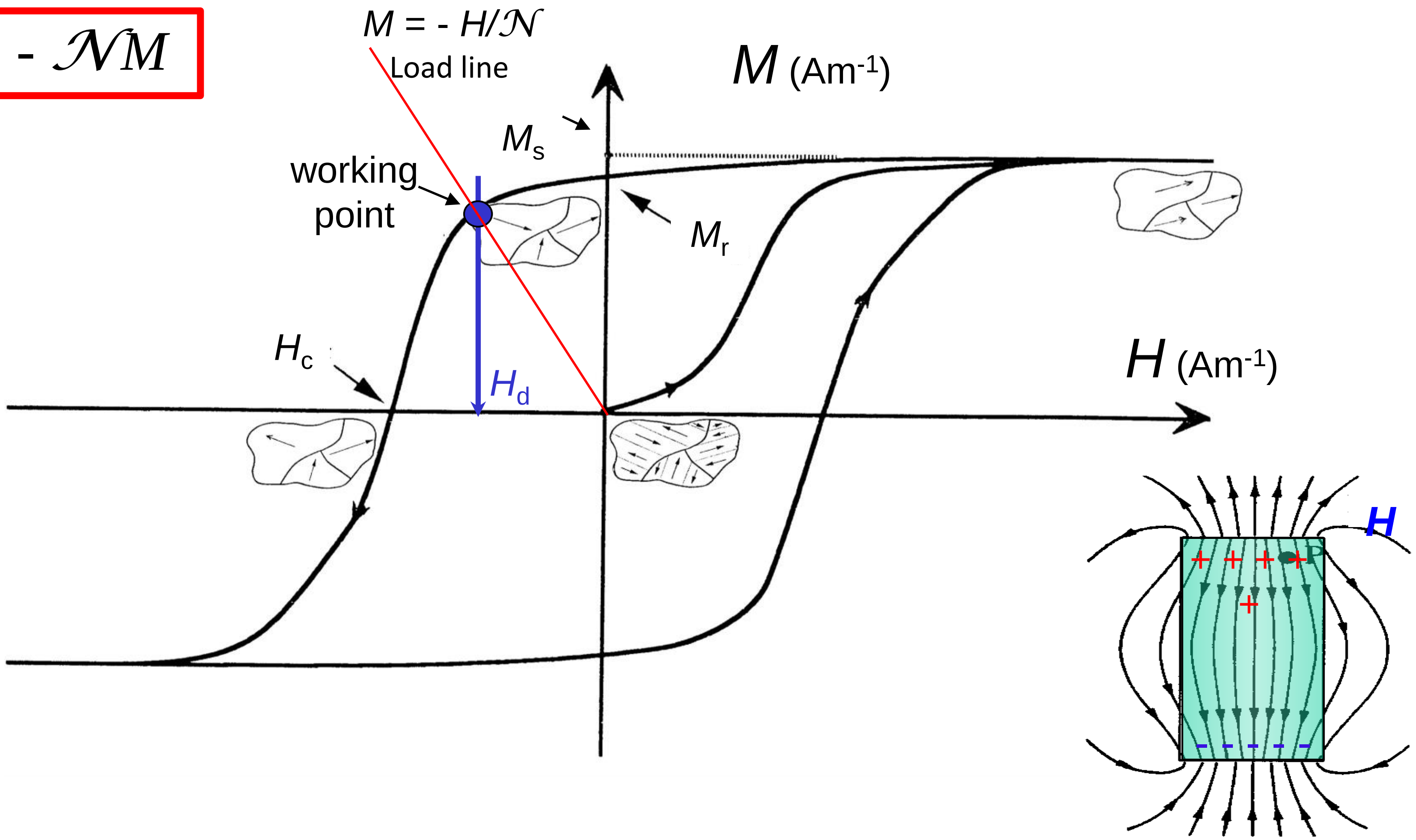
$\mathcal{N} = 0.5$

New icon for permanent magnets! ⇒



The shape barrier ovecome!

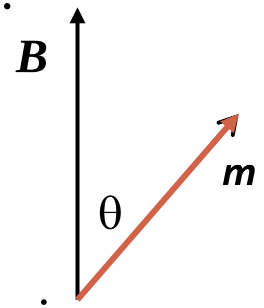
$$\boxed{H_d = - \mathcal{N}M}$$



The working point of the magnet is always in the second quadrant.

2.5 Energy and force on a magnetic moment

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



$\mathcal{E} = - \boldsymbol{m} \,.\, \boldsymbol{B}$ (i.e. $- |\boldsymbol{m}||\boldsymbol{B}|\cos\theta$)

- Differentiating gives the torque Γ = -

$\boldsymbol{\Gamma} = \boldsymbol{m} \times \boldsymbol{B}$ (i.e. $|\boldsymbol{m}||\boldsymbol{B}|\sin\theta$) (the compass is an example)

Note the moment *precesses* around the field when $\boldsymbol{m}$ is not parallel to $\boldsymbol{B}$. The magnetic moment is due to electric currents, and the Lorentz force $\boldsymbol{F}$ on a moving electron [$\boldsymbol{F} = -e(\boldsymbol{v} \times \boldsymbol{B})$] 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 $\boldsymbol{l}$

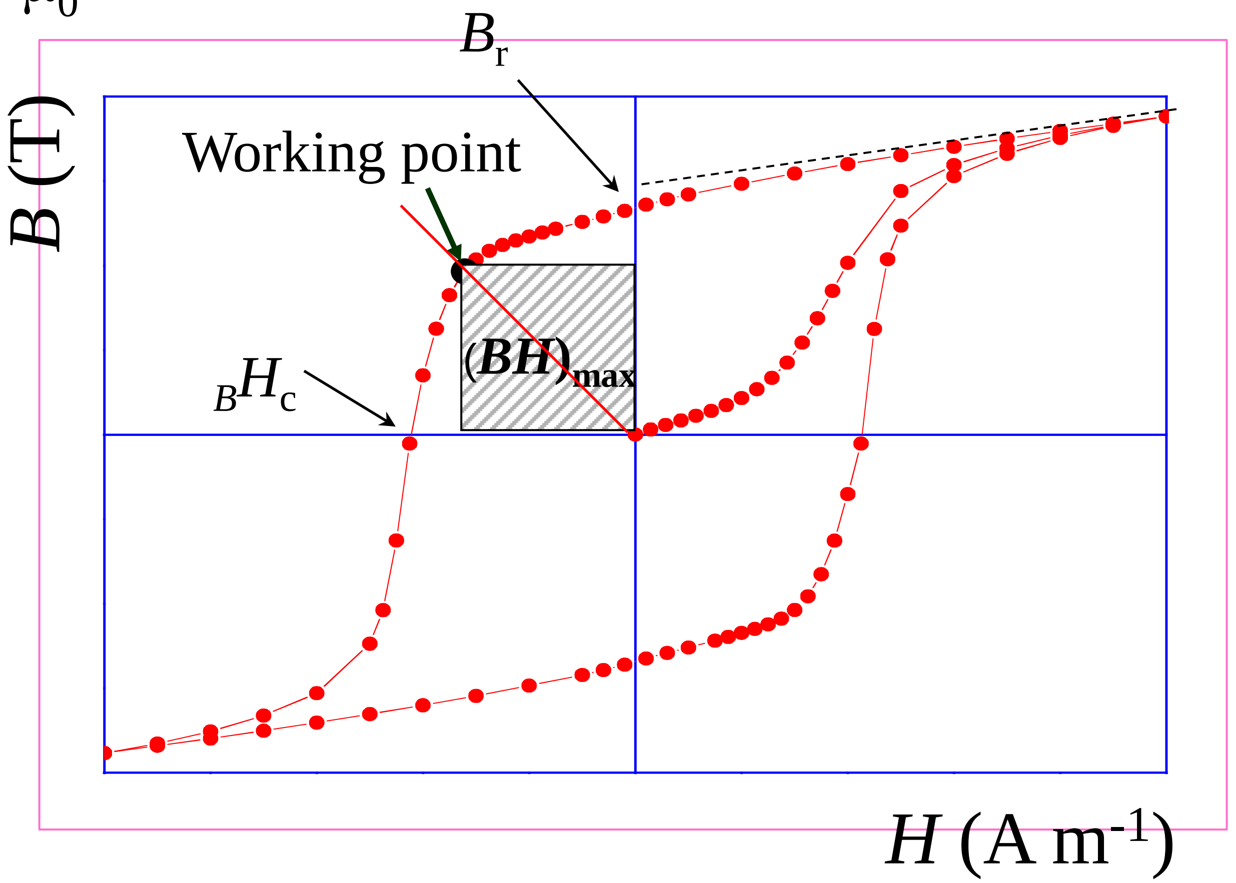
$\boldsymbol{m} = \gamma \boldsymbol{l}$ where is the gyromagnetic ratio

- The force on a magnetic moment $\boldsymbol{f} = -\nabla E = \nabla(\boldsymbol{m} \,.\, \boldsymbol{B})$ 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 μ_0



slope = μ_0

Note 1: ${}_BH_c \neq H_c$

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

Some expressions involving ***B***

$\boldsymbol{F} = q(\boldsymbol{E} + \mathbf{v} \times \boldsymbol{B})$	Force on a charged particle *q* *See* How Special Relativity Makes Magnets Work*
$\boldsymbol{F} = \boldsymbol{B}\, i\, \boldsymbol{l}$	Force on current-carrying wire
$emf = -nA\,dB/dt$	Faraday’s law of electromagnetic induction
$\varepsilon = -\, \boldsymbol{m}.\boldsymbol{B}$	Energy of a magnetic moment
$\boldsymbol{F} = \nabla\, \boldsymbol{m}.\boldsymbol{B}$	Force on a magnetic moment
$\boldsymbol{\Gamma} = \boldsymbol{m} \times \boldsymbol{B}$	Torque on a magnetic moment

Note: Whenever ***H*** interacts with matter, μ_0 comes in.

*https://www.youtube.com/watch?v=1TKSfAkWWN0

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 multi-meter and the oscilloscope
- It is possible to check the dimensions of any expression by inspection.
- They are almost universally used in teaching
- Units of $\boldsymbol{B}$, $\boldsymbol{H}$, Φ or $\frac{d\Phi}{dt}$ have been introduced.

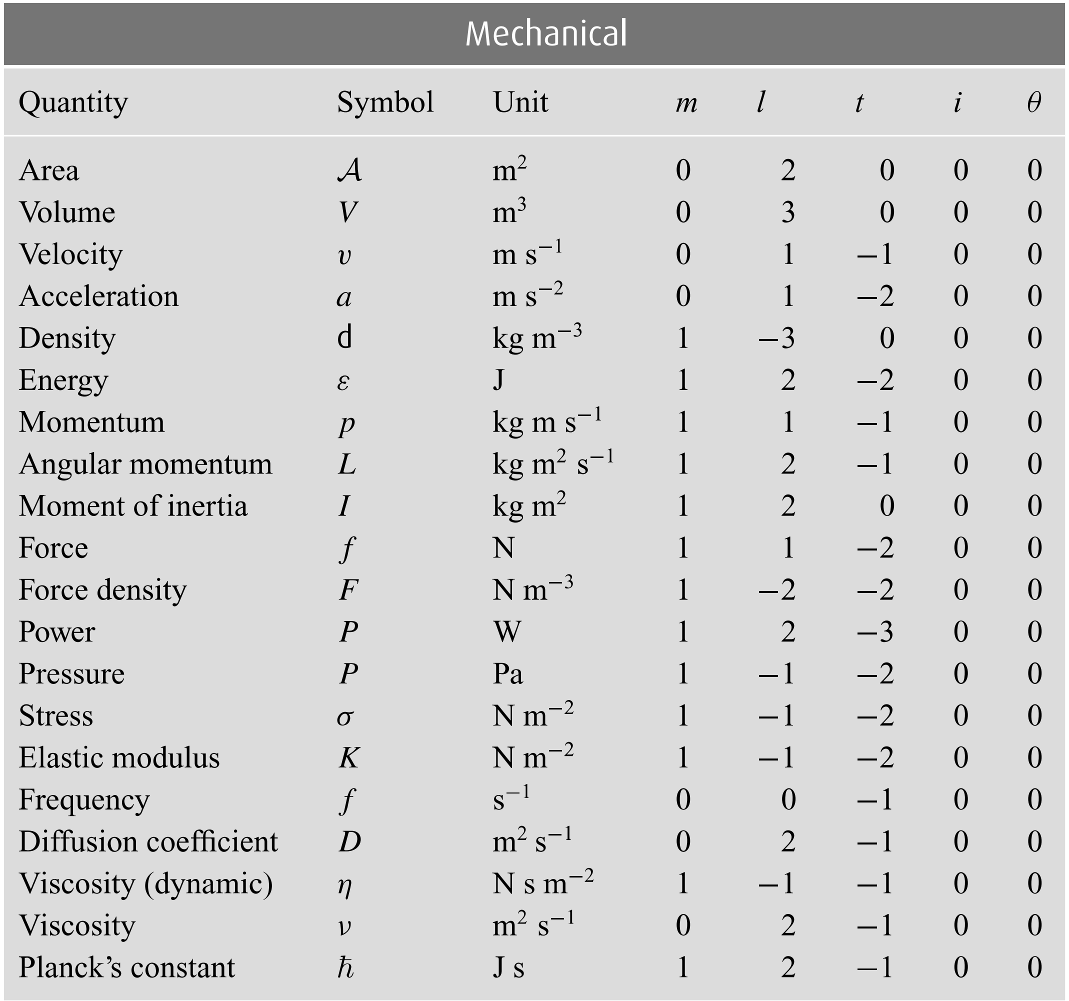
BUT

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

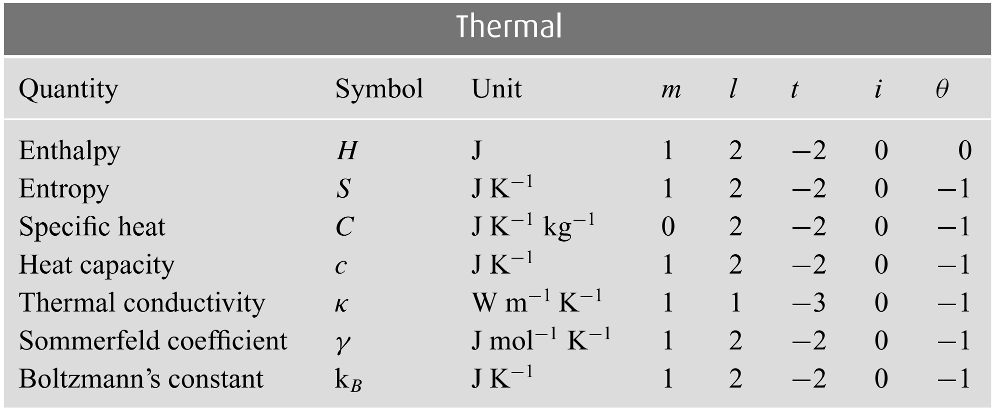
SI / cgs conversions:

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

Dimensions



Mechanical							
Quantity	Symbol	Unit	m	l	t	i	θ
Area	$\mathcal{A}$	m^2	0	2	0	0	0
Volume	V	m^3	0	3	0	0	0
Velocity	v	m s^{-1}	0	1	−1	0	0
Acceleration	a	m s^{-2}	0	1	−2	0	0
Density	d	kg m^{-3}	1	−3	0	0	0
Energy	ε	J	1	2	−2	0	0
Momentum	p	kg m s^{-1}	1	1	−1	0	0
Angular momentum	L	kg m^2 s^{-1}	1	2	−1	0	0
Moment of inertia	I	kg m^2	1	2	0	0	0
Force	f	N	1	1	−2	0	0
Force density	F	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	σ	N m^{-2}	1	−1	−2	0	0
Elastic modulus	K	N m^{-2}	1	−1	−2	0	0
Frequency	f	s^{-1}	0	0	−1	0	0
Diffusion coefficient	D	m^2 s^{-1}	0	2	−1	0	0
Viscosity (dynamic)	η	N s m^{-2}	1	−1	−1	0	0
Viscosity	ν	m^2 s^{-1}	0	2	−1	0	0
Planck's constant	$\hbar$	J s	1	2	−1	0	0



Thermal							
Quantity	Symbol	Unit	m	l	t	i	θ
Enthalpy	H	J	1	2	−2	0	0
Entropy	S	J K^{-1}	1	2	−2	0	−1
Specific heat	C	J K^{-1} kg^{-1}	0	2	−2	0	−1
Heat capacity	c	J K^{-1}	1	2	−2	0	−1
Thermal conductivity	κ	W m^{-1} K^{-1}	1	1	−3	0	−1
Sommerfeld coefficient	γ	J mol^{-1} K^{-1}	1	2	−2	0	−1
Boltzmann's constant	k_B	J K^{-1}	1	2	−2	0	−1

The dimensions of any physical quantity can be expresses as a product of the dimensions of some fundamental physical quantities.

These are, in the SI system

Mass – m

Length – l

Time – t

Current – i

Temperature – θ e.g Area – l^{2}

Density – $m\,l^{-3}$ etc.

Electrical

Quantity	Symbol	Unit	m	l	t	i	θ
Current	I	A	0	0	0	1	0
Current density	j	$\mathrm{A\ m^{-2}}$	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	Ω	1	2	−3	−2	0
Resistivity	ϱ	Ω m	1	3	−3	−2	0
Conductivity	σ	$\mathrm{S\ m^{-1}}$	−1	−3	3	2	0
Dipole moment	p	C m	0	1	1	1	0
Electric polarization	P	$\mathrm{C\ m^{-2}}$	0	−2	1	1	0
Electric field	E	$\mathrm{V\ m^{-1}}$	1	1	−3	−1	0
Electric displacement	D	$\mathrm{C\ m^{-2}}$	0	−2	1	1	0
Electric flux	Ψ	C	0	0	1	1	0
Permittivity	ε	$\mathrm{F\ m^{-1}}$	−1	−3	4	2	0
Thermopower	S	$\mathrm{V\ K^{-1}}$	1	2	−3	−1	−1
Mobility	μ	$\mathrm{m^2\ V^{-1}\ s^{-1}}$	−1	0	2	1	0

Magnetic

Quantity	Symbol	Unit	m	l	t	i	θ
Magnetic moment	$\mathfrak{m}$	$\mathrm{A\ m^2}$	0	2	0	1	0
Magnetization	M	$\mathrm{A\ m^{-1}}$	0	−1	0	1	0
Specific moment	σ	$\mathrm{A\ m^2\ kg^{-1}}$	−1	2	0	1	0
Magnetic field strength	H	$\mathrm{A\ m^{-1}}$	0	−1	0	1	0
Magnetic flux	Φ	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)	χ		0	0	0	0	0
Permeability (B/H)	μ	$\mathrm{H\ m^{-1}}$	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)	$\mathrm{J\ m^{-3}}$	1	−1	−2	0	0
Anisotropy energy	K	$\mathrm{J\ m^{-3}}$	1	−1	−2	0	0
Exchange stiffness	A	$\mathrm{J\ m^{-1}}$	1	1	−2	0	0
Hall coefficient	R_H	$\mathrm{m^3\ C^{-1}}$	0	3	−1	−1	0
Scalar potential	φ	A	0	0	0	1	0
Vector potential	A	T m	1	1	−2	−1	0
Permeance	P_m	$\mathrm{T\ m^2\ A^{-1}}$	1	2	−2	−2	0
Reluctance	R_m	$\mathrm{A\ T^{-1}\ m^{-2}}$	−1	−2	2	2	0

Examples

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

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

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

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

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

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

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

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

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

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

$$\begin{aligned} [\gamma_w] &= [\varepsilon A^{-1}] \\ &= [1, 2, -2, 0, 0] \\ &\quad - [0, 2, 0, 0, 0\ ] \\ &= [1, 0, -2, 0, 0] \end{aligned}$$

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

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

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

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

$$\begin{aligned}[F] &= [F V^{-1}] \\ &= [1, 1, -2, 0, 0] \\ &\quad - \frac{[0, 3, 0, 0, 0]}{[1, -2, -2, 0, 0]}\end{aligned}$$

$$\begin{aligned}[\sigma] &= [-1, -3, 3, 2, 0] \\ [v] &= [0, 1, -1, 0, 0] \\ [B^2] &= \frac{2[1, 0, -2, -1, 0]}{[1, -2, -2, 0, 0]}\end{aligned}$$

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

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

$$\begin{aligned}[\mu_0] &= [1, 1, -2, -2, 0] \\ [M], [H] &= \frac{[0, -1, 0, 1, 0]}{[1, 0, -2, -1, 0]}\end{aligned}$$

(6) Maxwell's equation $\nabla \times \boldsymbol{H} = \boldsymbol{j} + \mathrm{d}\boldsymbol{D}/\mathrm{d}t$.

$$\begin{aligned}[\nabla \times \boldsymbol{H}] &= [H r^{-1}] \\ &= [0, -1, 0, 1, 0] \\ &\quad -[\,0, 1, 0, 0, 0] \\ &= [0, -2, 0, 1, 0]\end{aligned}$$

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

$$\begin{aligned}[\mathrm{d}\boldsymbol{D}/\mathrm{d}t] &= [D t^{-1}] \\ &= [0, -2, 1, 1, 0] \\ &\quad -[0, 0, 1, 0, 0] \\ &= [0, -2, 0, 1, 0]\end{aligned}$$

(7) Ohm's Law $V = I R$

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

$$\begin{aligned}&[0, 0, 0, 1, 0] \\ &+[1, 2, -3, -2, 0] \\ &= [1, 2, -3, -1, 0]\end{aligned}$$

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

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

$$\begin{aligned}&[1, 2, -2, -1, 0] \\ &-[0, 0, 1, 0, 0] \\ &= [1, 2, -3, -1, 0]\end{aligned}$$

Calculation of the field of a dipole (current loop)

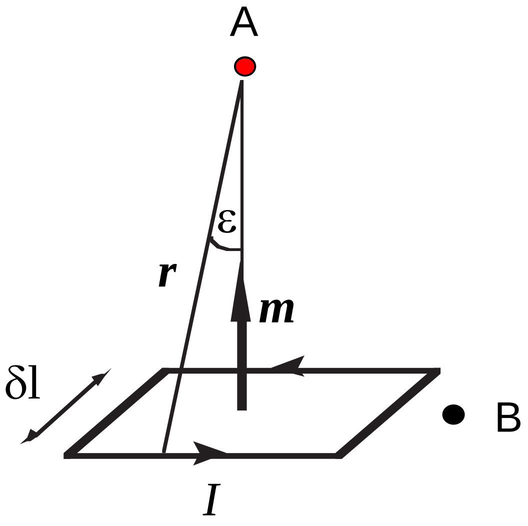
At point A – magnetic field above the center of a perfect square loop (B_A):

Use **Biot-Savart Law**

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

Also note:

$\sin\varepsilon = \delta l / 2r \qquad m = I(\delta l)^2$



$B_A = (4\,\mu_0\, I/4\pi r^3)\ \delta l\ \mathbf{r}\sin\varepsilon$

Add up the four contributions from each part of the loop and evaluate the cross product

$B_A = (4\,\mu_0\, I/4\pi r^3)\ \delta l\ \mathbf{r}\ \delta l/2r$

Substitute the expression for $\sin\varepsilon$ as given in the greenbox

$B_A = (2\,\mu_0\, I/4\pi r^3)\ \delta l^{\,2}$

Tidy the expression

Hence :

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

Use the fact from the green box

$m = I(\delta l)^2$

Calculation of the field of a dipole (current loop)

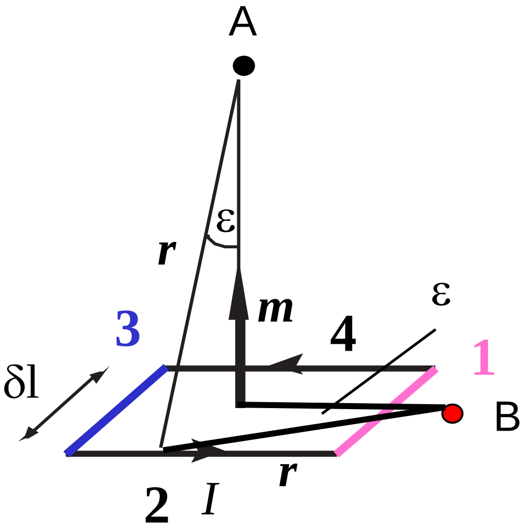
At point B – magnetic field outside in line the center of a perfect square loop (B_B):

Use **Biot-Savart Law**

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

Here we first must work out the contribution to the magnetic field at point B due to each part of the loop separately.

Note that for 1 & 3: $\delta \boldsymbol{l} \perp \boldsymbol{r}$



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

Contribition from 1

Contribition from 3

Contribitions from 2 & 4

Calculation of the field of a dipole (current loop)

At point B – magnetic field in the plane outside the center of a perfect square loop (B_A):

Use **Biot-Savart Law**

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

Also note:

$\sin\varepsilon = \delta l/2r \qquad m = I(\delta l)^2$

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

Add up the four contributions from each part of the loop and take r^2 outside the curly brackets

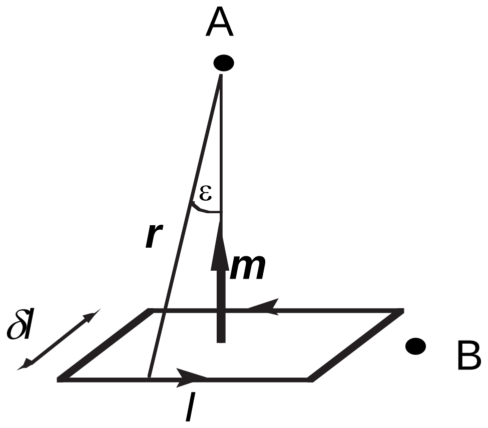
$$B_B = (\mu_0 I \delta l/4\pi r^2)\{(1 + \delta l/r) - (1 - \delta l/r) - \delta l/r\}$$

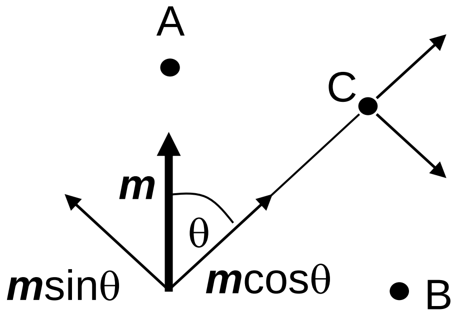
Substitute the expression for $\sin\varepsilon$ as given in the green box and Taylor expand the first two terms assuming

Hence : $$\boxed{B_B = \frac{\mu_0}{4\pi}\frac{m}{r^3}}$$

Use the fact from the green box $m = I(\delta l)^2$

Calculation of the field of a dipole (current loop)





What we found:

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

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

Now we can write down the B-field due to the loop at a generic point C in polar coordinates

$$\boldsymbol{B}_C = B_A\cos\theta\,\mathbf{e}_r + B_B\sin\theta\,\mathbf{e}_\theta\}$$

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

Magnetic Dipole Field Equation!

Now re-express the formula for B in terms of components of along ***m*** and ***r***

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

Homework

Prove that result is true

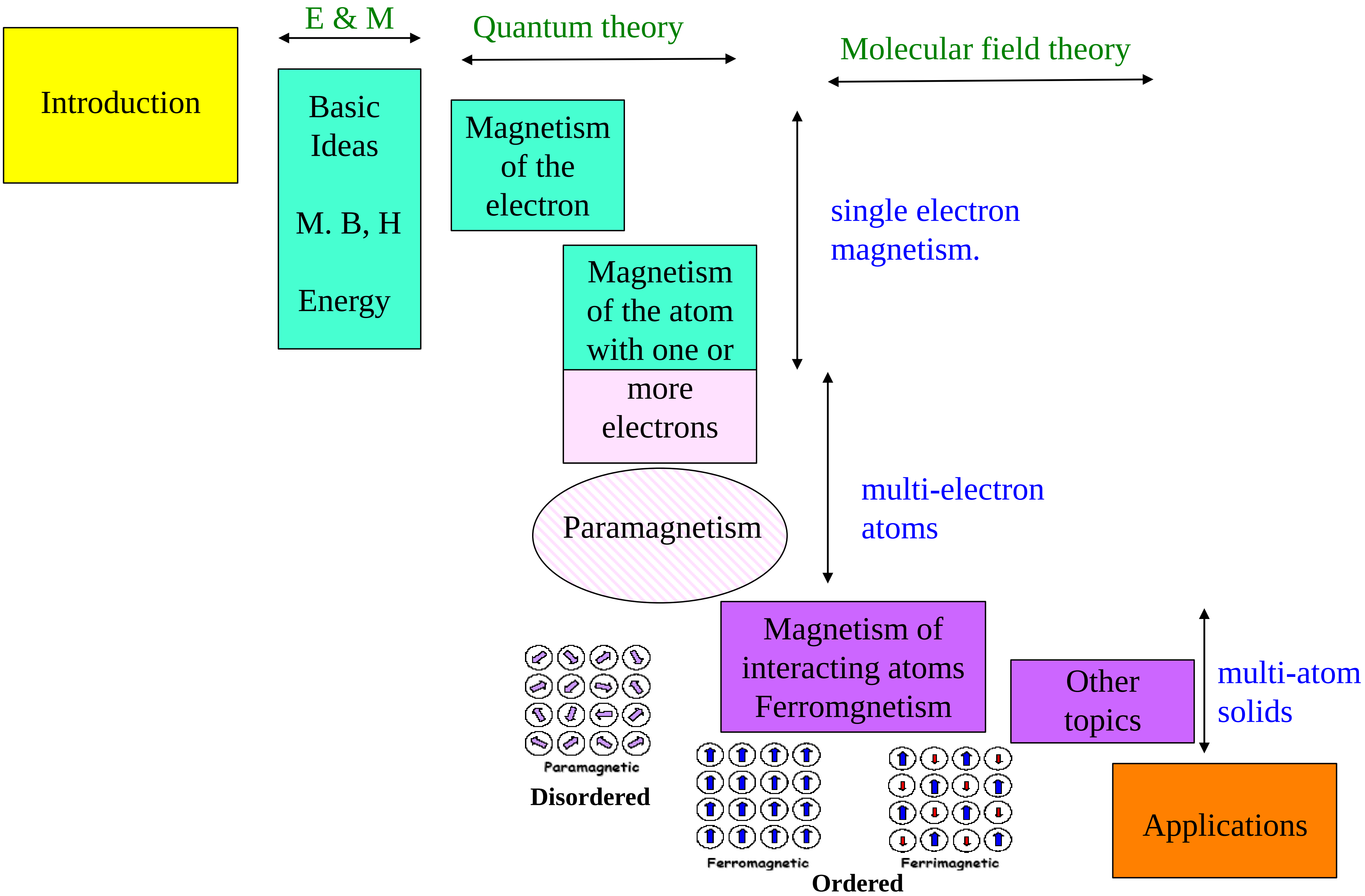
MOOC 2.1. 13’

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



Introduction

E & M

Basic Ideas

M. B, H

Energy

Quantum theory

Magnetism of the electron

Magnetism of the atom with one or more electrons

Paramagnetism

Molecular field theory

single electron magnetism.

multi-electron atoms

Magnetism of interacting atoms Ferromgnetism

Other topics

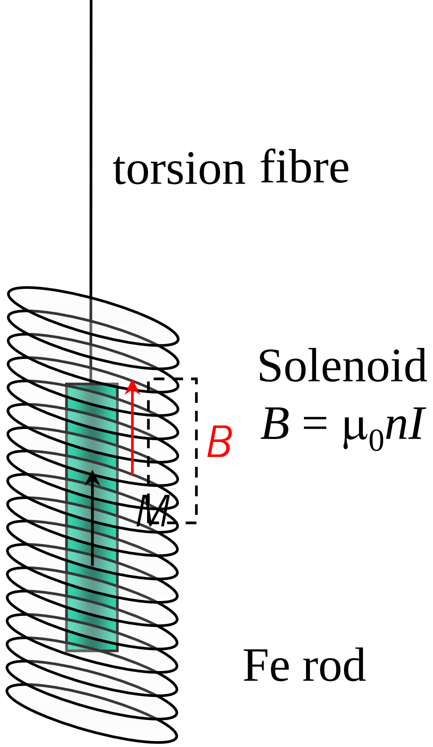
multi-atom solids

Disordered

Ordered

Applications

Einstein-de Haas experiment



This demonstrates the reality of the relation between the magnetic moment of a body and its angular momentum.

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

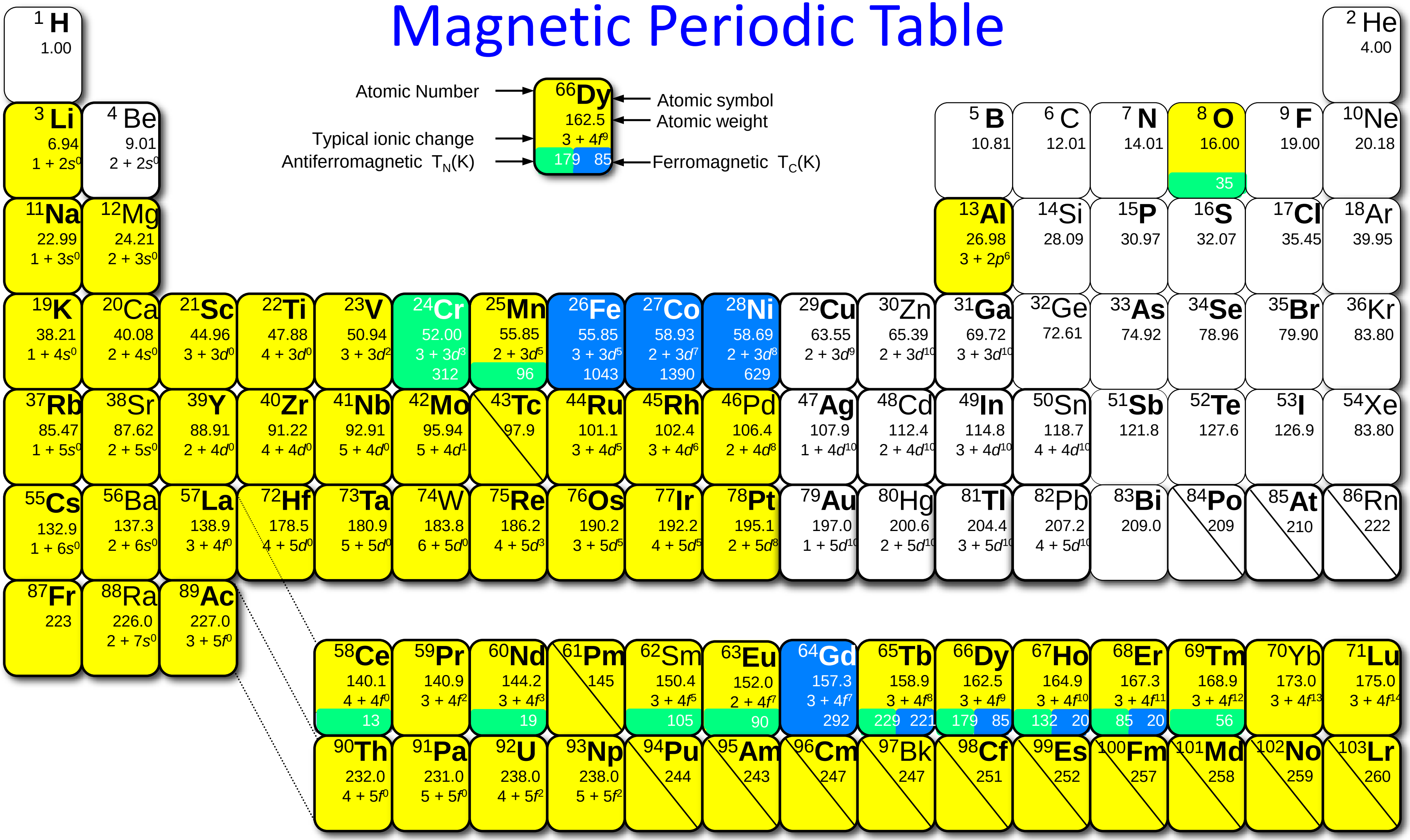
An iron rod is suspended on a torsion fibre. The field in the solenoid is reversed, changing the direction of magnetization of the iron. It rotates, to conserve angular momentum as the angular momenta of the electrons are reversed.

In Fe the moment is essentially due to the spin of the electrons. An electron has a spin moment of one Bohr magneton ($1\mu_B = 9.27\ 10^{-24}$ Am^2).

However, m per Fe atom is only 2.2 μ_B. There are *only* ~ *two* electrons with an unpaired spin, although the number of electrons per atom in iron is Z = 26

Iron 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



1 **H** 1.00																	2 He 4.00
3 **Li** 6.94 $1 + 2s^0$	4 Be 9.01 $2 + 2s^0$											5 **B** 10.81	6 C 12.01	7 **N** 14.01	8 **O** 16.00 35	9 **F** 19.00	10 Ne 20.18
11 **Na** 22.99 $1 + 3s^0$	12 Mg 24.21 $2 + 3s^0$											13 **Al** 26.98 $3 + 2p^6$	14 Si 28.09	15 **P** 30.97	16 **S** 32.07	17 **Cl** 35.45	18 Ar 39.95
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▭	Nonmetal	⬜	Diamagnet	🟦	Ferromagnet $T_C > 290$K
▭	Metal	🟨	Paramagnet	🟩	Antiferromagnet with $T_N > 290$K
⧄	Radioactive	**BOLD**	Magnetic atom	🟩🟦	Antiferromagnet/Ferromagnet with $T_N/T_C < 290$ K

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.

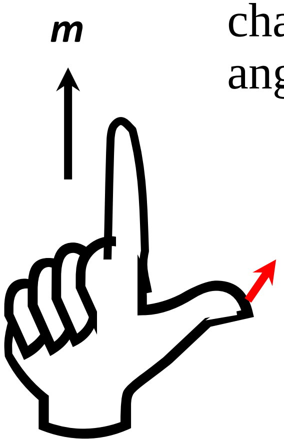
We focus on localized magnetism in this part of the course, where an *integral* number of electrons are localized on each atom

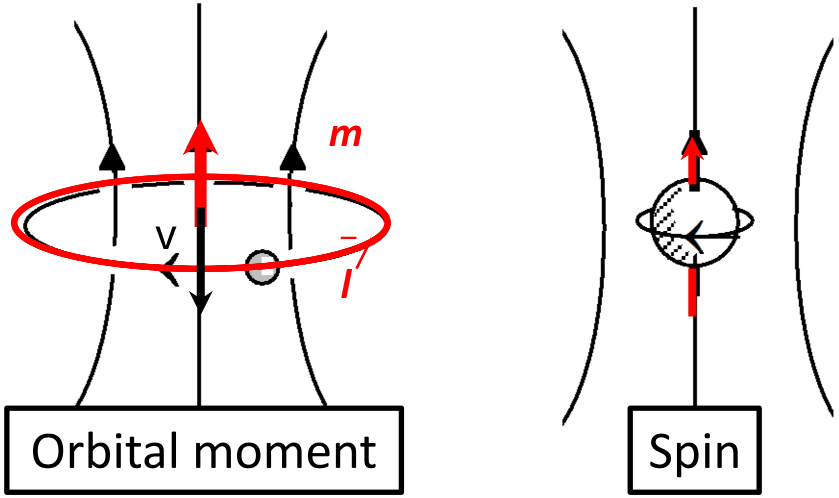
3.1 Spin and orbital moments of the electron

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 ≈ 1000 times smaller).

An electron possesses:

mass	$m_e = 9.109\ 10^{-31}$ kg
charge	$-e = -1.602\ \ 10^{-19}$ C
angular momentum *(spin)*	$\frac{1}{2}\hbar = 0.527\ 10^{-34}$ J s





On an atomic scale, magnetism is always associated with *angular momentum*. Electronic charge is negative, hence the angular momentum and magnetic moment are in *opposite* directions.

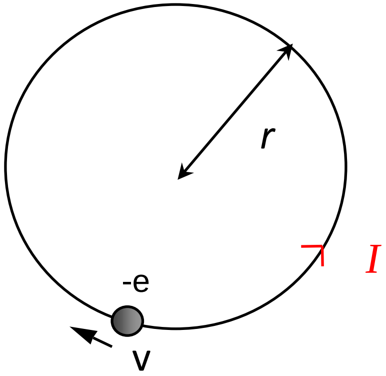
3.1.1 Orbital moment

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

The moment m: $m = IA$;

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

In Bohr's quantum theory, orbital angular momentum ***l*** is quantized in units of $\hbar$.



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

Planck's constant: $h = 6.62\ 10^{-34}$ J s.

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

The orbital angular momentum is $\boldsymbol{l} = \mathbf{r} \times m_e\mathbf{v}$ J s.

It is actually the *z-component* of $\boldsymbol{l}_z$ 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, ±1,±2 ... ,±l 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* (μ_B), the basic unit of atomic magnetism:

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

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 $s = ½$ .There are two magnetic states with $m_s = \pm ½$

The spin angular momentum is ***s***. The *z*-component s_z is quantized in units of $½\hbar$, taking only two values $\pm ½ \hbar$ along the z-axis

Yet, the magnetic moment associated with electron spin is also $1\ \mu_B$ (not $½\mu_B$)

$$m = -g\, m_s(e\hbar/2m_e), \text{ where } g = 2.$$

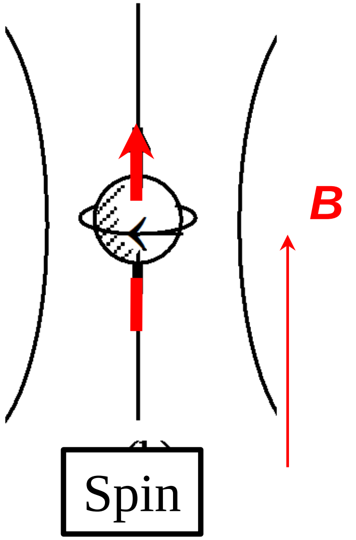
$$m_z = \pm 1\ \mu_B$$

The two states, ↓‘spin moment down’ and ↑ ’ spin moment up ‘ $m_s = \pm½$ have moments $m \mp 1\mu_B$ measured along the axis of quantization (z) usually defined by an external magnetic field.

$m_s = +½$ ↓ $\mathcal{E} = \mu_B B$

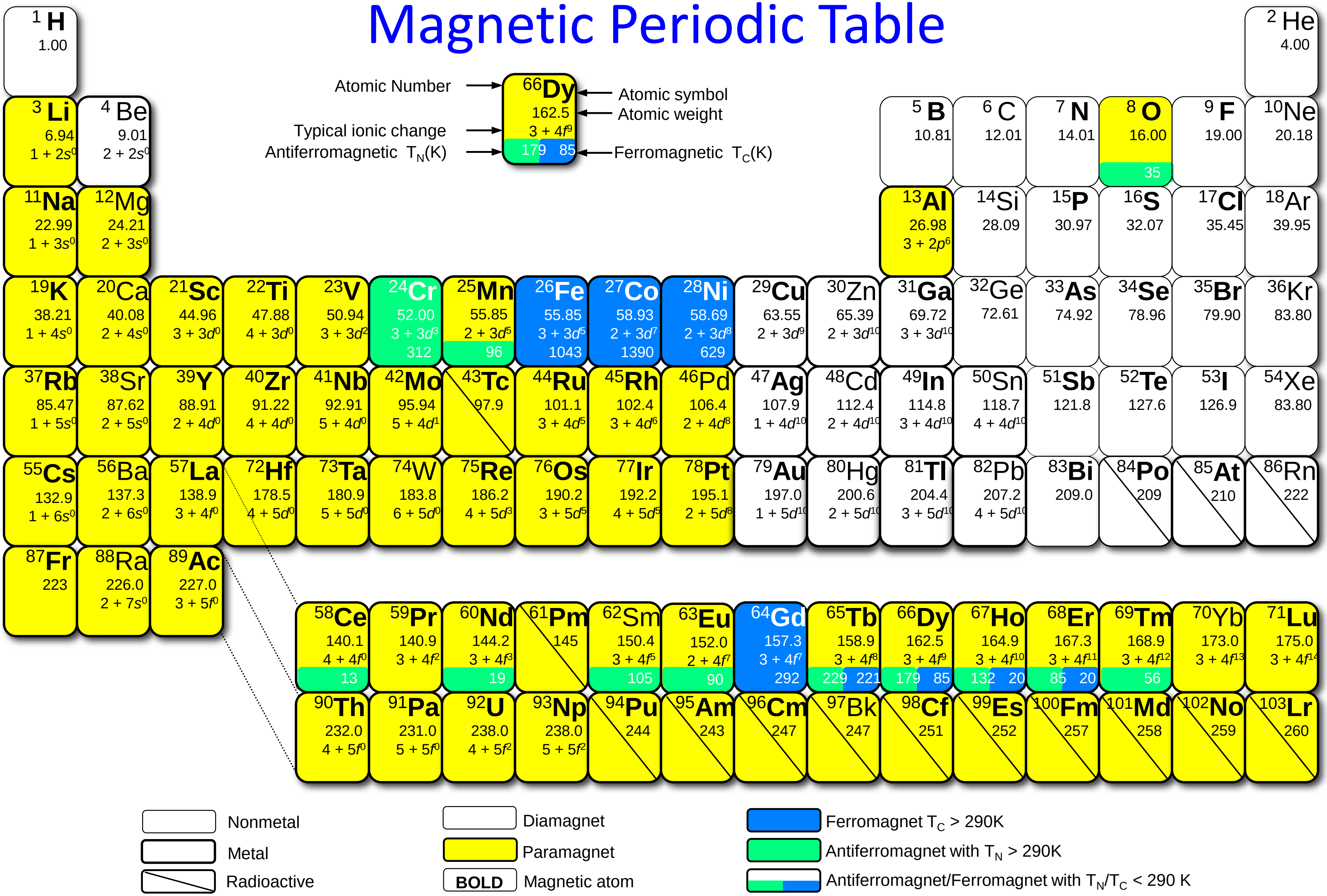
Zeeman splitting

$m_s = -½$. ↑ $\mathcal{E} = -\mu_B B$



If the orbital quantum number of the electron was $l = 1$, $m_l = -1, 0, 1$
Total umber of magnetic states in $(2l + 1) \times (2s + 1)$

Magnetic Periodic Table



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⧄ Radioactive	**BOLD** Magnetic atom	🟩🟦 Antiferromagnet/Ferromagnet with T_N/T_C < 290 K

The *gyromagnetic ratio* γ, is defined as the ratio of magnetic moment to angular momentum $\boldsymbol{m} = \gamma \boldsymbol{l}$, For orbital moments $m = -m_l\mu_B$. $l = m_l\hbar$.

* Hence for **orbital** angular momentum, the ratio of the z-components is

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

The *g-factor* is defined as the ratio of m (in units of μ_B) to $\boldsymbol{l}$ (in units of $\hbar$)

$$g = 1 \qquad \text{(for orbital motion)}$$

* For **spin** angular momentum $\gamma = -(e/m_e)$ ($m = -2m_l\mu_B$. $l = m_l\hbar$)

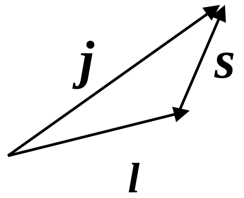
$$g = 2 \text{ for spin} \qquad \text{(after higher order corrections, 2.0023)}$$

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 add produce a total angular momentum $\boldsymbol{j}$,

$\boldsymbol{j} = \boldsymbol{l} + \boldsymbol{s}$; $m = -g_j(e/2m_e)\,\boldsymbol{j}$

Spin-orbit Interaction



3.2 Magnets in a field

Larmor precession

Classical derivation

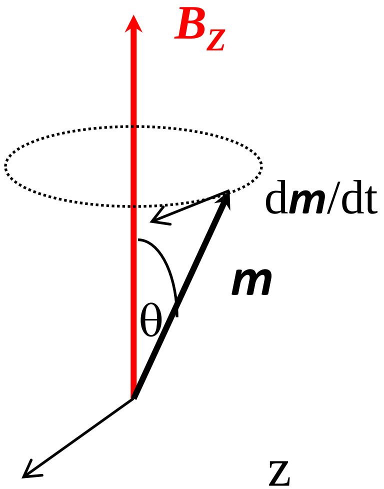
$\boldsymbol{m} = \gamma\ \boldsymbol{l}$

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

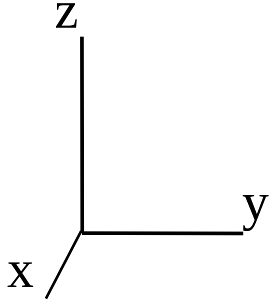
$\Gamma = \mathrm{d}\boldsymbol{l}/\mathrm{dt}$ (Newton's law)

$$\boxed{\mathrm{d}\boldsymbol{m}/\mathrm{dt} = \gamma\, \boldsymbol{m} \times \boldsymbol{B}}$$

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



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



$\mathrm{d}m_x/\mathrm{dt} = \gamma m_y B_z \quad \mathrm{d}m_y/\mathrm{dt} = -\gamma m_x B_z \quad \mathrm{d}m_z/\mathrm{dt} = 0$

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

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

28 GHz T^{-1} for spin

3.3 Magnetism of electrons in free atoms and solids.

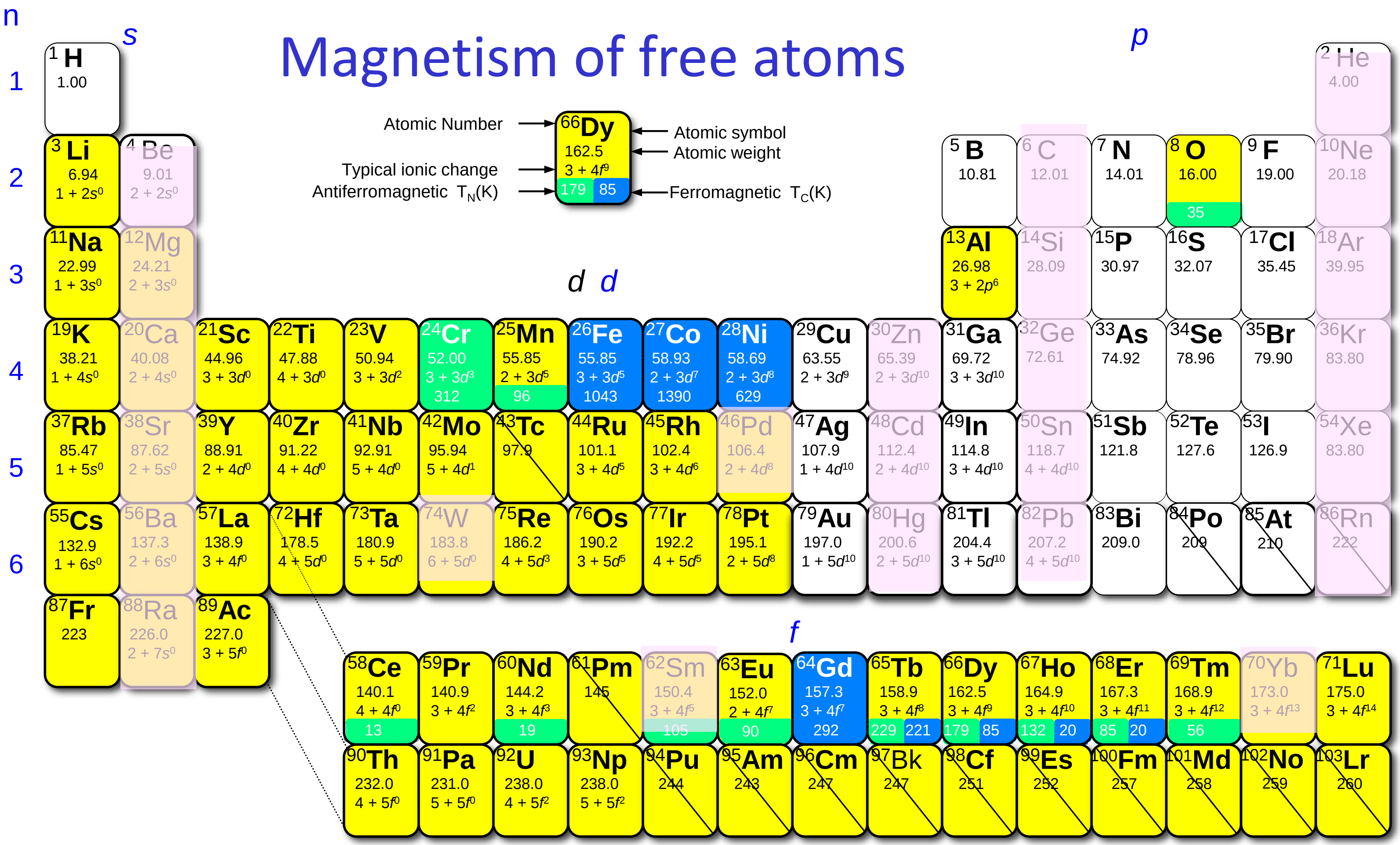
Magnetism in *free atoms* is reduced by shell filling.

Electrons in filled shells have paired spins with ↑ and ↓ 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. Na^+Cl^- both ions are $2p^6$
- covalent bond formation in semiconductors
- band formation in metals

Magnetism of free atoms



Atomic Number → 66 **Dy** ← Atomic symbol

162.5 ← Atomic weight

Typical ionic change → $3 + 4f^9$

Antiferromagnetic T_N(K) → 179 | 85 ← Ferromagnetic T_C(K)

n	s							d d									p	
1	1 **H** 1.00																	2 He 4.00
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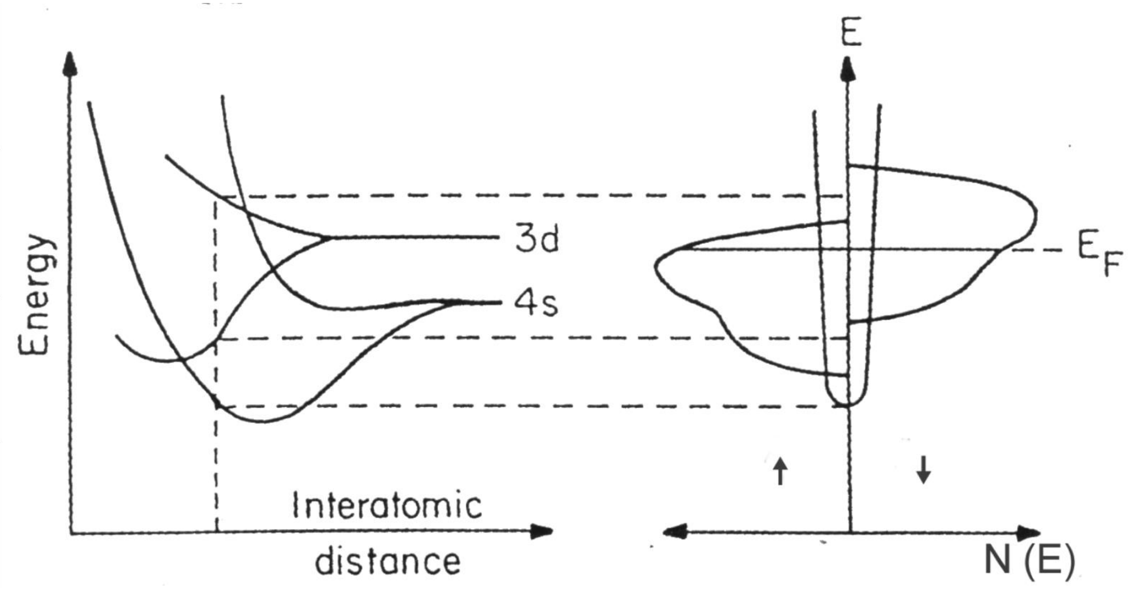
79 out of the 103 first elements are magnetic as free atoms Moments << $Z\mu_B$



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. Iron has a configuration $3d^{7.4}4s^{0.6}$. There are 2.2 unpaired 3d electrons, $m = 2.2\ \mu_B$.

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

γ-Fe_2O_3	**α-Fe**	**YFe_2**	**γ-Fe**	**YFe_2Si_2**
ferrimagnet	**ferromagnet**	**ferromagnet**	**antiferromagnet**	**Pauli paramagnet**
5.0	**2.2**	**1.45**	**unstable**	**0**

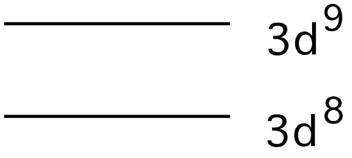
Table: *Atomic moments of iron in different compounds in Bohr magnetons/Fe.*

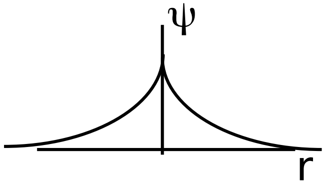
3.4 Localized and delocalized electrons

LOCALIZED MAGNETISM

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

Ni^{2+} 3d^8 **m** = 2 μ_B





$\psi \approx \exp(-r/a_0)$

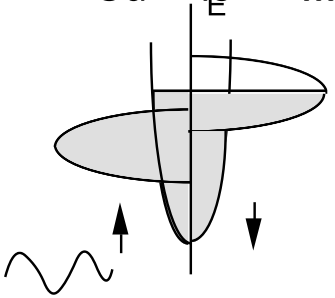
Boltzmann statistics

DELOCALIZED MAGNETISM

Nonintegral number of unpaired spins per atom.

Spin-polarized energy bands with strong correlations.

Ni 3d$^{9.4}$4s$^{0.6}$ **m** = 0.6 μ_B



$\psi \approx \exp(-i\mathbf{k}.\mathbf{r})$

Fermi-Dirac statistics

4*f* metals	*localized electrons*
4*f* compounds	*localized electrons*
3*d* compounds	*localized/delocalized electrons*
3*d* metals	*delocalized electrons.*

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

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

3.5.1 Orbital moment

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

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

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

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

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

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 $\boldsymbol{B}$ along **z**. Then the vector potential in component form is $\boldsymbol{A} = (1/2)(-yB, xB, 0)$,

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

$$\boldsymbol{A} = \tfrac{1}{2}\boldsymbol{B} \times \boldsymbol{r}$$

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

$$\mathcal{H}_1 = (\mu_B/\hbar)\boldsymbol{B}. \boldsymbol{l}$$

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

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 $\boldsymbol{\sigma}_i$, with coupled equations for electrons and positrons. The nonrelativistic limit of the theory, including the interaction with a magnetic field $\boldsymbol{B}$ represented by a vector potential $\boldsymbol{A}$ can be written as

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

- 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

$$\boxed{\mathcal{H}_Z = (\mu_B/\hbar)\boldsymbol{B}.(\boldsymbol{l} + 2\boldsymbol{s})}$$

The factor 2 is not quite exact. The expression is $2(1 + \alpha/2\pi - .....) \approx 2.0023$, where $\alpha = e^2/4\pi\varepsilon_0 hc \approx 1/137$ is the fine-structure constant.

- The fourth term is the spin-orbit ineteraction., which for a central potential $V(r) = -Ze^2/4\pi\varepsilon_0 r$ with Ze as the nuclear charge becomes $-Ze^2\mu_0 \boldsymbol{l.s}/8\pi m_e^{\,2} r^3$ since $\mu_0\varepsilon_0 = 1/c^2$. In an atom $<1/r^3> \approx (0.1\text{ nm})^3$ so the magnitude of the spin-orbit coupling λ 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 $(\boldsymbol{s} \times \nabla V)\boldsymbol{.}\,\boldsymbol{p}$

- 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

$$E = {}_{mec2}\sqrt{}[1 + (v^2/c^2)]$$

The order of magnitude of the velocity of electrons in solids is ©c. Expanding the equation in powers of c

$$E = m_e c^{2\,+} (1/2)\ \copyright^2 m_e c^2 - (1/8)\ \copyright^4 m_e c^2$$

Here the rest mass of the electron, $mc^2 = 511$ 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 spin and orbital angular momenta of the individual atoms 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.

Introduction

E & M

Basic Ideas

M. B, H

Energy

Quantum theory

Magnetism of the electron

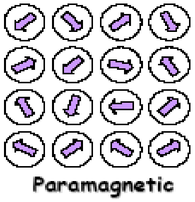
Magnetism of the atom with one or more electrons

single electron magnetism.

Molecular field theory

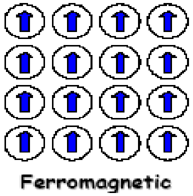
Paramagnetism

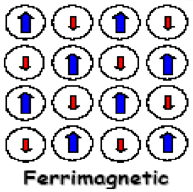
multi-electron atoms



Disordered

Magnetism of interacting atoms Ferromgnetism





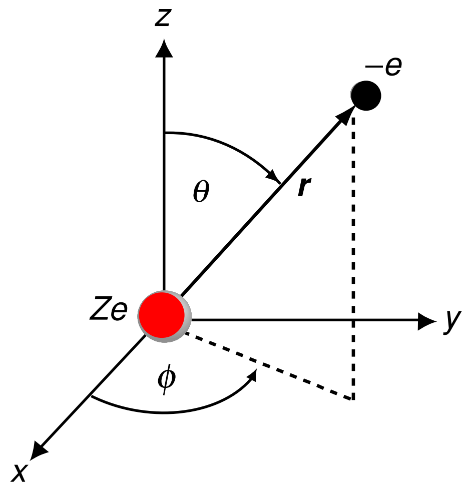
Ordered

Other topics

multi-atom solids

Applications

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,θ,ϕ)

$$\mathcal{H} = - (\hbar^2/2m_e)\nabla^2 - Ze^2/4\pi\varepsilon_0 r$$

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

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

$$\boldsymbol{l} = -i\hbar\begin{vmatrix} \mathbf{e}_x & \mathbf{e}_y & \mathbf{e}_z \\ x & y & z \\ \partial/\partial x & \partial/\partial y & \partial/\partial z \end{vmatrix}$$

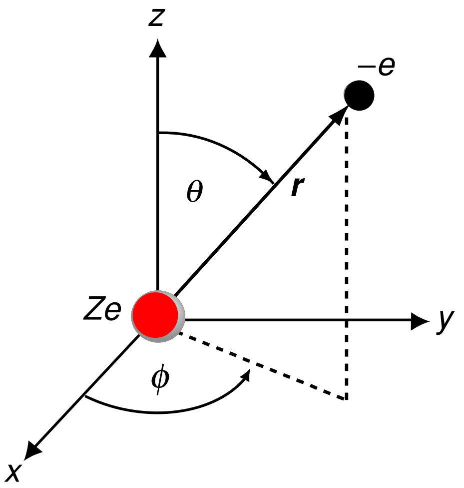
$$\nabla^2 = \partial^2/\partial r^2 + (2/r)\partial/\partial r + 1/r^2\{\partial^2/\partial\theta^2 + \cot\theta\,\partial/\partial\theta + (1/\sin^2\theta)\partial^2/\partial^2\phi\}$$

$$\boldsymbol{l} = \boldsymbol{r} \times \boldsymbol{p} = -i\hbar[(y\partial/\partial z - z\partial/\partial y)\boldsymbol{e}_x - (x\partial/\partial z - z\partial/\partial x)\boldsymbol{e}_y + (x\partial/\partial y - y\partial/\partial x)\boldsymbol{e}_z$$

$$= i\hbar[\sin\phi\,\partial/\partial\theta + \cot\theta\cos\phi\,\partial/\partial\phi)\boldsymbol{e}_x + (-\cos\phi\,\partial/\partial\theta + \cot\theta\sin\phi\,\partial/\partial\phi)\boldsymbol{e}_y - (\partial/\partial\phi)\boldsymbol{e}_z]$$

$\boldsymbol{l}^{2\cdot} = \boldsymbol{l}_x^{\,2} + \boldsymbol{l}_y^{\,2} + \boldsymbol{l}_z^{\,2} = \hbar^2\{\partial^2/\partial\theta^2 + \cot\theta\,\partial/\partial\theta + (1/\sin^2\theta)\partial^2/\partial^2\phi\}$ – the term in parentheses in ∇^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,θ,ϕ)



$$\boxed{\mathcal{H}\psi_i = E_i\,\psi_i}$$

$$[-(\hbar^2/2m_e)\nabla^2 - Ze^2/4\pi e_0 r]\;\psi_i = E_i\,\psi_i$$

Solutions for E_i are the eigenvalues (energy levels) of the atom.
The corresponding wavefunctions ψ_i are the eigenfunctions (orbitals) of the atom

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

The *basic property of angular momentum* is that $\boxed{[\boldsymbol{l}_x, \boldsymbol{l}_y] = i\hbar\,\boldsymbol{l}_z}$ etc. where $[\boldsymbol{l}_x, \boldsymbol{l}_y] = \boldsymbol{l}_x\boldsymbol{l}_y - \boldsymbol{l}_y\boldsymbol{l}_x$
$[\mathbf{X},\mathbf{Y}]$ 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 $[\boldsymbol{l}^2, \boldsymbol{l}_i] = 0$

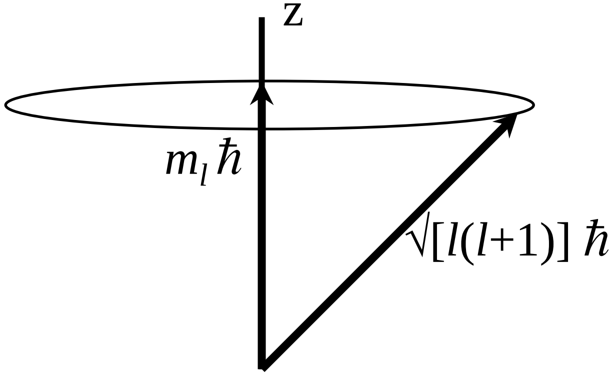
Vector model

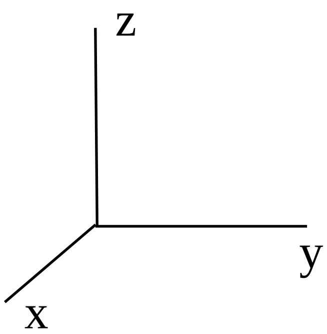
$\boldsymbol{l}^2$ the square of the orbital angular momentum operator of the electron in a central potential;
It has the eigenvalue $l(l+1)\hbar^2$. $\boldsymbol{l}^2 | l, m_l \rangle = l(l+1)]\hbar^2 | l, m_l \rangle$

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

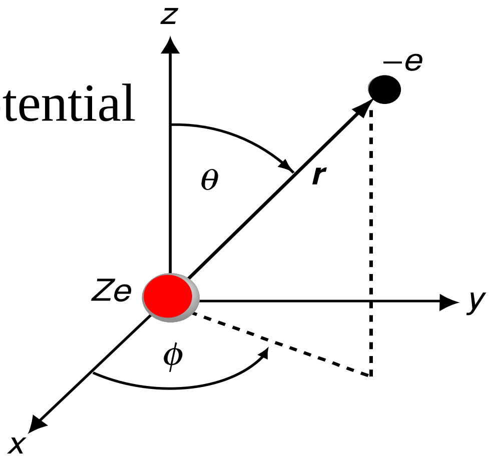
$\boldsymbol{l}_z$ the projection along **z** is the operator $-i\hbar(\partial/\partial\phi)$ which has eigenvalues $m_l\hbar$, which can have any value from $-l\hbar$ to $+l\hbar$. (2l + 1 different possible values). $\boldsymbol{l}_z | l, m_l \rangle = m_l \hbar | l, m_l \rangle$

We can model the total angular momentum as a vector which precesses around **z**.
$\boldsymbol{l}_x$ and $\boldsymbol{l}_y$ are indeterminate.





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



$$\boxed{\psi_{n,l,ml}(r,\theta,\phi) = \underbrace{R_{n,l}(r)}_{\text{radial part}}\underbrace{Y_l^{ml}(\theta,\phi)}_{\text{angular part}}}$$

- The angular part $Y_l^{ml}(\theta,\phi)$ are *spherical harmonics* that depend on two integers l, m_l, where $|m_l| \leq l$. The pair l, m_l denote an *orbital*

Notation: $l = 0$; *s* – orbital $l = 1$; *p* – orbital $l = 2$; *d* – orbital $l = 3$; *f* - orbital

The spherical harmonics are each a product of terms $\Theta(\theta)$ and $\Phi(\phi)$; $Y_l^{ml}(\theta,\phi) = \Theta(\theta)\Phi(\phi)$

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

The z-component of orbital angular momentum, represented by the operator $\boldsymbol{l}_z = -i\hbar(\partial/\partial\phi)$, has eigenvalues $\langle\Phi|\, \boldsymbol{l}_z \,|\Phi\rangle = \int \exp(-im_l\phi)\, -i\hbar(\partial/\partial\phi)\, \exp(im_l\phi) = m_l\hbar$.

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

Spherical harmonics

s $Y_0^0 = \surd(1/4\pi)$

p $Y_1^0 = \surd(3/4\pi)\cos\theta$ $Y_1^{\pm 1} = \pm\surd(3/8\pi)\sin\theta\, e^{\pm i\phi}$

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

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

- The radial part R(*r*) depends on *l* , also on n the principal quantum number where $l < n$; hence $l = 0, 1, \ldots, (n-1)$.

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

$V_1^0 = 1$. Here $a_0 = 4\pi\varepsilon_0\hbar^2/m_e e^2 = 52.9$ pm is the first *Bohr radius*, the basic length scale in atomic physics. The energy levels of the one-electron atom are

$$\boxed{E = -Zme^4/8h^2\varepsilon_0{}^2n^2 = -ZR/n^2}$$

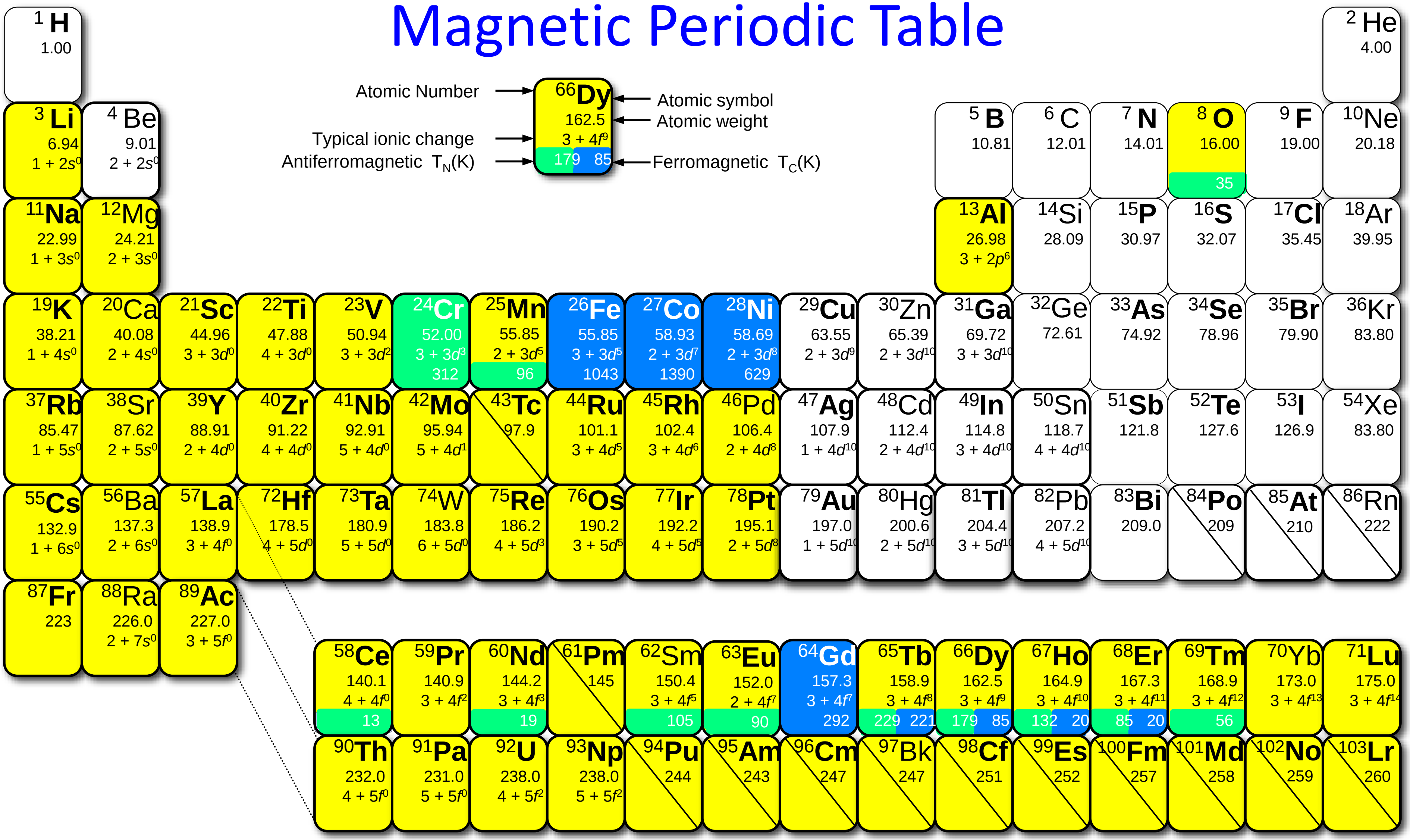
The quantity $R = m_e e^4/8h^2\varepsilon_0 = 13.6$ eV is the Rydberg, the basic energy unit in atomic physics. For the central Coulomb potential $\phi_{e,}$ the potential energy V(*r*) depends *only* on *r*, not on θ or φ. E depends *only* on n.

The three quantum numbers n, l, m_l denote an *orbital*, a spatial distribution of electronic charge. Orbitals are denoted nX, X = s, p, d, f for $l = 0, 1, 2, 3$. Each orbital can accommodate up to two electrons with spin $m_s = \pm½$. The hydrogenic orbitals are listed in the table

	n	l	m_l	m_s	No of orbitals
1s	**1**	**0**	**0**	**±½**	**2**
2s	**2**	**0**	**0**	**±½**	**2**
2p	**2**	**1**	**0,±1**	**±½**	**6**
3s	**3**	**0**	**0**	**±½**	**2**
3p	**3**	**1**	**0,±1**	**±½**	**6**
3d	**3**	**2**	**0,±1,±2**	**±½**	**10**
4s	**4**	**0**	**0**	**±½**	**2**
4p	**4**	**1**	**0,±1**	**±½**	**6**
4d	**4**	**2**	**0,±1,±2**	**±½**	**10**
4f	**4**	**3**	**0,±1,±2,±3**	**±½**	**14**

- 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.

Magnetic Periodic Table



Atomic Number → 66 **Dy** ← Atomic symbol

162.5 ← Atomic weight

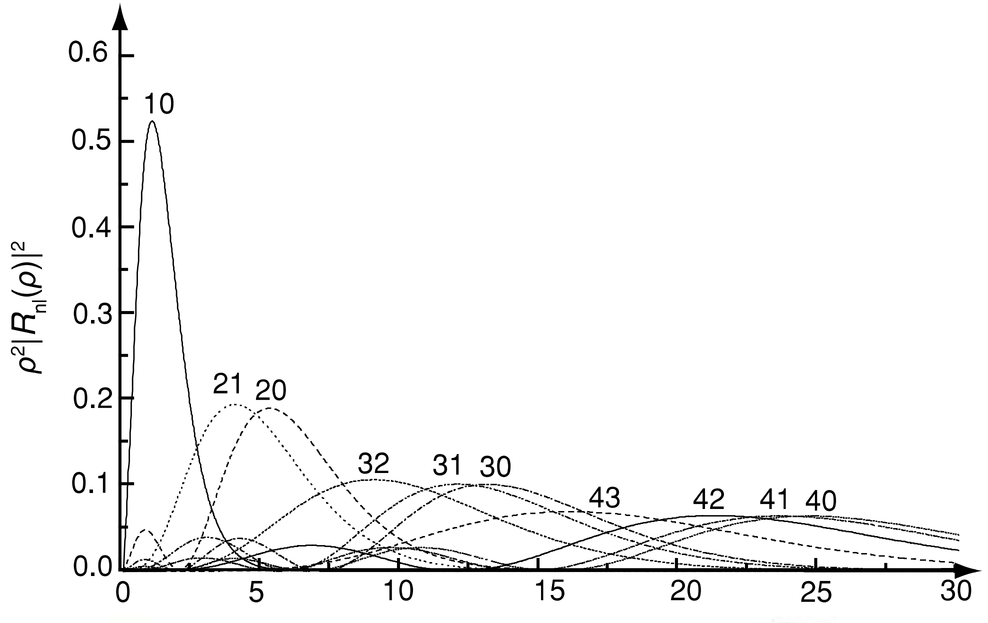
Typical ionic change → $3 + 4f^9$

Antiferromagnetic T_N(K) → 179 85 ← Ferromagnetic T_C(K)

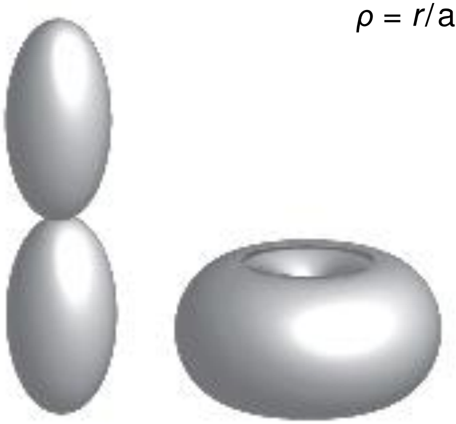
1 **H** 1.00																	2 He 4.00
3 **Li** 6.94 $1 + 2s^0$	4 Be 9.01 $2 + 2s^0$											5 **B** 10.81	6 C 12.01	7 **N** 14.01	8 **O** 16.00 35	9 **F** 19.00	10 Ne 20.18
11 **Na** 22.99 $1 + 3s^0$	12 Mg 24.21 $2 + 3s^0$											13 **Al** 26.98 $3 + 2p^6$	14 Si 28.09	15 **P** 30.97	16 **S** 32.07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

☐	Nonmetal	☐	Diamagnet	🟦	Ferromagnet T_C > 290K
☐	Metal	🟨	Paramagnet	🟩	Antiferromagnet with T_N > 290K
⧅	Radioactive	**BOLD**	Magnetic atom	🟩🟦	Antiferromagnet/Ferromagnet with T_N/T_C < 290 K

$R_{n,l}(r)$



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



$m_l = 0$

s orbital

$\ell = 0$

$m_l = 0$ $m_l = \pm 1$

p orbitals

$\ell = 1$

$m_l = 0$ $m_l = \pm 1$ $m_l = \pm 2$

d orbitals

$\ell = 2$

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

Schrodinger — wave mechanics, differential operators

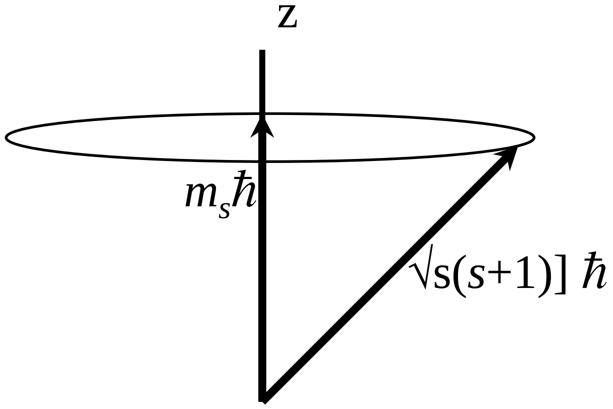
Heissenberg — matrix mechanics, n x n matrix operators, basis of n eigenstates,

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

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



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

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Schrodinger — wave mechanics, differential operators

Heissenberg — matrix mechanics, $n \times n$ matrix operators, basis of n eigenstates,

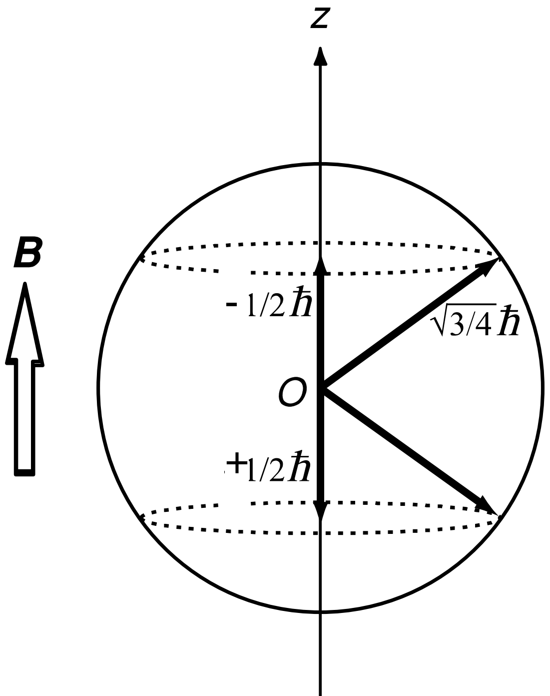
If a matrix is *diagonal*, the eigenvalues are the the diagonal elements.

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

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

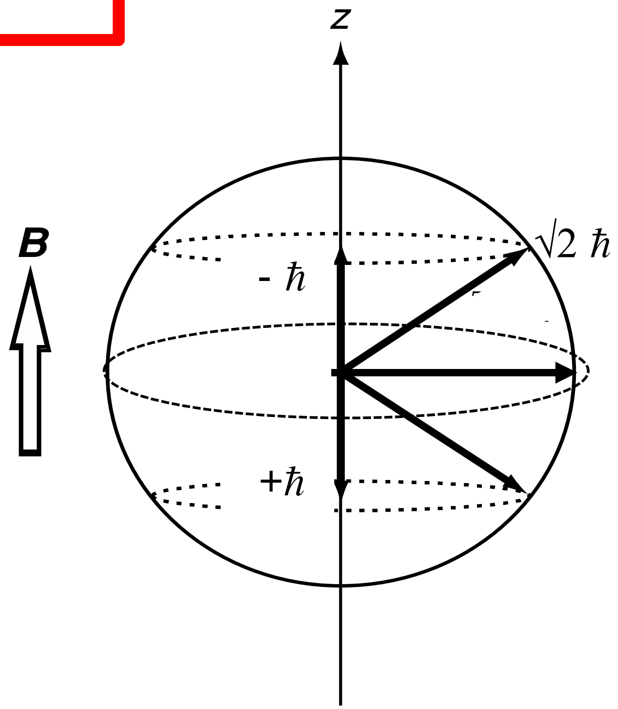
$$\mathbf{s}^2 = \mathbf{s}_x{}^2 + \mathbf{s}_y{}^2 + \mathbf{s}_s{}^2 = \begin{bmatrix} 1 & 0 \\ 0 & 1 \end{bmatrix} 3\hbar^2/4$$

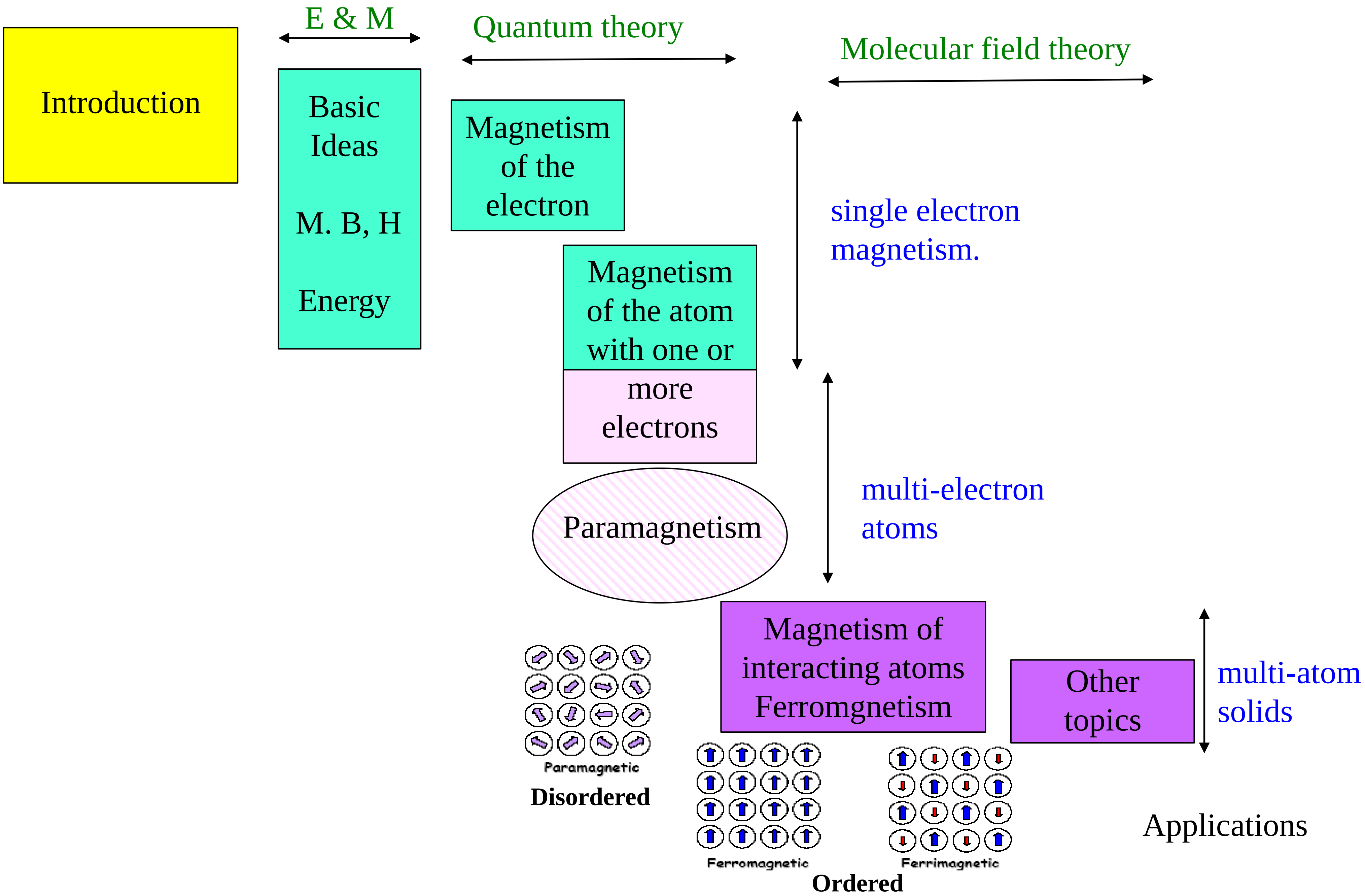


For orbital angular momentum, the basis set are the $2l + 1$ orbital wave functions
For example, if $l = 1$, there are three orbital wave functions, with $m_l = -1, 0, 1$

$$\boldsymbol{l}_x = \begin{vmatrix} 0 & 1 & 0 \\ 1 & 0 & 1 \\ 0. & 1 & 0 \end{vmatrix} \hbar/\sqrt{2} \qquad \boldsymbol{l}_y = \begin{vmatrix} 0 & -i. & 0 \\ i & 0 & -i \\ 0 & i & 0 \end{vmatrix} \hbar/\sqrt{2} \qquad \boldsymbol{l}_z = \begin{vmatrix} 1 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & -1 \end{vmatrix} \hbar$$

$$\boldsymbol{l}^2 = \boldsymbol{l}_x{}^2 + \boldsymbol{l}_y{}^2 + \boldsymbol{l}_z{}^2 = \begin{vmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{vmatrix} 2\hbar^2$$





Introduction

E & M

Basic Ideas

M. B, H

Energy

Quantum theory

Magnetism of the electron

Magnetism of the atom with one or more electrons

Molecular field theory

single electron magnetism.

multi-electron atoms

Paramagnetism

Magnetism of interacting atoms Ferromgnetism

Other topics

multi-atom solids

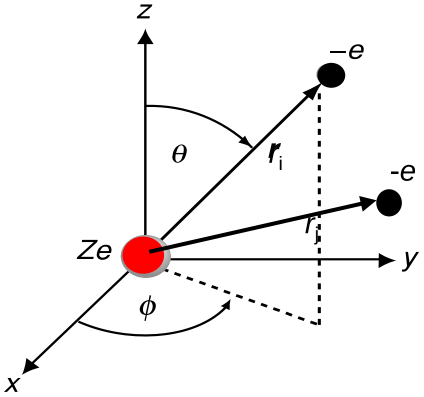
Disordered

Ordered

Applications

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,θ,ϕ. When there are several electrons, they interact via inter-electronic Coulomb interactions. Terms like $e^2/4\pi e_0|r_i - r_j|$ have to be added to the Hamiltonian. A many-body problem!



$$\mathcal{H} = \Sigma_i(p_i^2/2m) + \Sigma_I(Ze^2/4\pi e_0 r_i) + (1/2)\Sigma_{i\neq j}(e^2/4\pi e_0|r_i - r_j|)$$

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

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

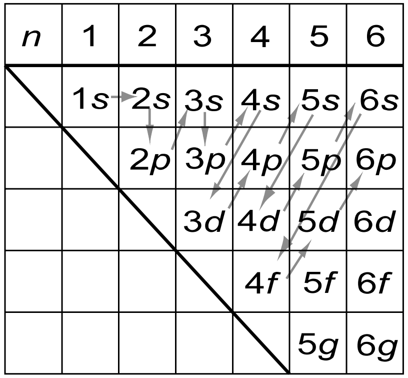
The potential with many electrons is not a simple Coulomb potential well; the degeneracy of electrons with different *l* is raised. The 4*s* shell, for example, is then lower in energy than the 3*d* shell, which defines the shape of the periodic table.

The quantities $V_I(r)$ must be determined self-consistently (the Hartree-Foch approximation)

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

$[\mathcal{H},\mathbf{S}^2] = 0$, $[\mathcal{H},\mathbf{S}_z] = 0$ where $\mathbf{S} = \Sigma_I \boldsymbol{s}_\mathbf{i}$ a sum of the spin moments

$[\mathcal{H},\mathbf{L}^2] = 0$, $[\mathcal{H},\mathbf{L}_z] = 0$ where $\mathbf{L} = \Sigma_I \boldsymbol{l}_\mathrm{i}$ a sum of the orbital moments

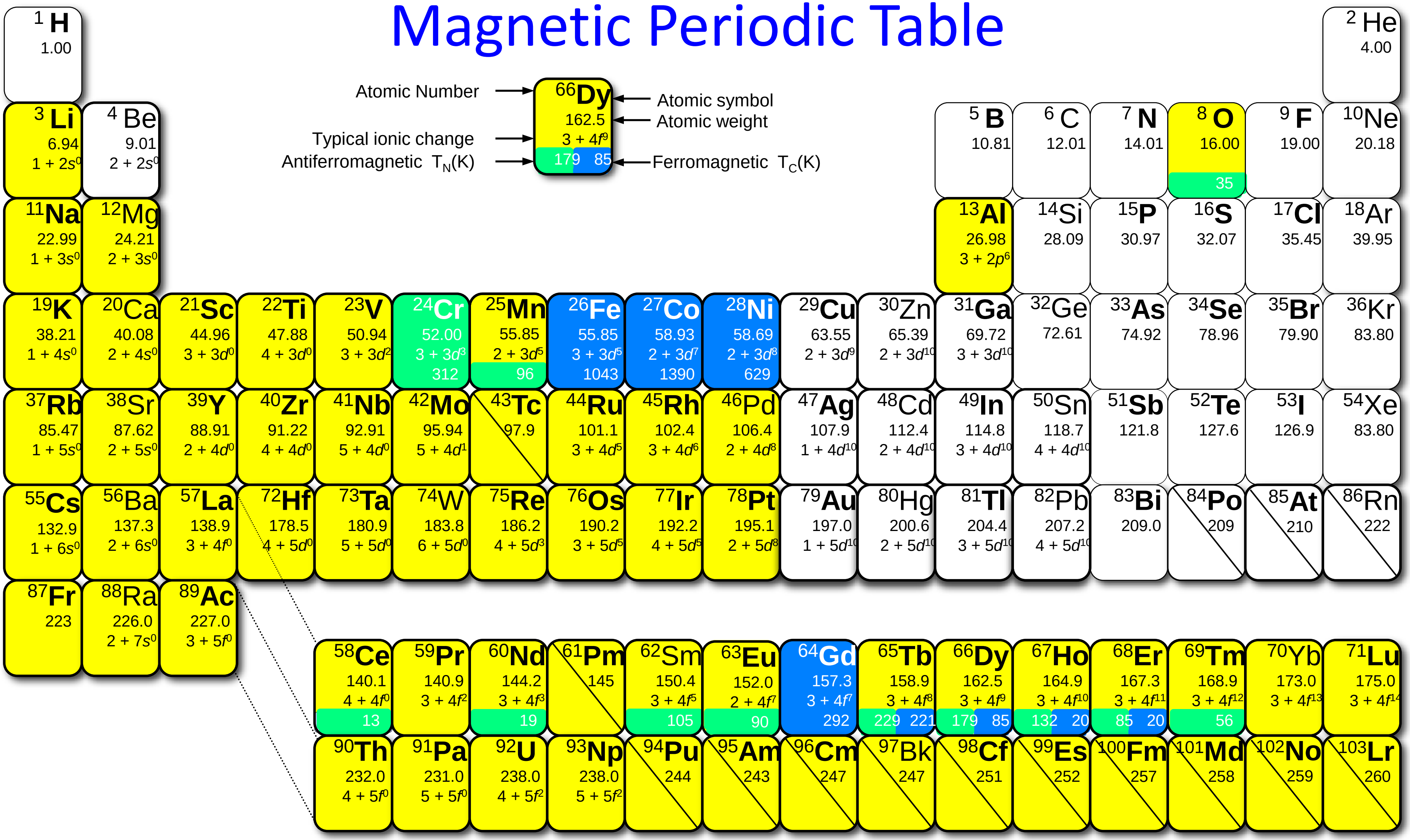


n	1	2	3	4	5	6
	1*s*	2*s*	3*s*	4*s*	5*s*	6*s*
		2*p*	3*p*	4*p*	5*p*	6*p*
			3*d*	4*d*	5*d*	6*d*
				4*f*	5*f*	6*f*
					5*g*	6*g*

The sums have the greatest values consistent with the Pauli principle (no two electrons can have the same four quantum numbers n, l, m_l, m_s)

The quantum numbers $S = \Sigma_i m_{s\,i}$ $L = \Sigma_i m_{l\,i}$ (again consistent with Pauli principle)

Magnetic Periodic Table



Atomic Number → 66 **Dy** ← Atomic symbol

162.5 ← Atomic weight

Typical ionic change → 3 + $4f^9$

Antiferromagnetic T_N(K) → 179 85 ← Ferromagnetic T_C(K)

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

☐ Nonmetal

☐ Metal

⧅ Radioactive

☐ Diamagnet

🟨 Paramagnet

BOLD Magnetic atom

🟦 Ferromagnet T_C > 290K

🟩 Antiferromagnet with T_N > 290K

🟩🟦 Antiferromagnet/Ferromagnet with T_N/T_C < 290 K

Each eigenstate of $\mathscr{H}$ 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 $\psi^{\alpha}_{LSM_LM_S}$

Eigenvalues $E^{\alpha}_{LSM_LM_S}$

$$\mathscr{H}|\psi^{\alpha}_{LSM_LM_S}\rangle = E^{\alpha}_{LSM_LM_S}|\psi^{\alpha}_{LSM_LM_S}\rangle$$

$$\mathbf{L}^2|\psi^{\alpha}_{LSM_LM_S}\rangle = L(L+1)\hbar^2|\psi^{\alpha}_{LSM_LM_S}\rangle \qquad \mathbf{L}_z|\psi^{\alpha}_{LSM_LM_S}\rangle = M_L\hbar|\psi^{\alpha}_{LSM_LM_S}\rangle$$

$$\mathbf{S}^2|\psi^{\alpha}_{LSM_LM_S}\rangle = S(S+1)\hbar^2|\psi^{\alpha}_{LSM_LM_S}\rangle \qquad \mathbf{S}_z|\psi^{\alpha}_{LSM_LM_S}\rangle = M_S\hbar|\psi^{\alpha}_{LSM_LM_S}\rangle$$

The eigenstates for different M_L or M_S values are degenerate in the absence of a magnetic field, but the states for different L, S are separated. (In a field there is Zeeman splitting) Hence each (L,S) state is (2L+1)(2S+1) times degenerate.

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

spin degeneracy

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

Notation $\boxed{{}^{2S+1}L}$

Example: ^{3}D 'triplet D' means S = 1, L = 2, total degeneracy 3 × 5 = 15

The energy splitting of the terms is of order 1 eV. In spectroscopy the energy unit cm^{-1} is often used; Useful energy conversions are 1 eV ≡ 11605 K and 1 cm^{-1} ≡ 1.44 K ($E = p^2/2m_e$ $p = h/\lambda$)

4.3 Addition of angular momenta

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

i.e. $\boldsymbol{j}_1^2\, |j_1, m_1\rangle = j_1(j_1+1)\,\hbar^2 |j_1, m_1\rangle$ $\quad$ $\boldsymbol{j}_{1z}\, |j_1, m_1\rangle = m_1\hbar |j_1, m_1\rangle$ $\quad$ $[2j_1 + 1$ of them$]$

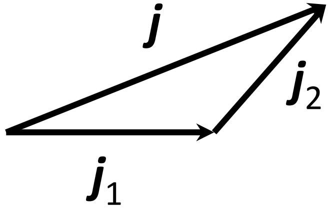
$\boldsymbol{j}_2^2\, |j_2, m_2\rangle = j_2(j_2+1)\,\hbar^2 |j_2, m_2\rangle$ $\quad$ $\boldsymbol{j}_{2z}\, |j_2, m_2\rangle = m_2\hbar |j_2, m_2\rangle$. $\quad$ $[2j_2 + 1$ of them$]$

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

Now $-j_1 \le m_1 \le j_1$ and $-j_2 \le m_2 \le j_2$ 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 $\boldsymbol{j}^2$ and $\boldsymbol{j}_z$ are $|j_1, j_2, j\,, m\,\rangle$ with $|\, j_1 - j_2\,| \le j \le |\, j_1 + j_2\,|$

(Triangle rule)



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

Their spin and orbital angular momenta each add to give resultants consistent with the Pauli principle

$\mathbf{S} = \Sigma\mathbf{s}_\mathrm{i}$, $\quad$ $\mathbf{L} = \Sigma\boldsymbol{l}_i$. $\quad$ *Apply triangle rule, subject to constraint of Pauli principle*

$\mathbf{S}_\mathrm{z} = \Sigma\mathbf{s}_\mathrm{zi}$, $\quad$ $\mathbf{L}_\mathrm{z} = \Sigma\boldsymbol{l}_\mathrm{zi}$. $\quad$ *The z-components just add up.*

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 $l = 1$, $\mathbf{L} = \boldsymbol{l}_1 + \boldsymbol{l}_2$ Hence $|l_1 - l_2| \le L \le |l_1 + l_2|$; $0 \le L \le 2$, $L = 0, 1, 2$

Also $s = ½$, $\mathbf{S} = \boldsymbol{s}_1 + \boldsymbol{s}_2$ Hence $|s_1 - s_2| \le S \le |s_1 + s_2|$; $0 \le S \le 1$, $S = 0, 1$

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
	↓	↓	-1	-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)

The case of Carbon; $1s^2 2s^2 2p^6$

$M_s \backslash M_l$	-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*. $\psi_{total}^2(1,2) = \psi_{total}^2(2,1)$

$$\boxed{\psi_{total}(1,2) = \pm\ \psi_{total}(2,1)}$$

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

$S = 0,\ M_s = 0$ $\quad \psi_{spin} = [|\uparrow\downarrow\rangle - |\downarrow\uparrow\rangle]/\sqrt{2}$ antisymmetric $\quad \psi_{spin}(1,2) = -\ \psi_{spin}(2,1)$

$S = 1,\ M_s = 1$ $\quad \psi_{spin} = |\uparrow\uparrow\rangle$

$M_s = 0$ $\quad \psi_{spin} = [|\uparrow\downarrow\rangle + |\downarrow\uparrow\rangle]/\sqrt{2}$ symmetric $\quad \psi_{spin}(1,2) = +\ \psi_{spin}(2,1)$

$M_s = -1$ $\quad \psi_{spin} = |\downarrow\downarrow\rangle$

SPIN Antisymmetric when S = 0

Symmetric when S = 1

ORBIT Antisymmetric when L = 1, *3, 5 .....*

Symmetric when L = 0, 2, *4, 6 .....*

The total wavefunction must be antisymmetric, $\quad \psi_{total} = \psi_{spin}\psi_{orbit}$

L=0, S=0 (^{1}S) ~~L=0, S=1 (^{3}S)~~

~~L=1, S=0 (^{1}P)~~ L=1, S=1 (^{3}P)

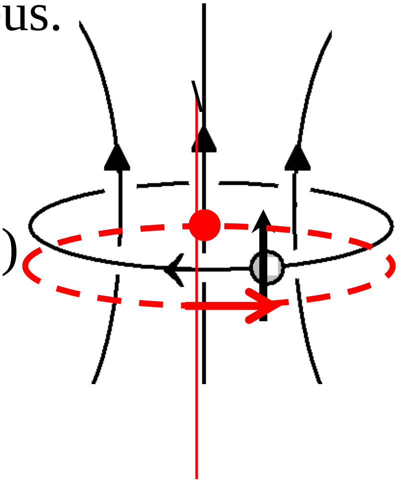
L=2, S=0 (^{1}D) ~~L=2, S=1 (^{3}D)~~

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 a magnetic field $\boldsymbol{B}_{orb}$ created by the relative orbital motion of the nucleus.



$$\mathcal{H}_{so} = -\boldsymbol{m}.\boldsymbol{B}_{orb} = -\mu_B.\boldsymbol{B}_{orb}$$

The field due to a current loop is $B = \mu_0 I/2r$ where $I = \mathrm{Z}ev/2\pi r$ (p.49)

$B_{orb} = \mu_0 Zev/4\pi r^2$. $\quad E_{so} = -\mu_0\mu_B Zev/4\pi r^2$.

Also $l = \mathrm{m}_e \mathrm{v r} \approx \hbar$. $\quad E_{so} = -\mu_0\mu_B Ze\hbar/4\pi \mathrm{m}_e r^3$

Since $r \approx a_0/\mathrm{Z}$ in the hydrogenic atom $E_{so} = -\mu_0\mu_B{}^2 \mathrm{Z}^4/2\pi a_o{}^3$

The interaction varies approximately as Z^4 for the innermost electrons.

It is most important for heavy elements.

The interaction is usually written in terms of the orbital moment as

$$\boxed{\mathcal{H}_{so} = -\lambda \boldsymbol{l}.\boldsymbol{s}}$$ where the spin-orbit coupling constant λ has units of $\mathrm{J}/\hbar^2$

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.

$\boldsymbol{l}$ and $\boldsymbol{s}$ couple to form the total angular momentum $\boldsymbol{j}$. $j = l \pm \mathrm{s} = l \pm ½$ $\qquad l, s, j, m_j$

In multi-electron atoms the spin-orbit interaction is

$$\mathcal{H}_{so} = -\,\Lambda \boldsymbol{L}.\boldsymbol{S}$$

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

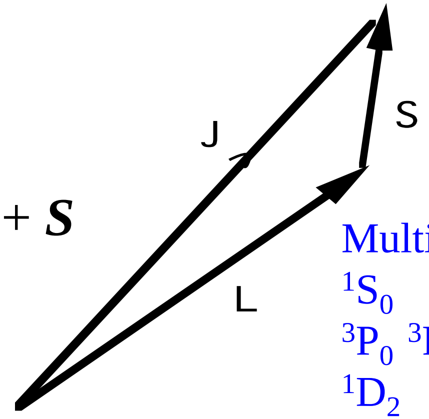
$$L - S \leq J \leq L + S$$

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

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

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

$$\boldsymbol{J} = \boldsymbol{L} + \boldsymbol{S}$$



Multiplets for C
${}^1S_0$
${}^3P_0$ ${}^3P_1$ ${}^3P_2$
${}^1D_2$

Addition of **L** and **S** in the vector model

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

	ion	**Λ**
$3d^1$	**Ti^{3+}**	**229**
$3d^2$	**V^{3+}**	**153**
$3d^3$	**Cr^{3+}**	**131**
$3d^4$	**Mn^{3+}**	**125**
$3d^6$	**Fe^{2+}**	**-164**
$3d^7$	**Co^{2+}**	**-272**
$3d^8$	**Ni^{2+}**	**-494**

$4f^1$	**Ce^{3+}**	**920**
$4f^2$	**Pr^{3+}**	**540**
$4f^3$	**Nd^{3+}**	**430**
$4f^5$	**Sm^{3+}**	**350**
$4f^8$	**Tb^{3+}**	**-410**
$4f^9$	**Dy^{3+}**	**-550**
$4f^{10}$	**Ho^{3+}**	**-780**
$4f^{11}$	**Er^{3+}**	**-1170**
$4f^{12}$	**Tm^{3+}**	**-1900**
$4f^{13}$	**Yb^{3+}**	**-4140**

4.3.2 Atomic multiplets, Hunds rules, examples

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

Answer: Use Hund's rules: These are an empirical prescription deduced from study of optical spectra which gives the lowest energy multiplet $\boxed{^{2S+1}L_J}$

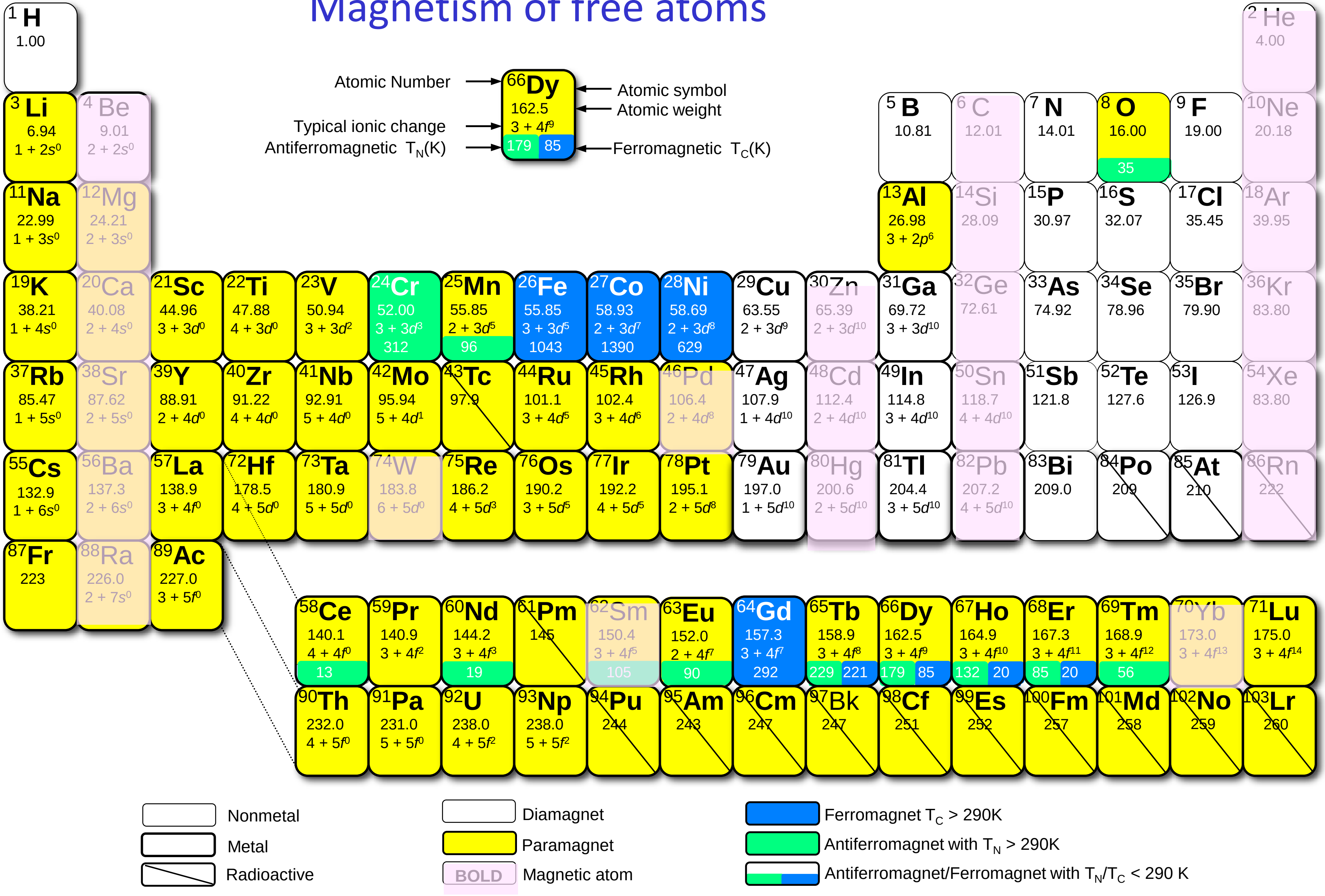
i) → First maximize S for the configuration
ii) → Then maximize L, consistent with that value of S
iii) → Finally, couple L and S; $J = L - S$ if shell is < half-full; $J = L + S$ if shell is > half-full.

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 our carbon atom is $^3P_0$, which is nonmagnetic ! ($J = 0$).

Magnetism of free atoms



66 Dy 162.5 $3 + 4f^9$ 179 85

Atomic Number
Atomic symbol
Atomic weight
Typical ionic change
Antiferromagnetic T_N(K)
Ferromagnetic T_C(K)

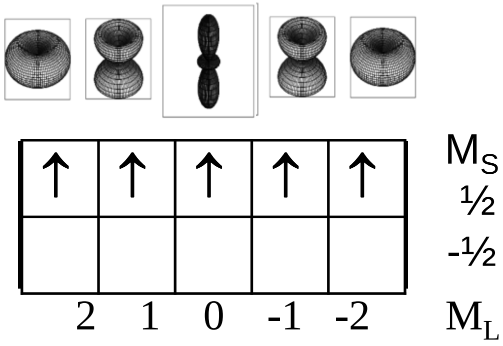
1 H 1.00																	2 He 4.00
3 Li 6.94 $1 + 2s^0$	4 Be 9.01 $2 + 2s^0$											5 B 10.81	6 C 12.01	7 N 14.01	8 O 16.00 35	9 F 19.00	10 Ne 20.18
11 Na 22.99 $1 + 3s^0$	12 Mg 24.21 $2 + 3s^0$											13 Al 26.98 $3 + 2p^6$	14 Si 28.09	15 P 30.97	16 S 32.07	17 Cl 35.45	18 Ar 39.95
19 K 38.21 $1 + 4s^0$	20 Ca 40.08 $2 + 4s^0$	21 Sc 44.96 $3 + 3d^0$	22 Ti 47.88 $4 + 3d^0$	23 V 50.94 $3 + 3d^2$	24 Cr 52.00 $3 + 3d^3$ 312	25 Mn 55.85 $2 + 3d^5$ 96	26 Fe 55.85 $3 + 3d^5$ 1043	27 Co 58.93 $2 + 3d^7$ 1390	28 Ni 58.69 $2 + 3d^8$ 629	29 Cu 63.55 $2 + 3d^9$	30 Zn 65.39 $2 + 3d^{10}$	31 Ga 69.72 $3 + 3d^{10}$	32 Ge 72.61	33 As 74.92	34 Se 78.96	35 Br 79.90	36 Kr 83.80
37 Rb 85.47 $1 + 5s^0$	38 Sr 87.62 $2 + 5s^0$	39 Y 88.91 $2 + 4d^0$	40 Zr 91.22 $4 + 4d^0$	41 Nb 92.91 $5 + 4d^0$	42 Mo 95.94 $5 + 4d^1$	43 Tc 97.9	44 Ru 101.1 $3 + 4d^5$	45 Rh 102.4 $3 + 4d^6$	46 Pd 106.4 $2 + 4d^8$	47 Ag 107.9 $1 + 4d^{10}$	48 Cd 112.4 $2 + 4d^{10}$	49 In 114.8 $3 + 4d^{10}$	50 Sn 118.7 $4 + 4d^{10}$	51 Sb 121.8	52 Te 127.6	53 I 126.9	54 Xe 83.80
55 Cs 132.9 $1 + 6s^0$	56 Ba 137.3 $2 + 6s^0$	57 La 138.9 $3 + 4f^0$	72 Hf 178.5 $4 + 5d^0$	73 Ta 180.9 $5 + 5d^0$	74 W 183.8 $6 + 5d^0$	75 Re 186.2 $4 + 5d^3$	76 Os 190.2 $3 + 5d^5$	77 Ir 192.2 $4 + 5d^5$	78 Pt 195.1 $2 + 5d^8$	79 Au 197.0 $1 + 5d^{10}$	80 Hg 200.6 $2 + 5d^{10}$	81 Tl 204.4 $3 + 5d^{10}$	82 Pb 207.2 $4 + 5d^{10}$	83 Bi 209.0	84 Po 209	85 At 210	86 Rn 222
87 Fr 223	88 Ra 226.0 $2 + 7s^0$	89 Ac 227.0 $3 + 5f^0$															

58 Ce 140.1 $4 + 4f^0$ 13	59 Pr 140.9 $3 + 4f^2$	60 Nd 144.2 $3 + 4f^3$ 19	61 Pm 145	62 Sm 150.4 $3 + 4f^5$ 105	63 Eu 152.0 $2 + 4f^7$ 90	64 Gd 157.3 $3 + 4f^7$ 292	65 Tb 158.9 $3 + 4f^8$ 229 221	66 Dy 162.5 $3 + 4f^9$ 179 85	67 Ho 164.9 $3 + 4f^{10}$ 132 20	68 Er 167.3 $3 + 4f^{11}$ 85 20	69 Tm 168.9 $3 + 4f^{12}$ 56	70 Yb 173.0 $3 + 4f^{13}$	71 Lu 175.0 $3 + 4f^{14}$
90 Th 232.0 $4 + 5f^0$	91 Pa 231.0 $5 + 5f^0$	92 U 238.0 $4 + 5f^2$	93 Np 238.0 $5 + 5f^2$	94 Pu 244	95 Am 243	96 Cm 247	97 Bk 247	98 Cf 251	99 Es 252	100 Fm 257	101 Md 258	102 No 259	103 Lr 260

☐	Nonmetal	☐	Diamagnet	🟦	Ferromagnet T_C > 290K
☐	Metal	🟨	Paramagnet	🟩	Antiferromagnet with T_N > 290K
⧄	Radioactive	BOLD	Magnetic atom	🟩🟦	Antiferromagnet/Ferromagnet with T_N/T_C < 290 K

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

4.3.3 Examples



Fe^{3+} $3d^5$

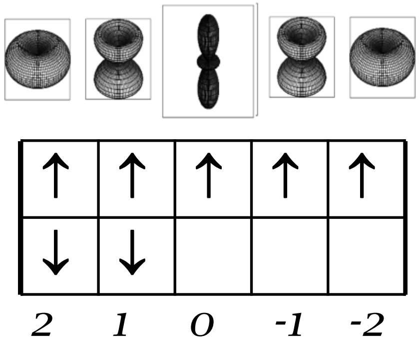
S = 5/2 L = 0 J = 5/2

$^6S_{5/2}$

Note: Maximizing S is equivalent to maximizing $M_s = \Sigma m_{si}$, since $M_s \leq S$

Same for L

Co^{2+} $3d^7$



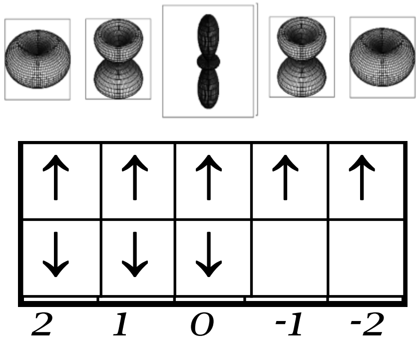
$S = 3/2$ $L = 3$ $J = 9/2$

$^4F_{9/2}$

Note: Maximizing L is equivalent to maximizing $M_L = \Sigma m_l$, since $M_L \leq L$

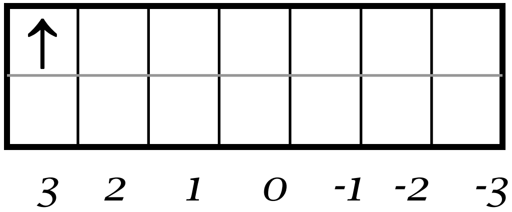
Ni^{2+} 3d^8

S = 1 L = 3 J = 4



$^3F_4$

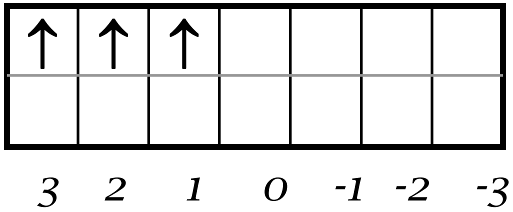
Ce^{3+} $4f^1$



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

$^2F_{5/2}$

Nd^{3+} $4f^3$

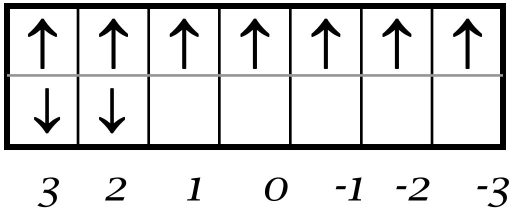


$S = 3/2$ $L = 6$ $J = 9/2$

$^4I_{9/2}$

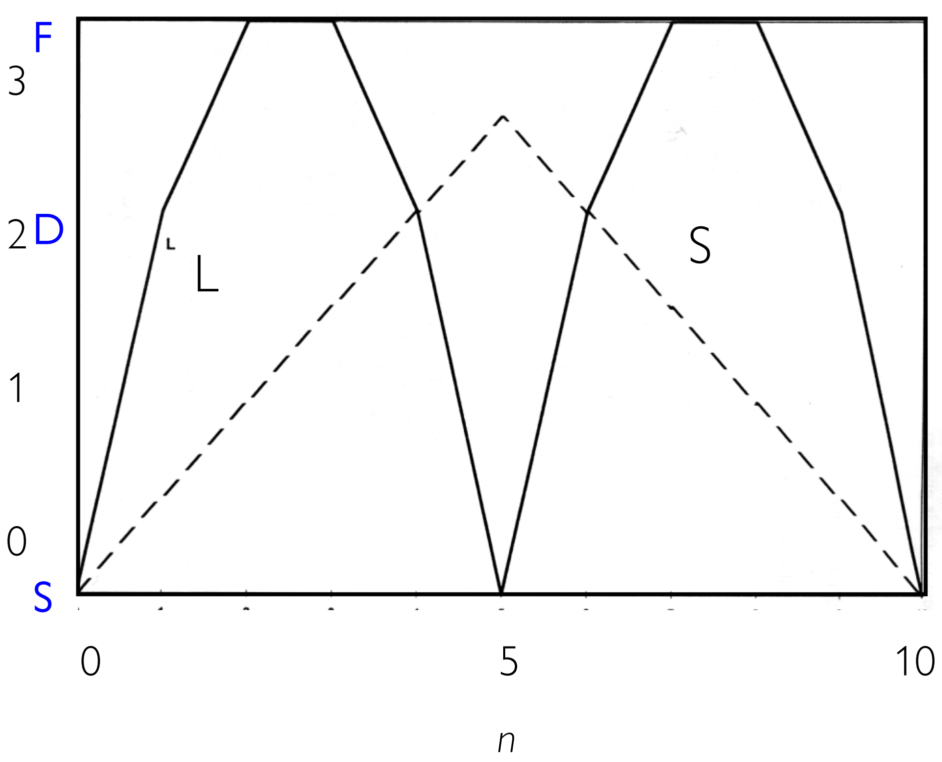
Dy^{3+} $4f^9$

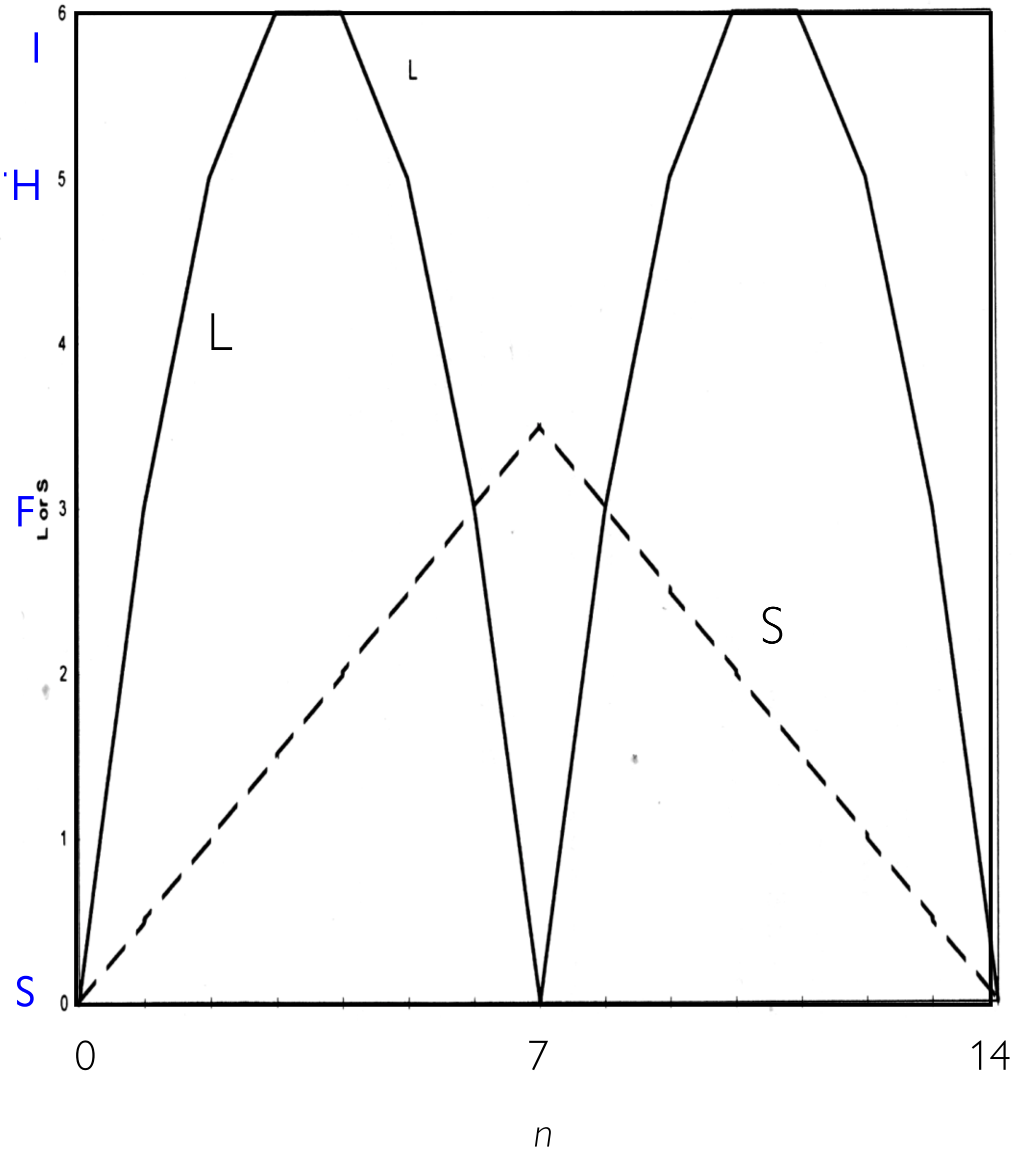
$S = 5/2$ $L = 5$ $J = 15/2$



$^6H_{15/2}$

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


3d series


4f series

4.4 Zeeman Splitting

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

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

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

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

$$\langle \mathrm{LSJM_J}|\,\boldsymbol{L} + 2\boldsymbol{S}\,|\mathrm{LSJM_J}\rangle = g_J\langle \mathrm{LSJM_J}|\,\boldsymbol{J}\,|\mathrm{LSJM_J}\rangle$$

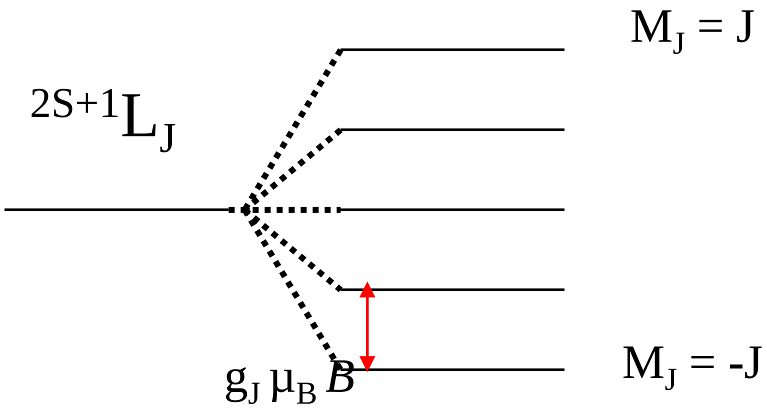
g_J is the Landé g-factor

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

$$\boldsymbol{m}_z = g_J\,\boldsymbol{J}_z\mu_B/\hbar$$

$$\boxed{\mathcal{H}_{\mathrm{Zeeman}} = g_J\,\boldsymbol{J}_z B(\mu_B/\hbar)}$$

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



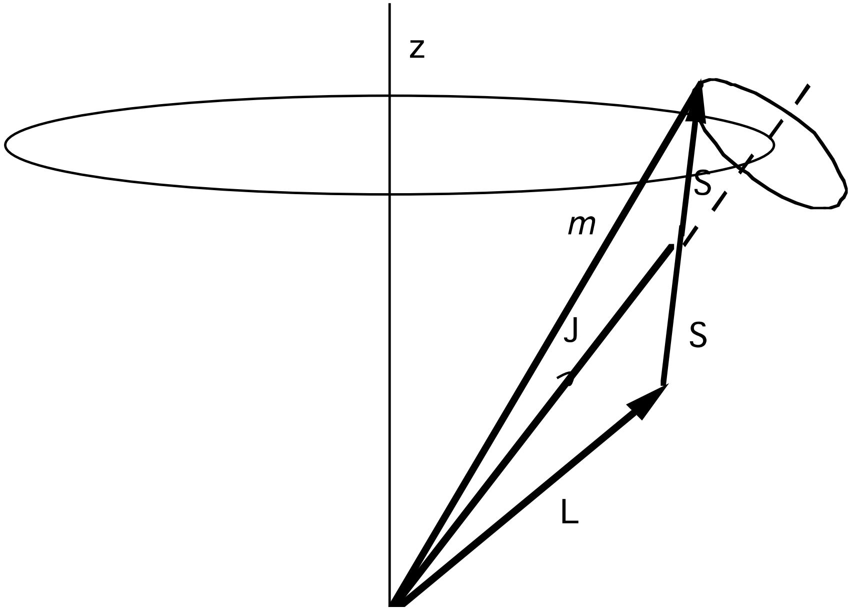
Example: $J = 2$

4.4.1 Landé g-factor

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

The g-factor for the atom or ion is the ratio of the component of magnetic moment along $\boldsymbol{J}$ in units of μ_B to the magnitude of the angular momentum in units of $\hbar$. From the W-E theorem,

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



$\boldsymbol{J}^2 = J(J + 1)\hbar^2$; $\boldsymbol{J}_z = M_J\hbar$

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

$g_J J^2 = -\hbar \boldsymbol{m}.\boldsymbol{J}/\mu_B$

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

but $\boldsymbol{m}.\boldsymbol{J} = -(\mu_B/\hbar)\{(\boldsymbol{L} + 2\boldsymbol{S}).(\boldsymbol{L} + \boldsymbol{S})\}$

$-(\mu_B/\hbar)\{(\boldsymbol{L}^2 + 3\boldsymbol{L}.\boldsymbol{S} + 2\boldsymbol{S}^2)\}$

$-(\mu_B/\hbar)\{(\boldsymbol{L}^2 + 2\boldsymbol{S}^2 + (3/2)(\boldsymbol{J}^2 - \boldsymbol{L}^2 - \boldsymbol{S}^2)\}$ since $\boldsymbol{J}^2 = (\boldsymbol{L} + \boldsymbol{S})^2 = \boldsymbol{L}^2 + \boldsymbol{S}^2 + 2\,\boldsymbol{L}\cdot\boldsymbol{S}$

$-(\mu_B/\hbar)\{((3/2)\boldsymbol{J}^2 - (1/2)\boldsymbol{L}^2 + (1/2)\boldsymbol{S}^2)\}$

$-(\mu_B/\hbar)\{((3/2)J(J + 1) - (1/2)L(L + 1) + (1/2)S(S + 1)\}$

hence

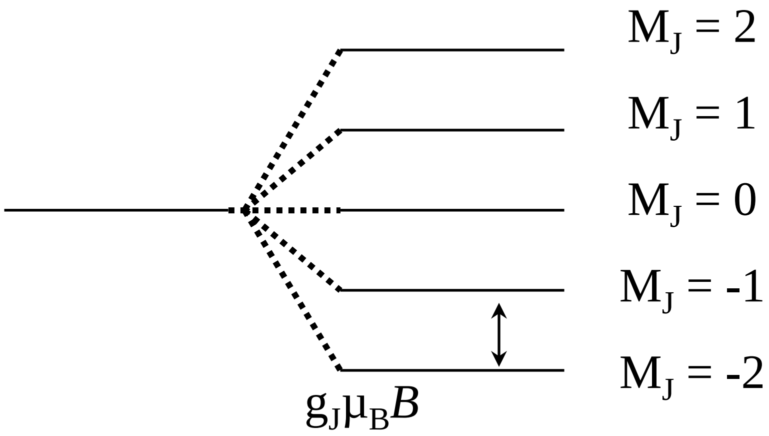
$$\boxed{g_J = 3/2 + \{S(S+1) - L(L+1)\}/2J(J+1)}$$

Check; $g_S = 2$, $g_L = 1$

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

The magnetic Zeeman energy is $E_Z = -m_z B$, $J_z = M_J \hbar$

Hence $\boxed{E_Z = g_J \mu_B M_J B}$



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

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

[$k_B = 1.38\ 10^{-23}$ 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 ν so that E = hν is sufficient to induce transitions between the Zeeman levels. Since h = 6.63 10^{-34} J s^{-1}, ν ≈ 28 GHz for resonance in 1 T. This is in the microwave range.

Note: It is possible to deduce the total moment from the susceptibility, which gives $m_{\mathrm{eff}} = g\sqrt{[J(J+1)]}\mu_B$ for free ions (see § 5.2.2) . The maximum value of $m_z = gJ\mu_B$ is deduced from the low-temperature saturation magnetization. Generally $m_{\mathrm{eff}} > m_z$

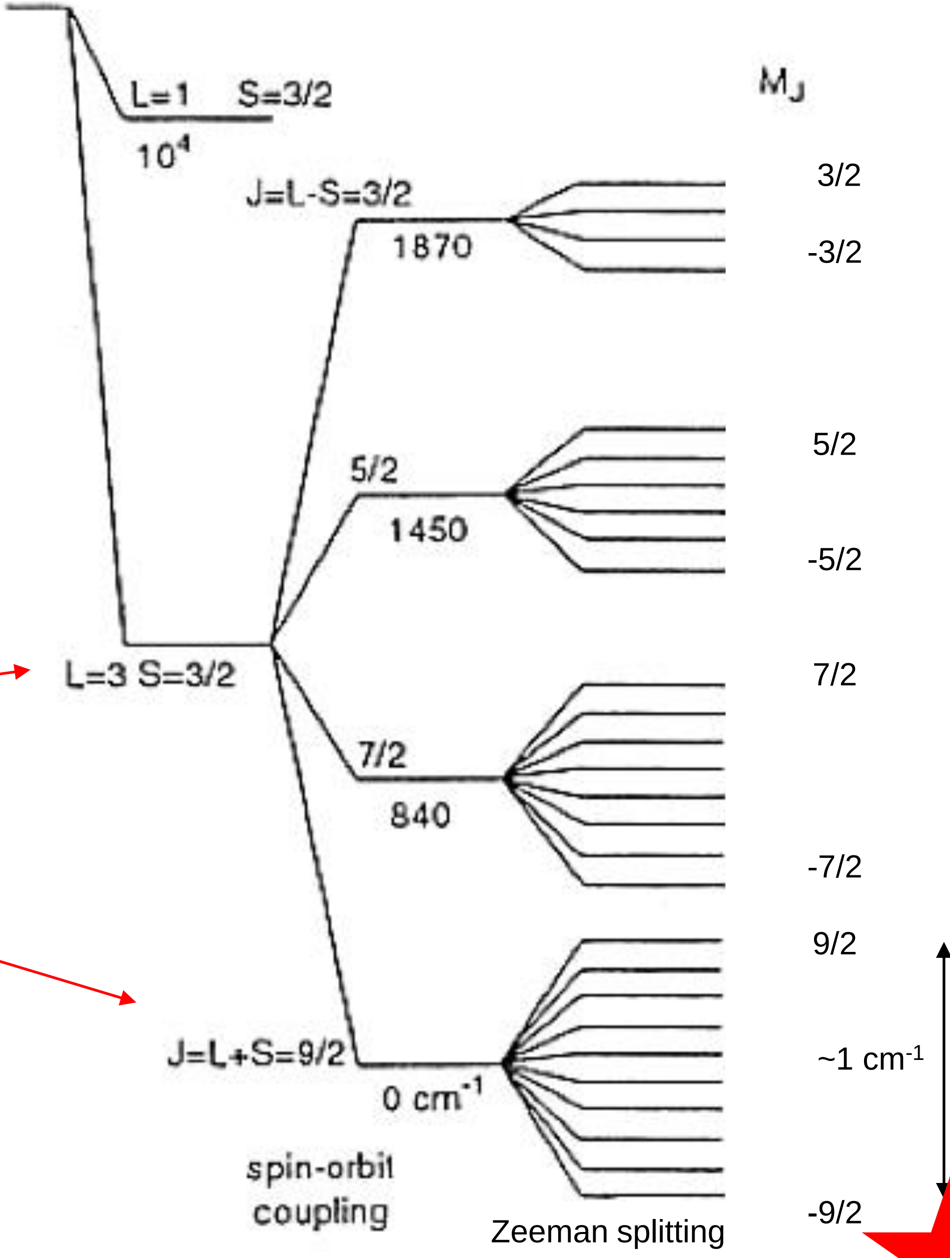
Summary: Example of Co^{2+}

↑	↑	↑	↑	↑
↓	↓			
2	1	0	-1	-2

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

Ground Term ^4F

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



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

NB. 1 cm^{-1} is equivalent to 1.44 K

4.5 Ions in Solids

Summarizing, for *free* ions;

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

ooOoo

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 3*d* ions is *quenched*. L = 0 and the spin-only moment is $\boldsymbol{m} \approx g\mu_B\mathbf{S}$, with g = 2.
- The 4*f* ions do behave like free ions, and J is the good quantum number, as above.
- 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)

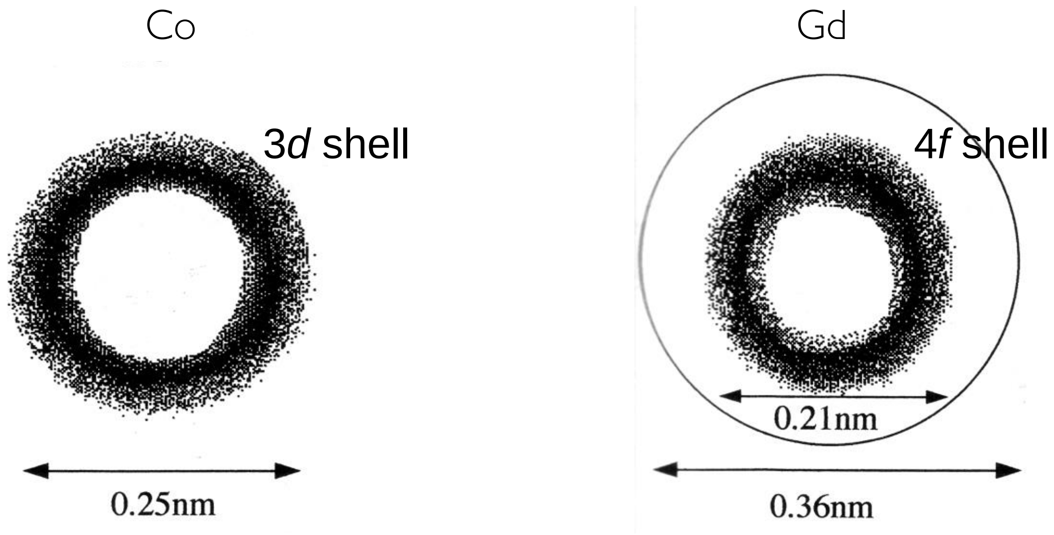
	$\mathcal{H}_0$	$\mathcal{H}_{so}$	$\mathcal{H}_{cf}$	$\mathcal{H}_Z$ **in 1 T**
3*d*	**1 - 5 10^4**	**10^2 -10^3**	**10^4**	**1**
4*f*	**1 - 6 10^5**	**1 - 5 10^3**	**≈3 10^2**	**1**

$\mathcal{H}_{so}$ must be considered before $\mathcal{H}_{cf}$ for 4*f* ions, and the converse for 3*d* ions.

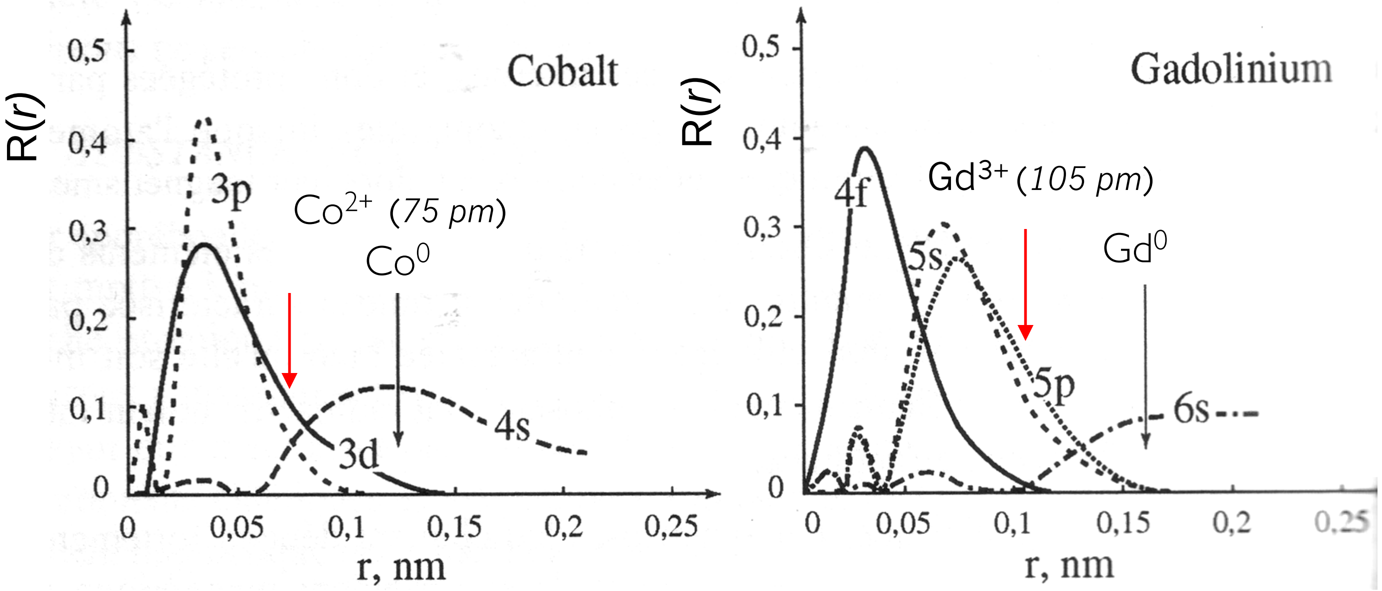
◆ For 4*f* ions in solids J is the good quantum number, but for 3*d* ions S is the good quantum number

◆ The 4*f* electrons are generally localized, and 3*d* electrons are localized in oxides and other ionic compounds, but they are delocalized in metals.

▨ Unpaired electrons



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

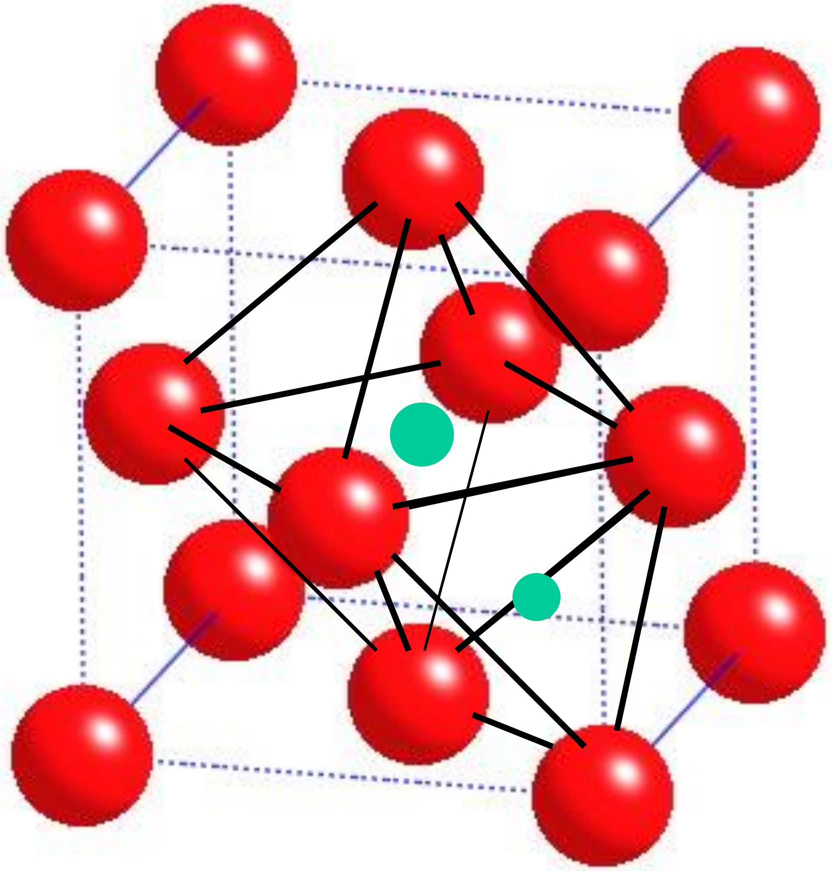


Radial wave function in the free atom

Oxides

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

$r_O = 140$ pm



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

Both have *cubic* symmetry if undistorted

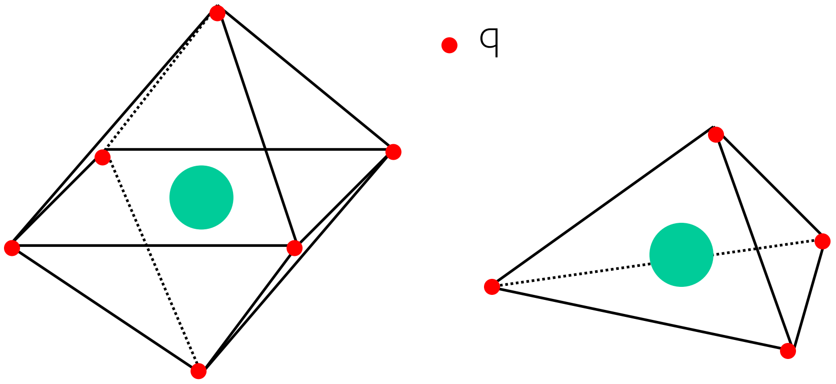
$R_{oct} = (\sqrt{2} - 1)r_O = 58$ pm

$R_{tet} = (\sqrt{(3/2)} - 1)r_O = 32$ pm

Cation radii in oxides:

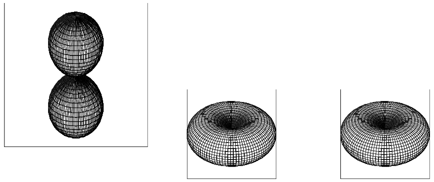
4-fold tetrahedral	pm	6-fold octahedral	pm	6-fold octahedral	pm	12-fold substitutional	pm
Mg^{2+}	53	Cr^{4+} $3d^2$	55	Ti^{3+} $3d^1$	67	Ca^{2+}	134
Zn^{2+}	60	Mn^{4+} $3d^3$	53	V^{3+} $3d^2$	64	Sr^{2+}	144
Al^{3+}	42			Cr^{3+} $3d^3$	62	Ba^{2+}	161
Fe^{3+} $3d^5$	52	Mn^{2+} $3d^5$	83	Mn^{3+} $3d^4$	65	Pb^{2+}	149
Si^{4-}	34	Fe^{2+} $3d^6$	78	Fe^{3+} $3d^5$	64	Y^{3+}	119
		Co^{2+} $3d^7$	75	Co^{3+} $3d^6$	61	La^{3+}	136
		Ni^{2+} $3d^8$	69	Ni^{3+} $3d^7$	60	Gd^{3+}	122

The radius of the O^{2-} anion is 140 pm



Octahedral and tetrahedral sites.

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



$$\psi^0 = R(r)\cos\theta$$

$$\psi^{\pm 1} = R(r)\sin\theta\exp\{\pm\imath\phi\}$$

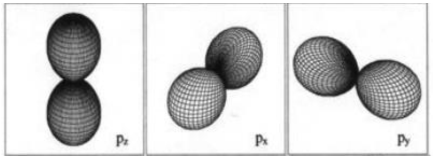
The functions are eigenstates in the central potential V (r) but they are not eigenstates of H_{cf}. Suppose the oxygens ● can be represented by point charges q at their centres, then for the octahedron,

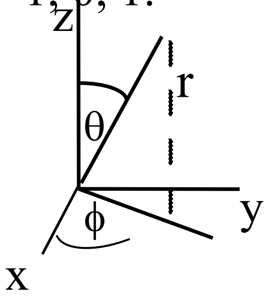
$$\mathscr{H}_{cf} = V_{cf} = D(x^4 + y^4 + z^4 - 3y^2z^2 - 3z^2x^2 - 3x^2y^2)$$

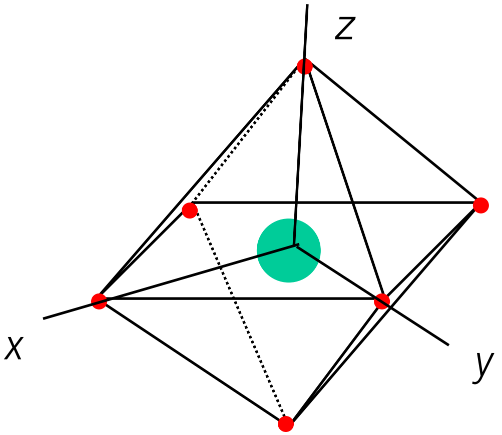
where $D \approx eq/4\pi\varepsilon_o a^6$. But $\psi^{\pm 1}$ are *not* eigenfunctions of $V_{cf,}$ e.g. $\int \psi_i^* V_{cf} \psi_j dv \neq \delta_{ij}$, where i,j = -1, 0, 1.

We seek linear combinations that are eigenfunctions, namely

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

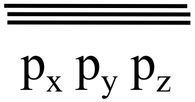






The 2*p* eigenfunctions are degenerate in an undistorted cubic environment

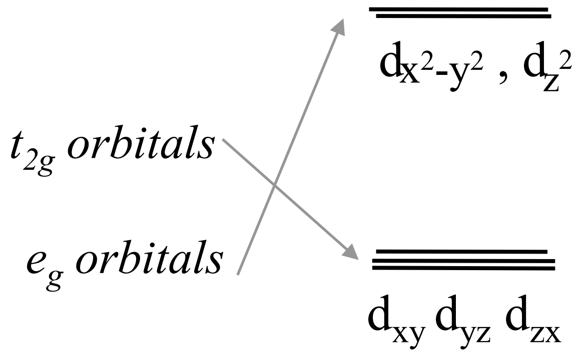
$$\psi^0 = R(r)\cos\theta = zR(r) = p_z$$
$$(1/\sqrt{2})(\psi^1 + \psi^{-1}) = R'(r)\sin\theta\cos\phi = yR(r) = p_x$$
$$(1/\sqrt{2})(\psi^1 - \psi^{-1}) = R'(r)\sin\theta\sin\phi = xR(r) = p_y$$


$p_x\ p_y\ p_z$

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

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

$$d_{xy} = (1/\sqrt{2})(\psi^2 - \psi^{-2}) = R'(r)\sin^2\theta\sin 2\phi \approx xyR(r)$$
$$d_{yz} = (1/\sqrt{2})(\psi^1 - \psi^{-1}) = R'(r)\sin\theta\cos\theta\sin\phi \approx yzR(r)$$
$$d_{zx} = (1/\sqrt{2})(\psi^1 + \psi^{-1}) = R'(r)\sin\theta\cos\theta\cos\phi \approx zxR(r)$$
$$d_{x^2-y^2} = (1/\sqrt{2})(\psi^2 + \psi^{-2}) = R'(r)\sin^2\theta\cos 2\phi \approx (x^2-y^2)R(r)$$
$$d_{3z^2-r^2} = \psi^0 = R'(r)(3\cos^2\theta - 1) \approx (3z^2-r^2)R(r)$$


$d_{x^2-y^2}\ ,\ d_{z^2}$

t_{2g} orbitals

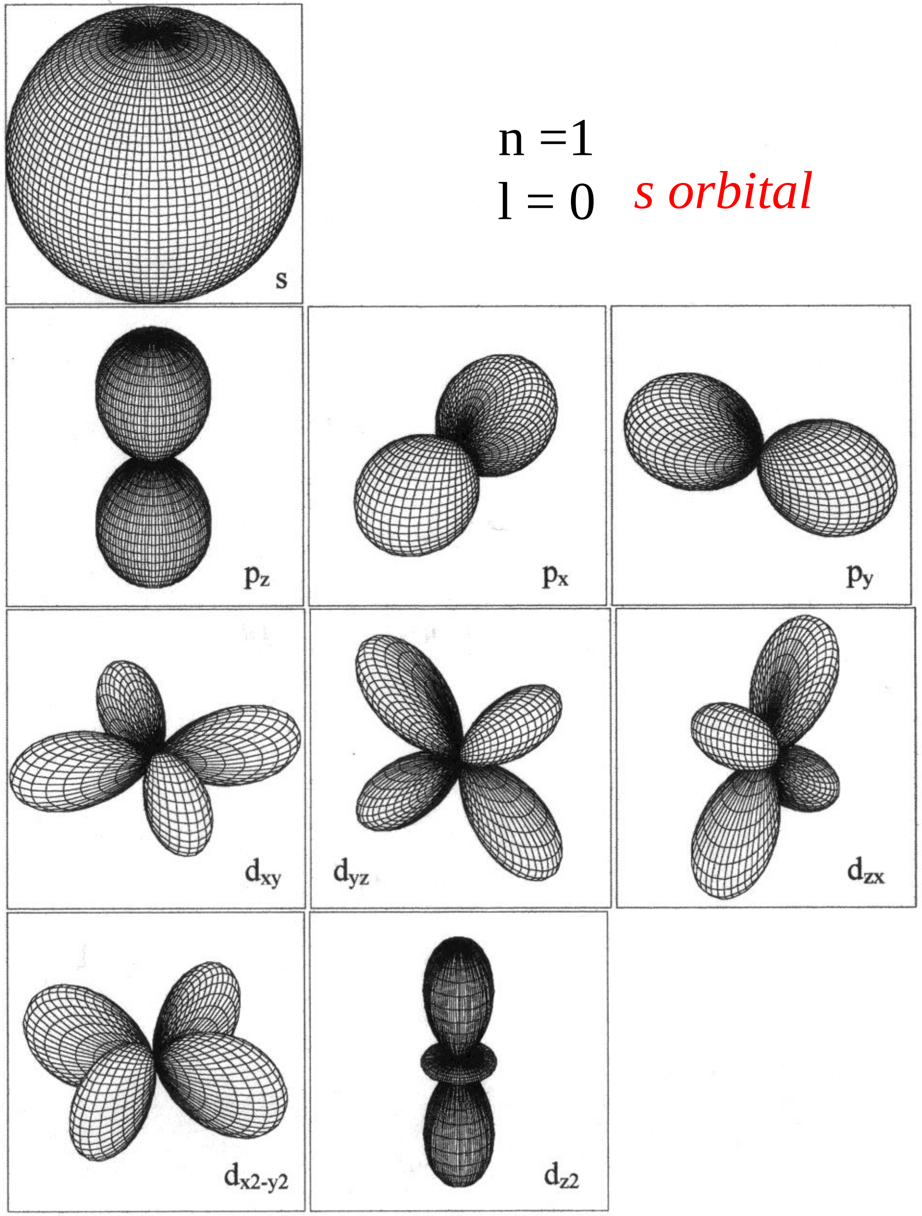
e_g orbitals

$d_{xy}\ d_{yz}\ d_{zx}$

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

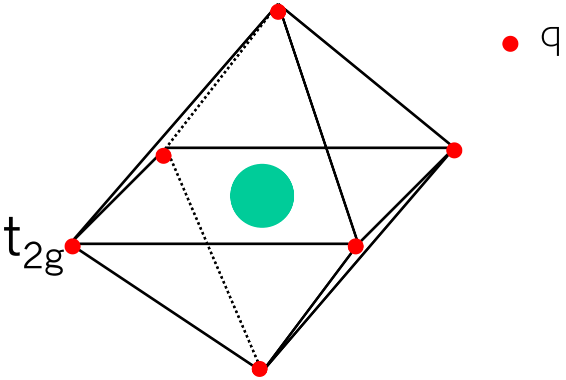
Notation; *a* or *b* denote a nondegenerate single-electron orbital, *e* a twofold degenerate orbital and *t* a threefold degenerate orbital. Capital letters refer to multi-electron states. *a*, *A* are nondegenerate and symmetric with respect to the principal axis of symmetry (the sign of the wavefunction 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

Orbitals in the crystal field



n =1
l = 0 *s orbital*

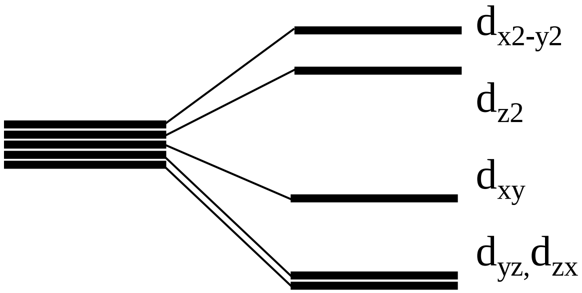
n =2
l = 1 *p orbitals*

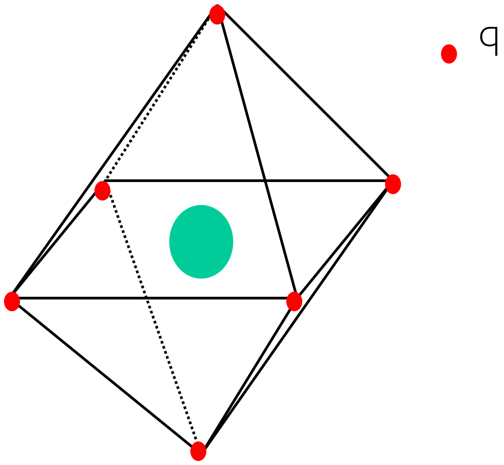


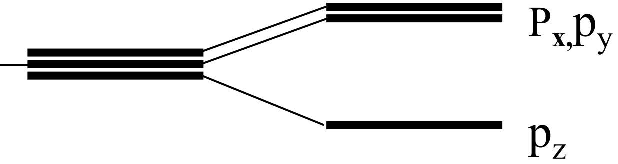
n =3
l = 2 *d orbitals*

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 1-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 ε, 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 susceptibility $\chi = M/H$ is positive. It follows a Curie-law $\chi = C/T$, which is calculated using either classical or quantum statistical mechanics.

Introduction

E & M

Basic Ideas

M. B, H

Energy

Quantum theory

Magnetism of the electron

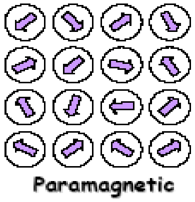
Molecular field theory

single electron magnetism.

Magnetism of the atom with one or more electrons

multi-electron atoms

Paramagnetism



Disordered

Magnetism of interacting atoms Ferromgnetism

Other topics

multi-atom solids

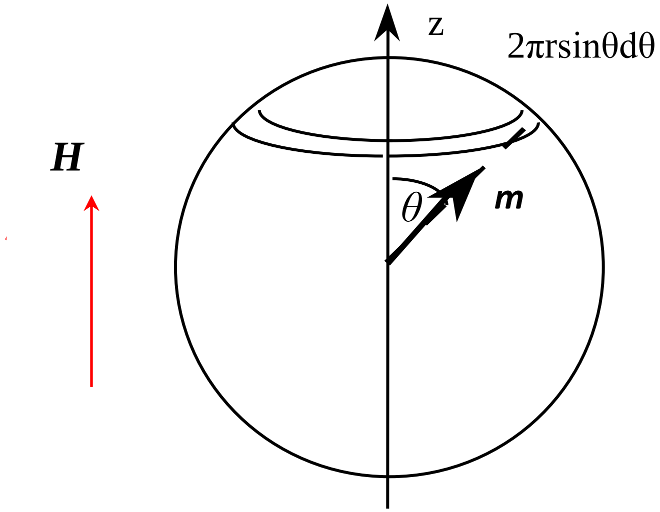
Applications

5.1 Classical limit; Langevin theory

We study the response of a magnetic moment $\boldsymbol{m}$ to an applied magnetic field $\boldsymbol{H}$.

Each particle has a small moment $\boldsymbol{m}$. which can adopt any orientation relative to the applied field $\boldsymbol{B} = \mu_0\boldsymbol{H}$. The energy is $-\boldsymbol{m}\,.\boldsymbol{B}$

$$E(\theta) = -\, \boldsymbol{m}\, \mu_0 H \cos\theta$$



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

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

where κ is determined by the normalization condition

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

$$\langle \boldsymbol{m}_z \rangle = \int_0^\pi \boldsymbol{m} \cos\theta\, P(\theta)\, d\theta \Big/ \int_0^\pi P(\theta)\, d\theta$$

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

$$\int_0^\pi P(\theta)\, d\theta = \int_0^\pi \kappa\, 2\pi \sin\theta \exp[-E(\theta)/k_B T]\, d\theta = -\kappa\, 2\pi \int_1^{-1} \exp[ax]\, da$$

$$= \kappa\, 2\pi \Big|_1^{-1} (1/x)\exp[ax] = \kappa\, 2\pi\, (1/x)\, \{\exp[-x] - \exp[x]\}$$

$$\int_0^\pi m \cos\theta\, P(\theta)\, d\theta = -\kappa\, 2\pi\, m \int_1^{-1} a \exp[ax]\, da$$

$$= \kappa\, 2\pi\, m \left\{ \Big|_1^{-1} (a/x) \exp[ax] - \int_1^{-1} (1/x) \exp[ax]\, da \right\}$$

$$= \kappa\, 2\pi\, m \left\{ \Big|_1^{-1} (a/x) \exp[ax] + \Big|_1^{-1} (1/x)^2 \exp[ax] \right\}$$

$$= \kappa\, 2\pi\, m\, (1/x) \left\{ -\{\exp[-x] + \exp[x]\} + (1/x)[\{\exp[-x] - \exp[x]\}\right\}$$

$$\langle \boldsymbol{m}_z \rangle = m \left\{ -\{\exp[-x] + \exp[x]\} / \{\exp[-x] - \exp[x]\} - (1/x) \right.$$

$$\boxed{\langle \boldsymbol{m}_z \rangle = m\, \{\coth x - (1/x)\}} = m\mathcal{L}(x);$$

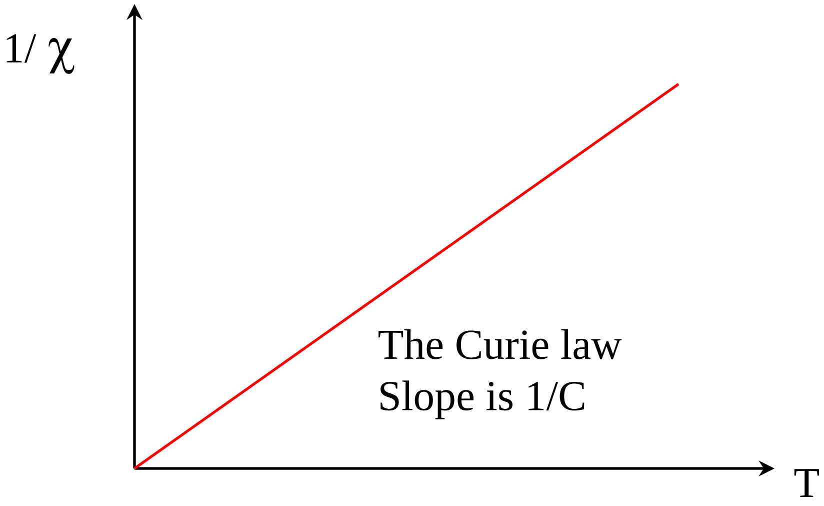
$\mathcal{L}(x)$ = coth x -1/x is the *Langevin function*

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

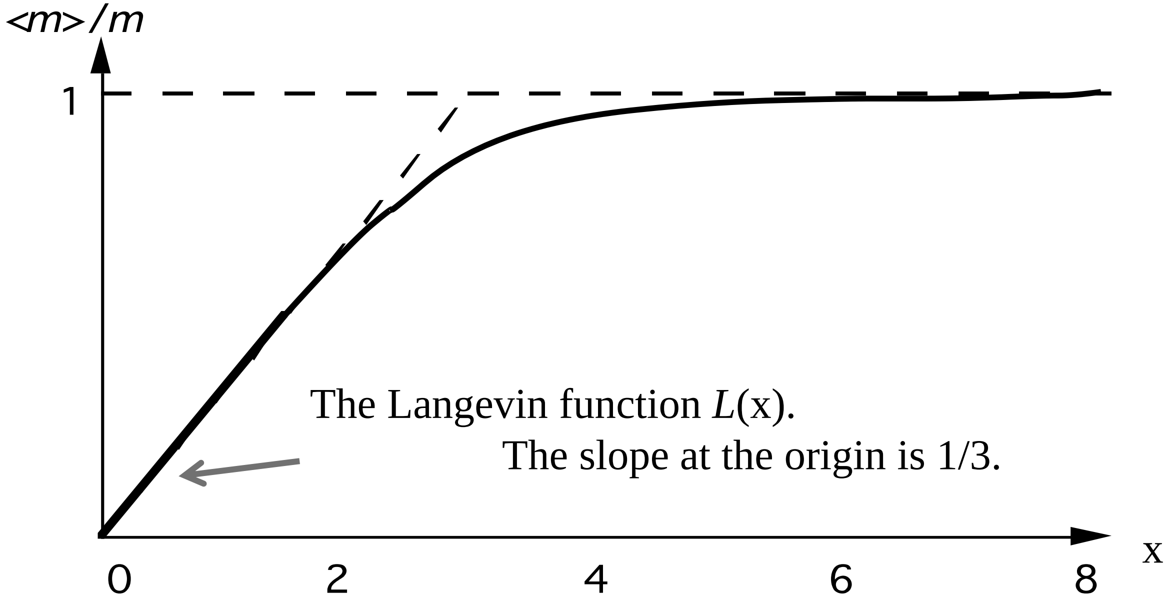
The susceptibility of an ensemble of N moments is $\chi = N\langle m\rangle/H$,

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

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



The Curie law
Slope is 1/C

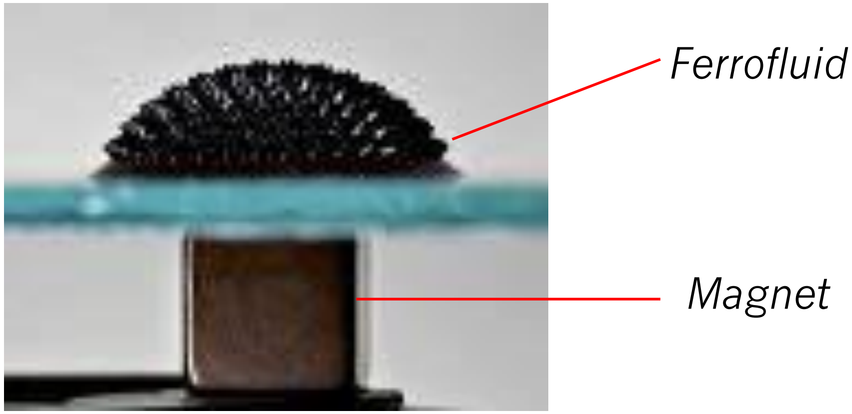


The Langevin function $L(x)$.
The slope at the origin is 1/3.

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

5.1.1 Ferrofluids

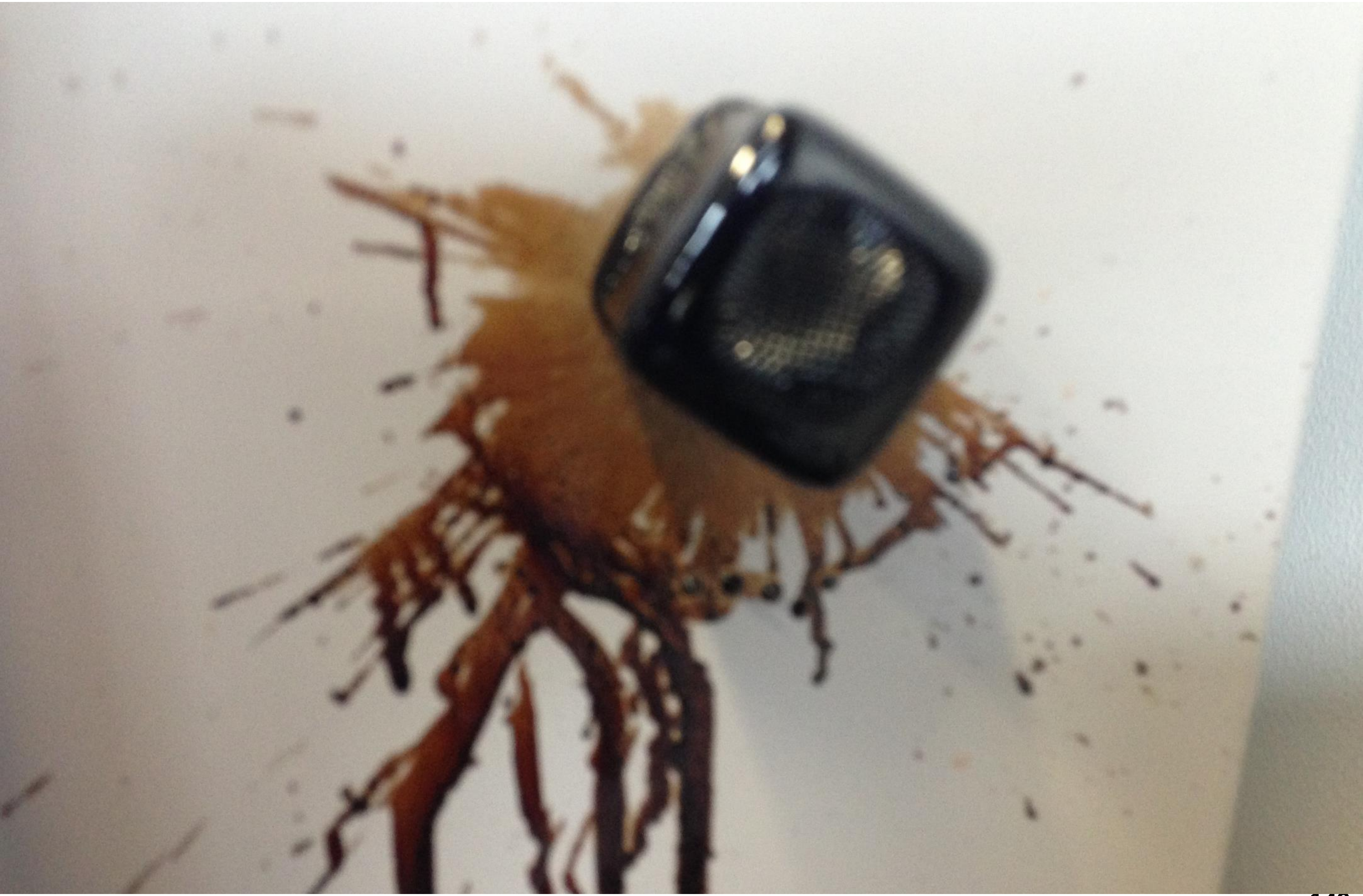
These are colloidal suspensions of superparamagnetic particles,



Energy barrier

Criterion for superparamagnetism: $KV < 25k_BT$ Particle size ≤ 15 nm.

Applications: Ferrofluids are used for hypothermia, and for rotation seals in high-vacuum systems.. Functionalized superparamagnetic iron oxide nanoparticles are used for magnetic separation of biological species,



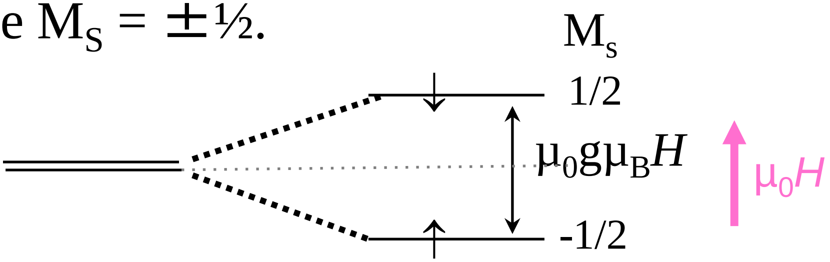
5.2 Quantum theory.

5.2.1 S = ½

The extreme quantum limit is the case J = ½.

This arises when S = ½, L = 0

There are only two energy levels $E_i = -\mu_0 g \mu_B M_S H$, where $M_S = \pm½$.



Two possible orientations of the moment of the ion 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 moment up' (↑) and 'spin moment down' (↓).

A single, localized electron has s = ½ and g = 2.

The spin angular momentum is $s = ½$, $m_s = \pm½$.

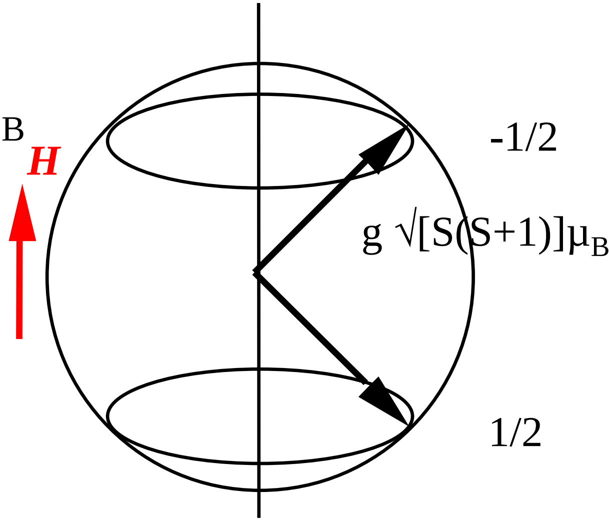
Eigenvalues of $\boldsymbol{s}_z$ are $\pm \hbar/2$ so $\mathbf{m}_i = \mp \mu_B$

The electrons have only two eigenstates, 'spin up' (↑, $m_s = -½$) and 'spin down' (↓, $m_s = ½$), 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 $\exp\{-E_i/k_BT\}$. The thermodynamic average $\langle m \rangle$ is evaluated from these Boltzmann populations.

$$\langle \boldsymbol{m}_z \rangle = \Sigma_i m_i \exp\{-E_i/k_BT\}/\ \Sigma_i \exp\{-E_i/k_BT\}$$

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

$\boxed{\langle \boldsymbol{m}_z \rangle = m \tanh(x)}$ where $x = -\mu_0\mu_B H/k_BT$; $m = g\mu_B s = \mu_B$



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

$$\boxed{\chi = \mu_0 N\mu_B^2/k_BT}$$

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 $6\ 10^{28}\ \mathrm{m}^{-3}$ gives $C \approx 0.5$ K. The Curie law susceptibility at room temperature is of order 10^{-3}.

At low fields, tanh(x) ≈ x

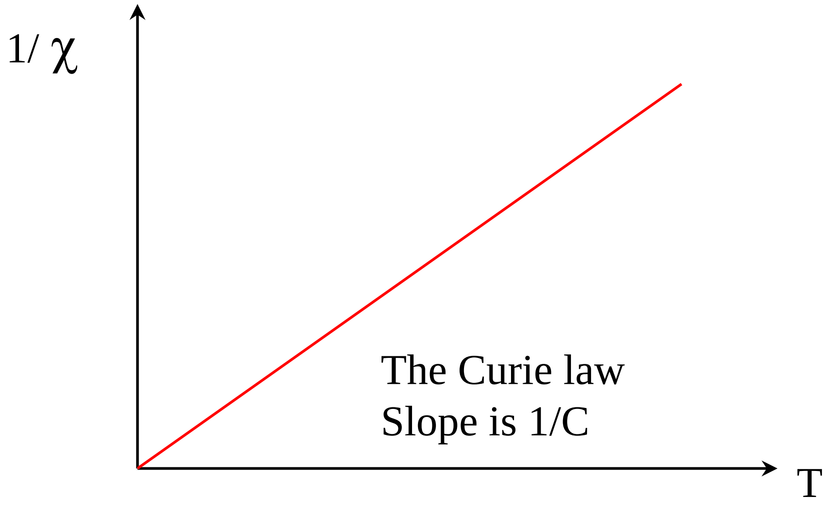
The Curie law is $\chi = C/T$
where $C = \mu_0 N \mu_B{}^2/k_B$,

Plotting $1/\chi$ vs T gives $1/C$

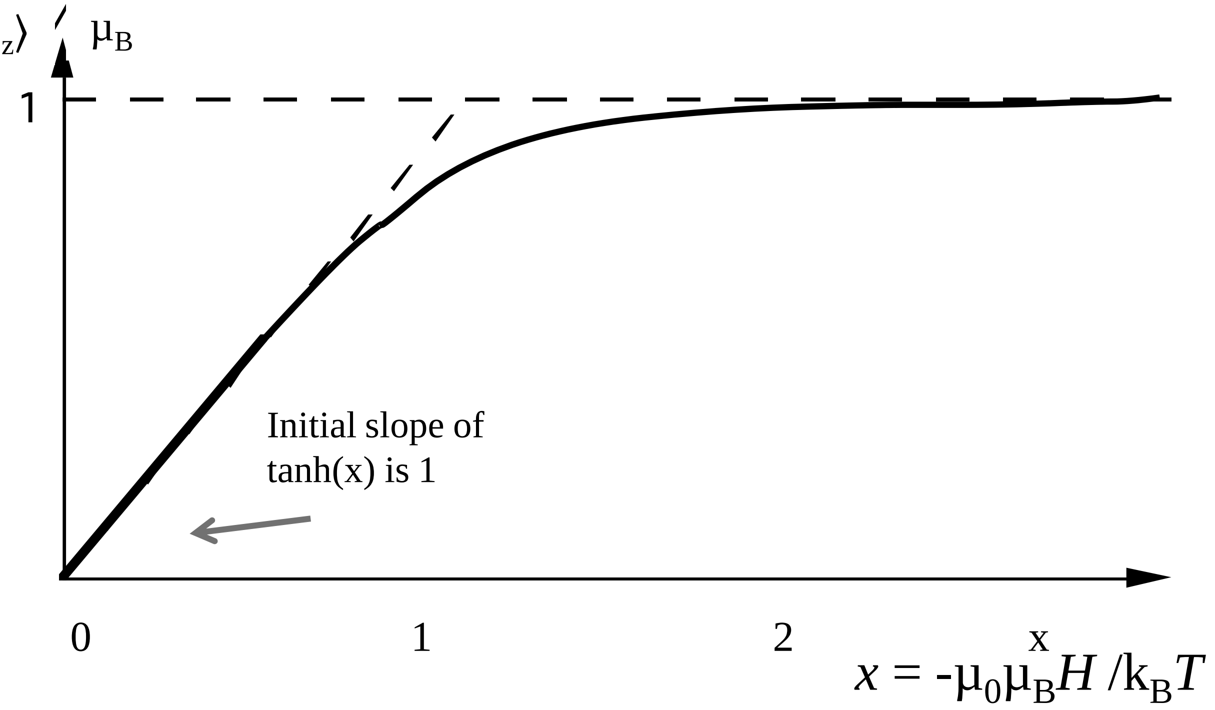
At high fields, tanh(x) → 1.

The magnetization saturates
Moments are then fully aligned

$\langle \boldsymbol{m}_z \rangle = 1\ \mu_B$



The Curie law
Slope is 1/C



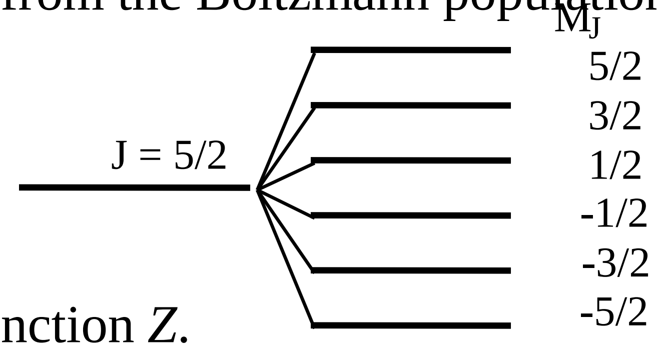
Initial slope of
tanh(x) is 1

Many ‘two-level systems’ in physics are treated by assigning them a ‘pseudospin’ s = ½.

5.2.2 General case

The general quantum case was treated by *Brillouin*; m is $g_J\mu_B J$, and x is defined as $x = m\,\mu_0 H/k_B T$. There are $2J + 1$ energy levels $E_i = -g_J\mu_B M_J\mu_0 H$, with moment $m_i = g_J\mu_B M_J$ 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 $\exp\{-E_i/k_BT\}$. The thermodynamic average $<m>$ is evaluated from the Boltzmann populations of the levels E_i.



$$\boxed{\langle \boldsymbol{m}_z\rangle = \Sigma_i m_i \exp\{-E_i/k_B T\}/ \Sigma_i \exp\{-E_i/k_B T\}}$$

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 $\exp(x) \approx 1 + x + ..$,

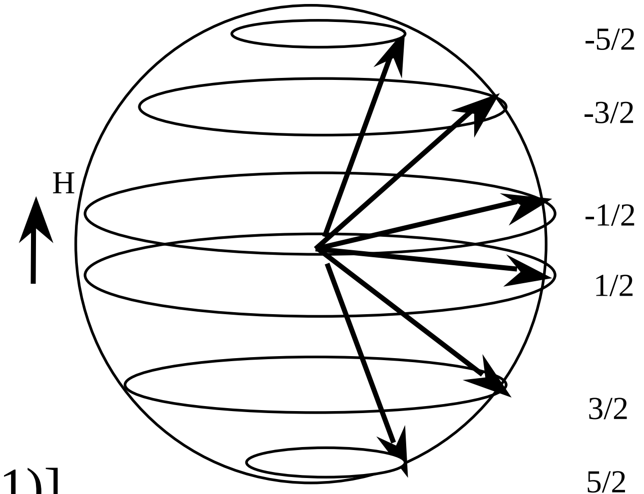
$$\langle \boldsymbol{m}_z\rangle = \Sigma_{-J}^{J}\, g_J\mu_B M_J(1 + g\mu_B M_J\,\mu_0 H/k_B T)/\, \Sigma_{-J}^{J}(1 + g\mu_B M_J\,\mu_0 H/k_B T)$$

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

Hence $\langle \boldsymbol{m}_z \rangle = g^2\mu_B{}^2BJ(J+1)(2J+1)/3(2J+1)k_BT$

The susceptibility is $N<m>/H$, where N is the number of atoms/m^3.

$$\boxed{\chi = \mu_0 N g^2 \mu_B{}^2 J(J+1)/3k_BT}$$



This is the general form of the Curie law.

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

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

A typical value of C for $J = 1$, $N = 8.10^{28}$ 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

$$\boxed{\chi = \mu_0 N m^2/3k_BT}$$

QM➔CM

Correspondence principle
for large quantum numbers

Ion 3d	$^{2S+1}$**L**$_J$	**L**	**S**	**J**	**g**	$m_{eff} = g\sqrt{J(J+1)}$ (m_B)	$m_s = 2\sqrt{S(S+1)}$ (m_B)	$m_{eff}{}^*$ (m_B)
Ti^{2+}, V^{4+} ($3d^1$)	$^2D_{3/2}$	2	1/2	3/2	4/5	1.549	1.73	1.7
Ti^{2+}, V^{3+} ($3d^2$)	$^3F_2$	3	1	2	2/3	1.633	2.83	2.8
V^{2+}, Cr^{3+} ($3d^3$)	$^4F_{3/2}$	3	3/2	3/2	2/5	0.775	3.87	3.8
Cr^{2+}, Mn^{3+} ($3d^4$)	$^5D_0$	2	2	0	-	-	4.90	4.9
Mn^{2+}, Fe^{3+}($3d^5$)	$^6S_{5/2}$	0	5/2	5/2	2	5.916	5.92	5.9
Fe^{2+}, Co^{3+} ($3d^6$)	$^5D_4$	2	2	4	3/2	6.708	4.90	5.4
Co^{2+}, Ni^{3+} ($3d^7$)	$^4F_{9/2}$	3	3/2	9/2	4/3	6.633	3.87	4.8
Ni^{2+} ($3d^8$)	$^3F_4$	3	1	4	5/4	5.590	2.83	3.2
Cu^{2+} ($3d^9$)	$^2D_{5/2}$	2	1/2	5/2	6/5	3.550	1.73	1.9

Ion 4f	$^{2S+1}$**L**$_J$	**L**	**S**	**J**	**g**	m_0=gJ (μ_B)	m_{eff}=g√(J(J+1)) (μ_B)	m_{eff} (μ_B)
Ce^{3+} ($4f^1$)	$^2F_{5/2}$	3	1/2	5/2	6/7	2.14	2.54	2.5
P^{3+} ($4f^2$)	$^3H_4$	5	1	4	4/5	3.20	3.58	3.5
Nd^{3+} ($4f^3$)	$^4I_{9/2}$	6	3/2	9/2	8/11	3.27	3.62	3.4
Pm^{3+}($4f^4$)	$^5I_4$	6	2	4	3/5	2.40	2.68	-
Sm^{3+}($4f^5$)	$^6H_{5/2}$	5	5/2	5/2	2/7	0.71	0.85	1.7
Eu^{3+} ($4f^6$)	$^7F_0$	3	3	0	-	0.00	0.00	3.4
Gd^{3+} ($4f^7$)	$^8S_{7/2}$	0	7/2	7/2	2	7.00	7.94	8.9
Tb^{3+} ($4f^8$)	$^7F_6$	3	3	6	3/2	9.00	9.72	9.8
Dy^{3+} ($4f^9$)	$^6H_{15/2}$	5	5/2	15/2	4/3	10.00	10.65	10.6
Ho^{3+} ($4f^{10}$)	$^5I_8$	6	2	8	5/4	10.00	10.61	10.4
Er^{3+} ($4f^{11}$)	$^4I_{15/2}$	6	3/2	15/2	6/5	9.00	9.58	9.5
Tm^{3+} ($4f^{12}$)	$^3H_6$	5	1	6	7/6	7.00	7.56	7.6
Yb^{3+} ($4f^{13}$)	$^2F_{7/2}$	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

$$\langle \boldsymbol{m}_z\rangle = g\mu_B \partial/\partial y[\ln\Sigma_{-J}^{J} \exp\{M_J y\}] \qquad [d(\ln z)/dy = (1/z)\, dz/dy]$$

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

$$\exp(Jy)\,\{1 + r + r^2 + ...r^{2J}\} \qquad \text{where } r = \exp\{-y\}$$

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

$$\therefore\ \Sigma_{-J}^{J} \exp\{M_J y\} = (\exp\{-(2J+1)y\} - 1)\exp\{Jy\}/(\exp\{-y\}-1)$$

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

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

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

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

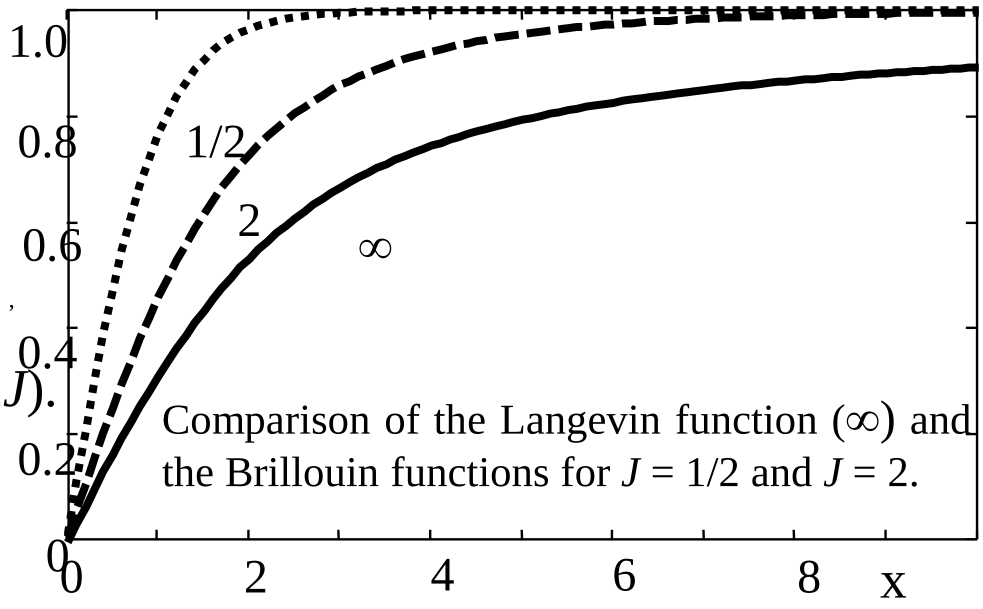
setting $x = Jy$, we obtain

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

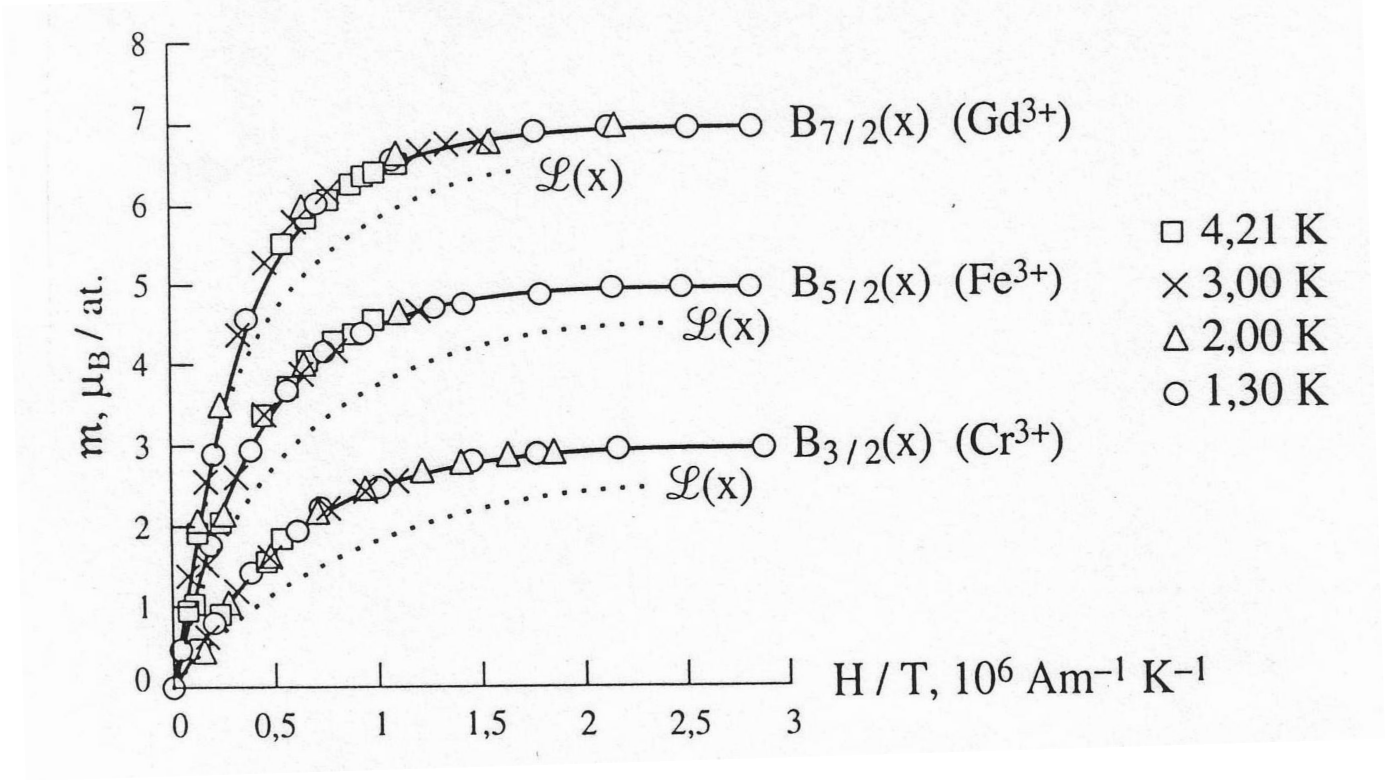
where the Brillouin function

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

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



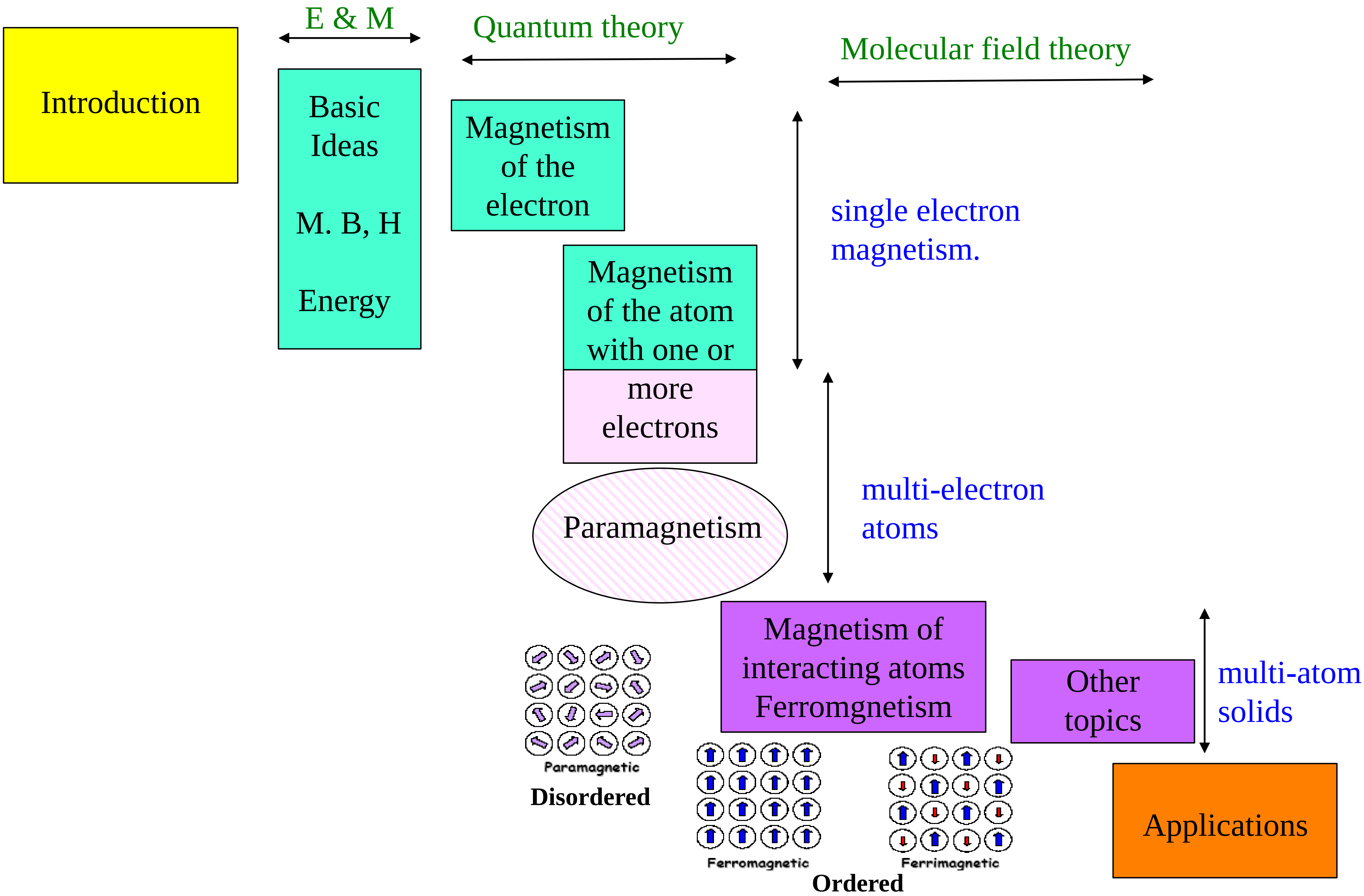
Comparison of the Langevin function (∞) and the Brillouin functions for $J = 1/2$ and $J = 2$.



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

The quantum theory of localized magnetism gives a good account of magnetically-dilute 3*d* and 4*f* 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 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 $x \approx H/T$ ★



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Ordered

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 $\boldsymbol{H}$, there is an internal 'molecular' field in a ferromagnet proportional to its magnetization.

$$\boxed{\boldsymbol{H}^{i} = n_W \boldsymbol{M}}$$

$\boldsymbol{H}^{i}$ must be immense in a ferromagnet like iron to be able to induce a significant fraction of saturation at room temperature; $n_W \approx 10 - 1000$. The origin of these huge fields remained a mystery until Heisenberg introduced the idea of the *exchange interaction* in 1928.

Spontaneous magnetization $M_s = N\langle \boldsymbol{m} \rangle$ is given by the Brillouin function, (no *external* field defines **z**)

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

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 $M_s = N\langle \boldsymbol{m} \rangle$

In zero external field, we have

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

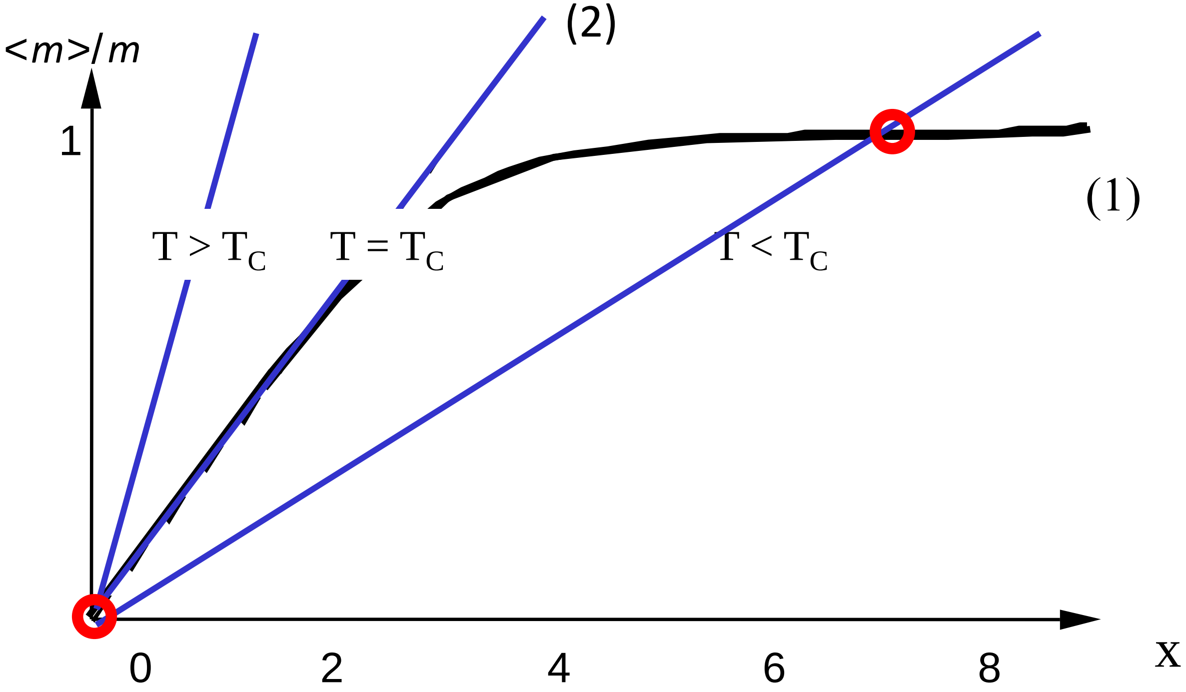
Also, eliminating H^i from the expressions for H^i ($H^i = n_W M_s$) and x ($H^i = k_B T x/\mu_0 m$) and using $M_0 = Nm$

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

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

$$M_s/M_0 = [T(J+1)/3CJn_W]x \qquad (2)$$

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 plotted in blue for $T < T_C$, $T = T_C$ 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. $\mathcal{B}_J(x) \approx [(J+1)/3J]x + \ldots$

hence $\boxed{T_C = n_W C}$

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 = 3.0×10^{28} m^{-3}; hence $C = 4.9$ K, $n_W = 59$.
The value of $M_0 = Ng\mu_B J$ is 1.95 MA m^{-1}.
Hence $\mu_0 H^i = 144$ T.
This is an enormous 'effective' field

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

For small x. $\mathcal{B}_J(x) \approx [(J+1)/3J]x + \ldots$

hence $\boxed{T_C = n_W C}$

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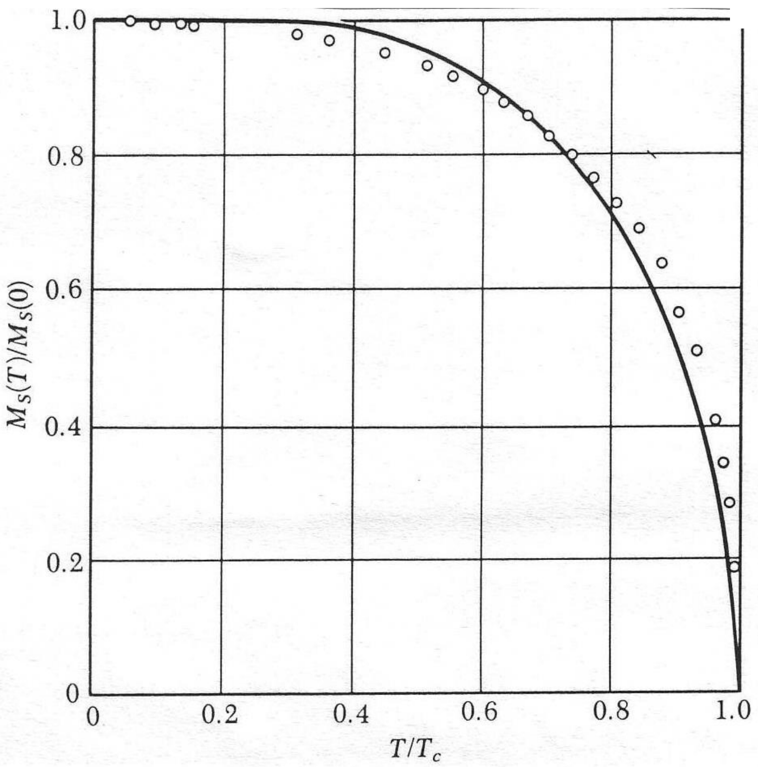
A typical value of T_C is a few hundred Kelvin. In practice, T_C is used to determine n_W.

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

The value of $M_0 = Ng\mu_B J$ is 1.95 MA m^{-1}. Hence $\mu_0 H^i$ = 144 T.
This is an enormous 'effective' field

The spontaneous magnetization for nickel, together with the theoretical curve for S = ½ from the mean field theory. The theoretical curve is scaled to give correct values at either end.



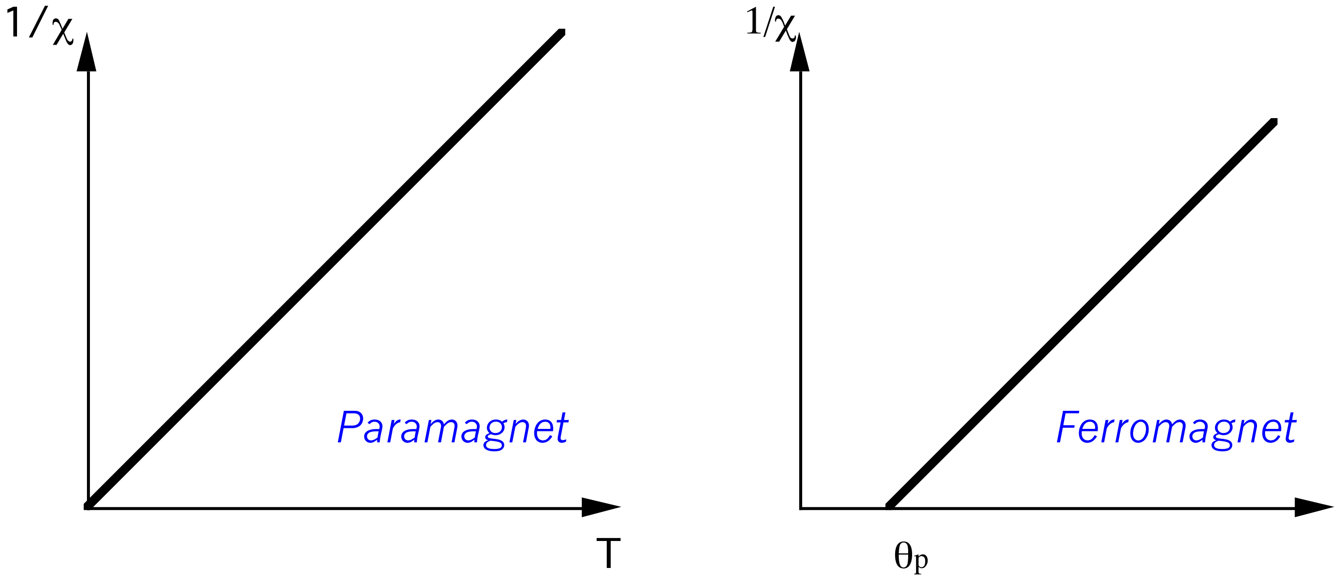
$T > T_C$

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

$$\boxed{\chi = C/(T - \theta_p)}$$

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

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



The Curie-law suceptibility 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.126, p151.

6.2 Exchange Interactions

What is the origin of the effective magnetic fields of ~100 T which are responsible for ferromagnetism ? They are *not* due to the atomic magnetic dipole moments. The field at distance ***r*** due to a moment ***m*** is

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

The order of magnitude of $B_{dip} = \mu_0 H_{dip}$ is $\mu_0 m/4\pi r^3$; taking $m = 1\ \mu_B$ and $r = 0.1$ nm gives $B_{dip} = 4\pi\ 10^{-7} \times 9.27.\ 10^{-24}/\ 4\pi\ 10^{-30} \approx 1$ 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 $\boldsymbol{H}^i$ 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 ↑↓ and ↑↑ 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.

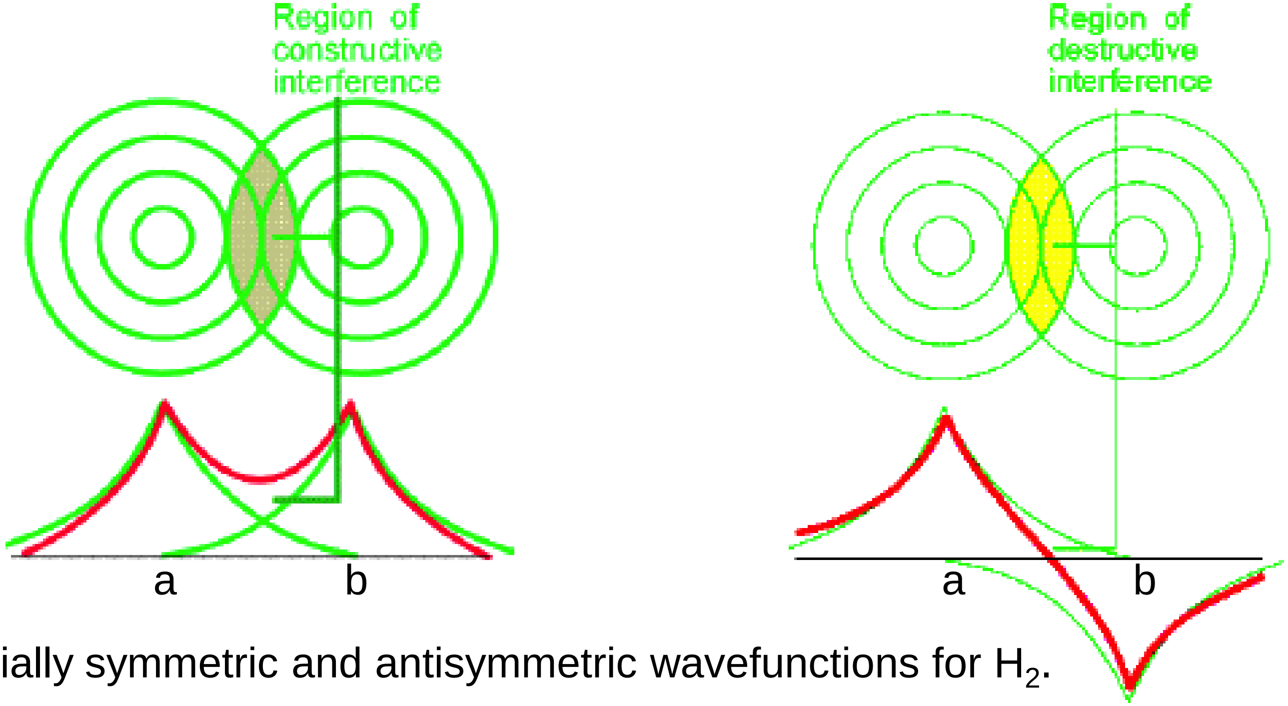
The Pauli principle requires the total wave function $\Phi(1,2)$ of a pair of electrons 1,2 to be *antisymmetric* on exchanging two electrons

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

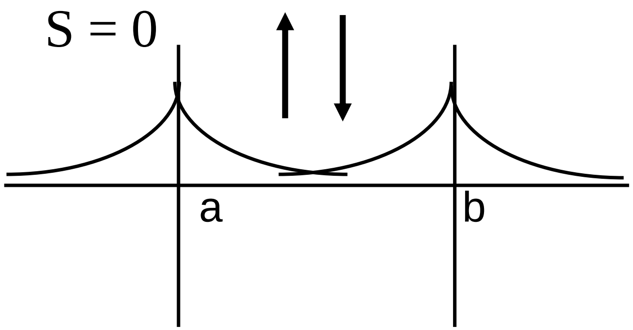
The total wavefunction is the product of functions of space and spin coordinates $\Psi(\mathbf{r}_1,\mathbf{r}_2)$ and $\chi(s_1, s_2)$, each of which must be either symmetric or antisymmetric. This follows because the electrons are indistinguishable particles, and the number in a small volume dV can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

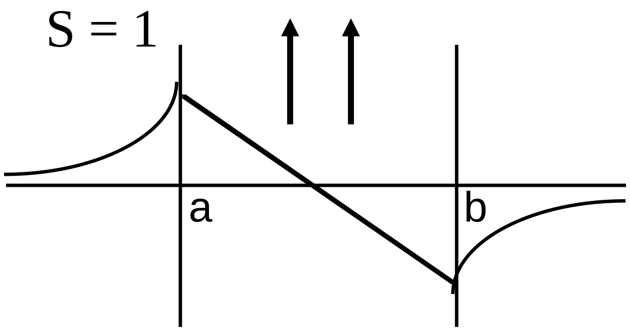
The simple example of the hydrogen molecule H_2 with two atoms a,b and two electrons 1,2 in hydrogenic 1*s* orbitals ψ_i gives the idea of the physics of exchange. There are two molecular orbits, one spatially symmetric Ψ_S, the other spatially antisymmetric Ψ_A.

$\Psi_S(1,2) = (1/\sqrt{2})(\psi_{a1}\psi_{b2} + \psi_{a2}\psi_{b1})$; $\Psi_A(1,2) = (1/\sqrt{2})(\psi_{a1}\psi_{b2} - \psi_{a2}\psi_{b1})$



The spatially symmetric and antisymmetric wavefunctions for H_2.





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

$\chi_S = |\uparrow_{1,}\uparrow_2>;\ \ (1/\sqrt{2})[|\uparrow_{1,}\downarrow_2> + |\downarrow_{1,}\uparrow_2>];\ \ |\downarrow_{1,}\downarrow_2>.$ $S = 1; M_S = 1, 0, -1$

$\chi_A = (1/\sqrt{2})[|\uparrow_{1,}\downarrow_2> - |\downarrow_{1,}\uparrow_2>]$ $S = 0; M_S = 0$

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

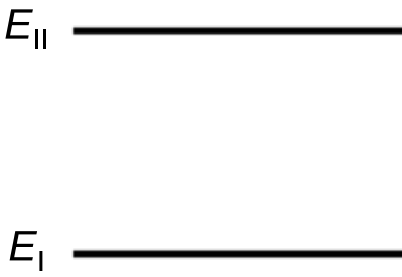
$$\Phi_I = \Psi_S(1,2)\chi_A(1,2); \quad \Phi_{II} = \Psi_A(1,2)\chi_S(1,2)$$

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

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

With no interaction of the electrons on atoms a and b, $H(\mathbf{r}_1, \mathbf{r}_2)$ is just

$$\mathcal{H}_0 = \mathcal{H}_1 + \mathcal{H}_2 = (-\hbar^2/2m)\{\nabla_1^2 + \nabla_2^2\} + V_1 + V_2.$$



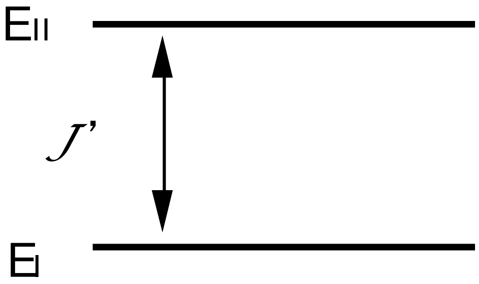
The two energy levels $E_{I,}$ $E_{,II}$ are degenerate, with energy E_0. However, if the electrons interact via a term $\mathcal{H}'_{12} = e^2/4\pi\varepsilon_0 r_{12}^2$, we find that the perturbed energy levels are $E_I = E_0 + 2\mathcal{J}$, $E_{II} = E_0 - 2\mathcal{J}$. The *exchange* integral is

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

and the separation $(E_{II} - E_I)$ is $4\mathcal{J}$. For the H_2 molecule, E_I is lies lower than E_{II}, the *bonding* orbital singlet state lies below the *antibonding* orbital triplet state $\mathcal{J}$ 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

$$\boxed{E = -2(\mathcal{J}'/\hbar^2)\,\mathbf{s}_1.\mathbf{s}_2}$$

The operator $\mathbf{s}_1.\mathbf{s}_2$ 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 ↑↓ singlet state (I) and the ↑↑ triplet state (II) is then $\mathcal{J}'$.



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 ***S***.

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

$\mathcal{J} > 0$ indicates a ferromagnetic interaction (favouring ↑↑ alignment).

$\mathcal{J} < 0$ indicates an antiferromagnetic interaction (favouring ↑↓ alignment).

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

The Heisenberg exchange constant $\mathcal{J}$ 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 neighours of S_i have an appreciable interaction with it. Then the site Hamiltonian is

$$\mathcal{H}_i = -2(\Sigma_j \mathcal{J}\mathbf{S}_j).\mathbf{S}_i \approx -\mu_0 H^i m_i = -\mu_0 H^i g\mu_B S_i$$

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

$$\boxed{T_C = 2Z\mathcal{J}S(S+1)/3k_B}$$

★

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

6.3 Ferromagnetic domains

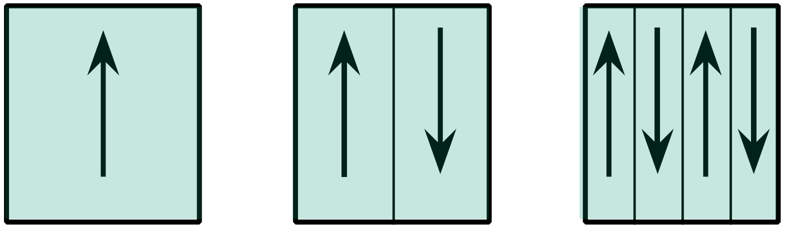
Weiss also explained why most pieces of iron, a paperclopfor example, do not appear ferromagnetic.They actually contain many ferromagnetic *domains,*magnetized in different directions. The domains form in order to reduce the magnetostatic self-energy.
This self-energy E_{ms} can be written in two equivalent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

$$E_{ms} = \tfrac{1}{2}\mu_0\int_{\text{all space}} H^2 dV \qquad \text{or} \qquad E_{ms} = -\tfrac{1}{2}\mu_0 \int_{\text{magnet}} \boldsymbol{M}.\boldsymbol{H} dV$$

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

$$\boxed{E_{ms} = \tfrac{1}{2}\mu_0 \mathcal{N} M^2 V}$$

Magnitude $10^5 - 10^6$ Jm^{-3}



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

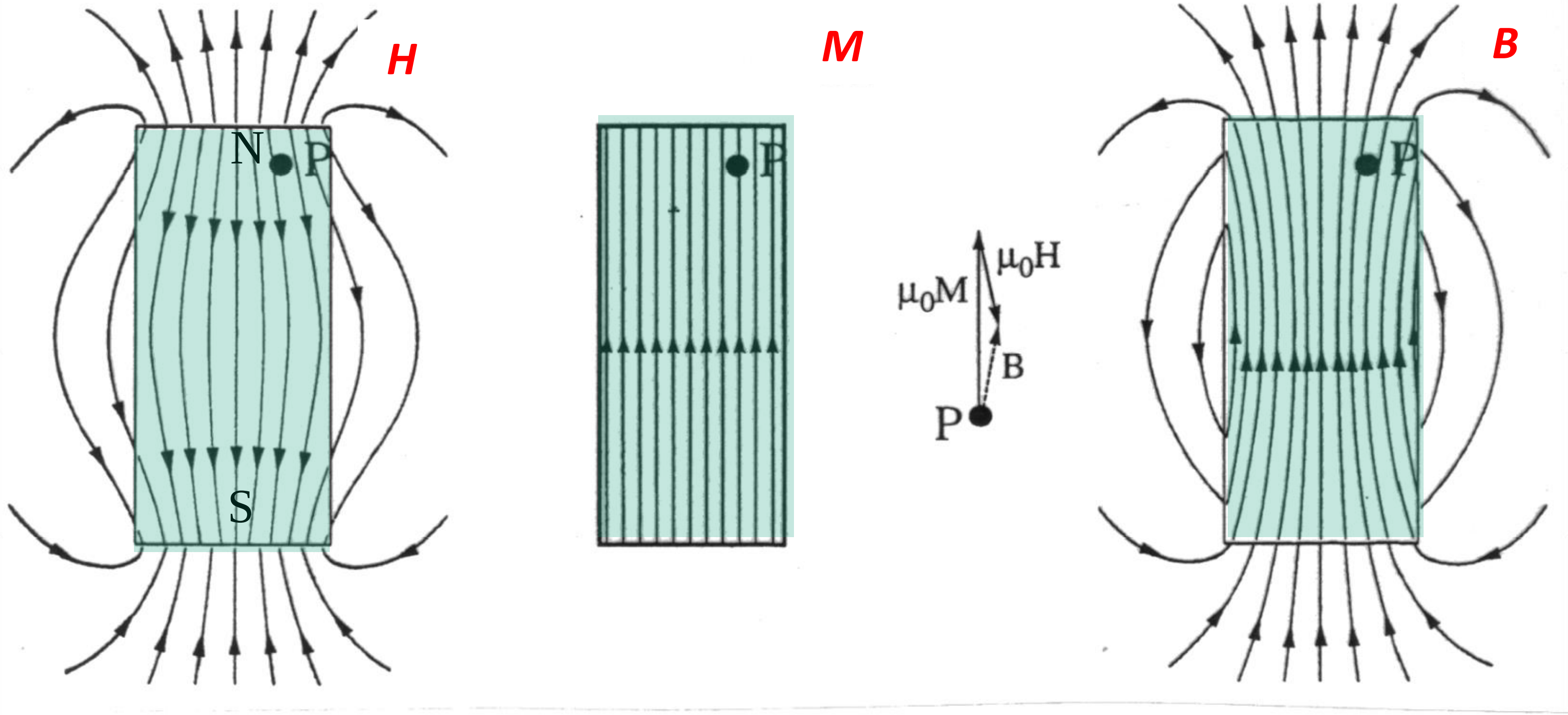
The particular domain structure adopted by a piece of ferromagnetic material is the result of minimizing the total energy, which in the sum of four terms

$$E_{tot} = E_{ex} + E_a + E_{ms} + E_Z$$

E_{ex} is the exchange energy. E_a is the anisotropy energy. E_Z is the Zeeman energy in an external field

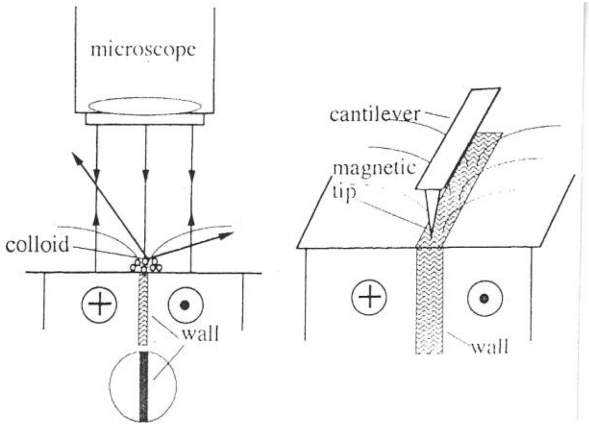
B, ***H*** *and* ***M*** *again*

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



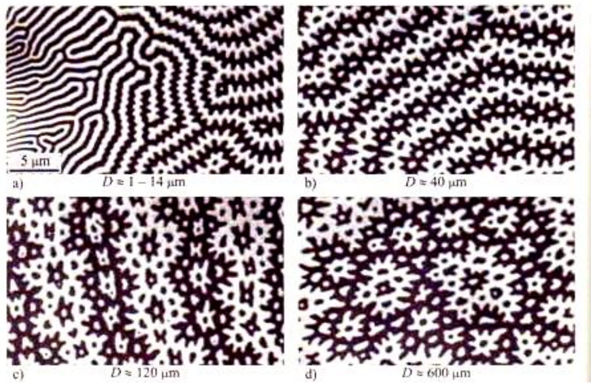
Some ways of visualizing domains:

— 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 ***M*** in the surface region]
— Lorentz (transmission electron) microscopy [depends on ***B*** in a thin foil]



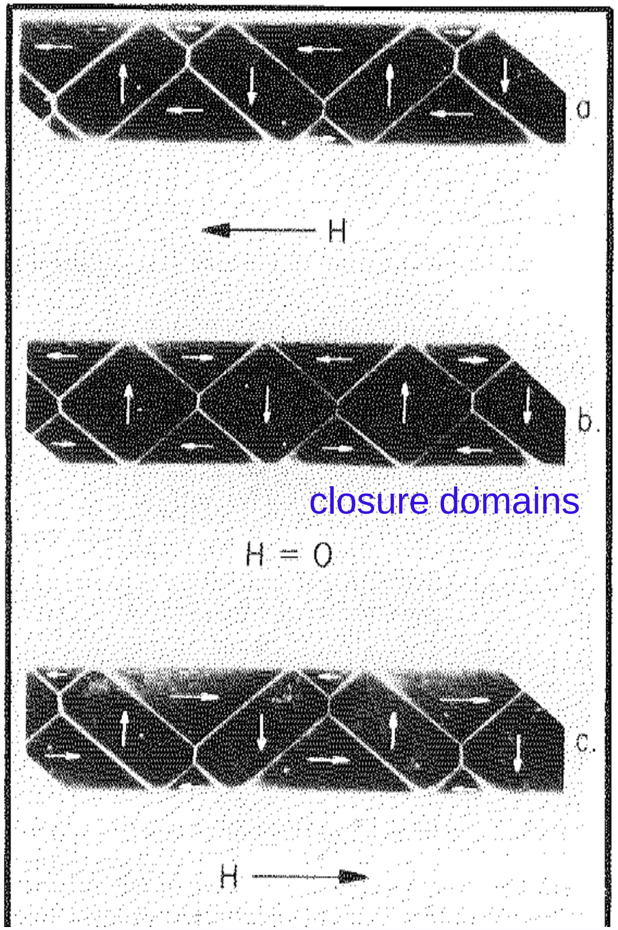
Bitter method (left) and MFM (right)

— Barkhausen heard them first !



Kerr images of domains

Domain patterns in a cubic iron crystal. The structure depends on the applied magnetic field *H*

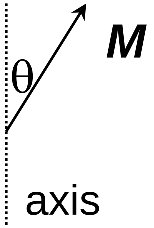


6.3.1 Anisotropy

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

$$\boxed{E_a = K_1 \sin^2\theta}$$



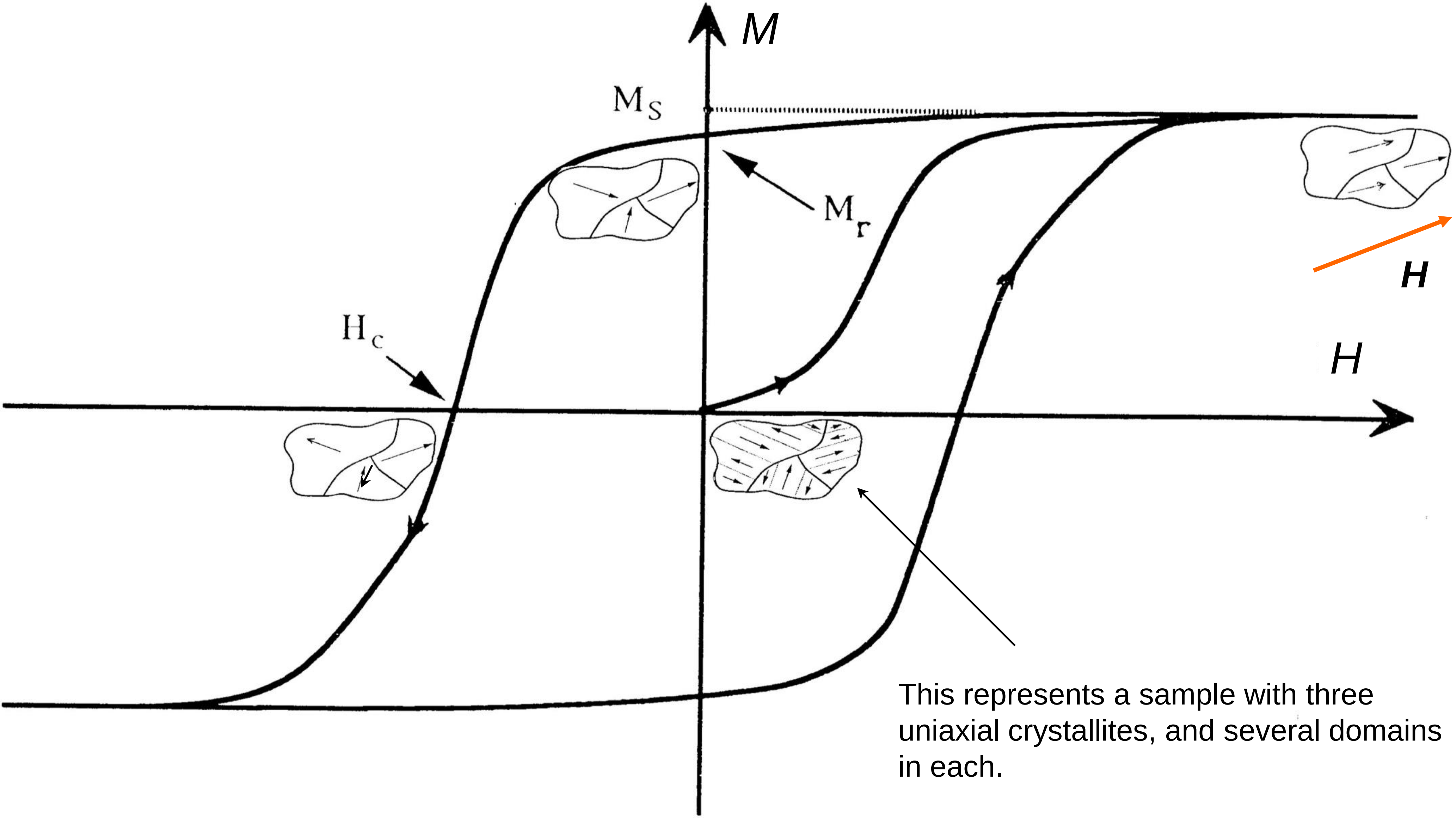
where θ is the angle between ***M*** and the anisotropy axis.
The anisotropy constant K_1 depends on temperature, and the anisotropy energy goes to zero at T_C. Units are J m^{-3}. Values typically range from 10^2 to 10^6 J m^{-3}.

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

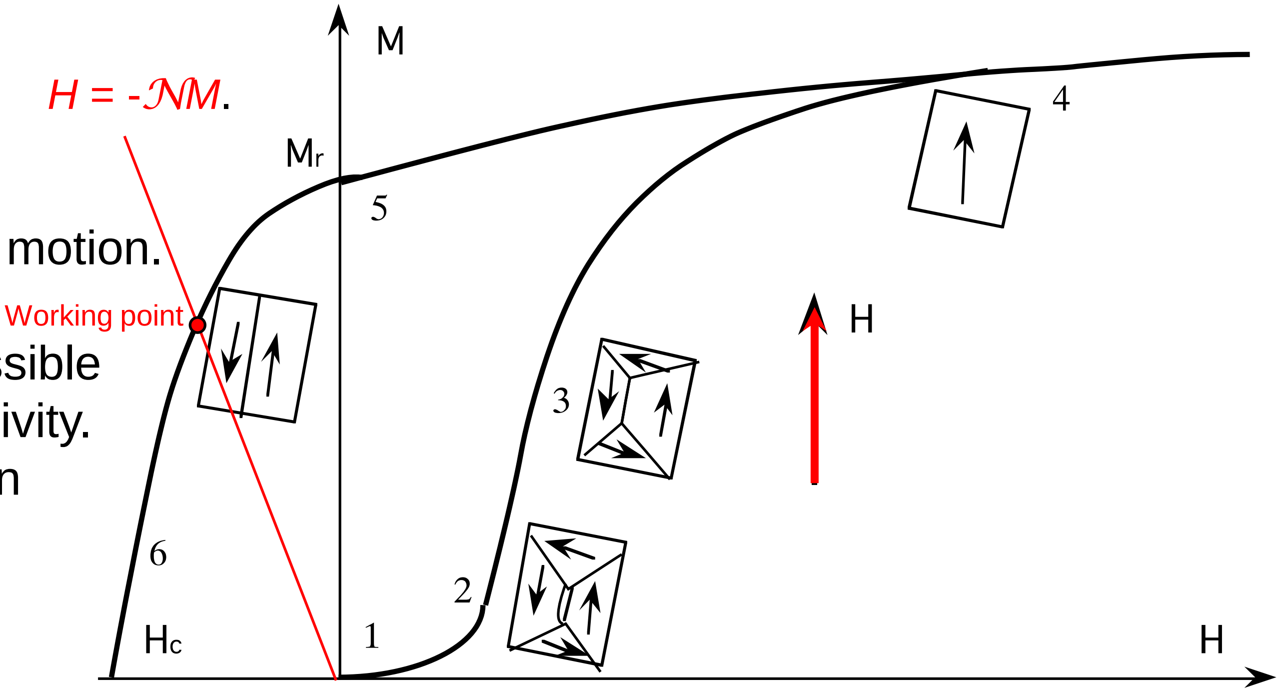


This represents a sample with three uniaxial crystallites, and several domains in each.

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 $\int_{loop}\mu_0 H \mathrm{d}M$.
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 $-\mathcal{N}M$.
If the magnet is to remain fully magnetized no matter what its shape, it should have a square loop with $H_c > M$

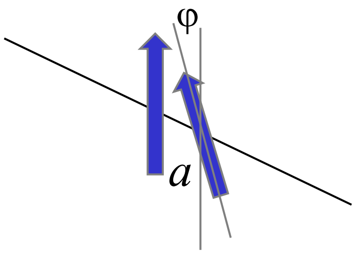
6.3.2 Domain walls

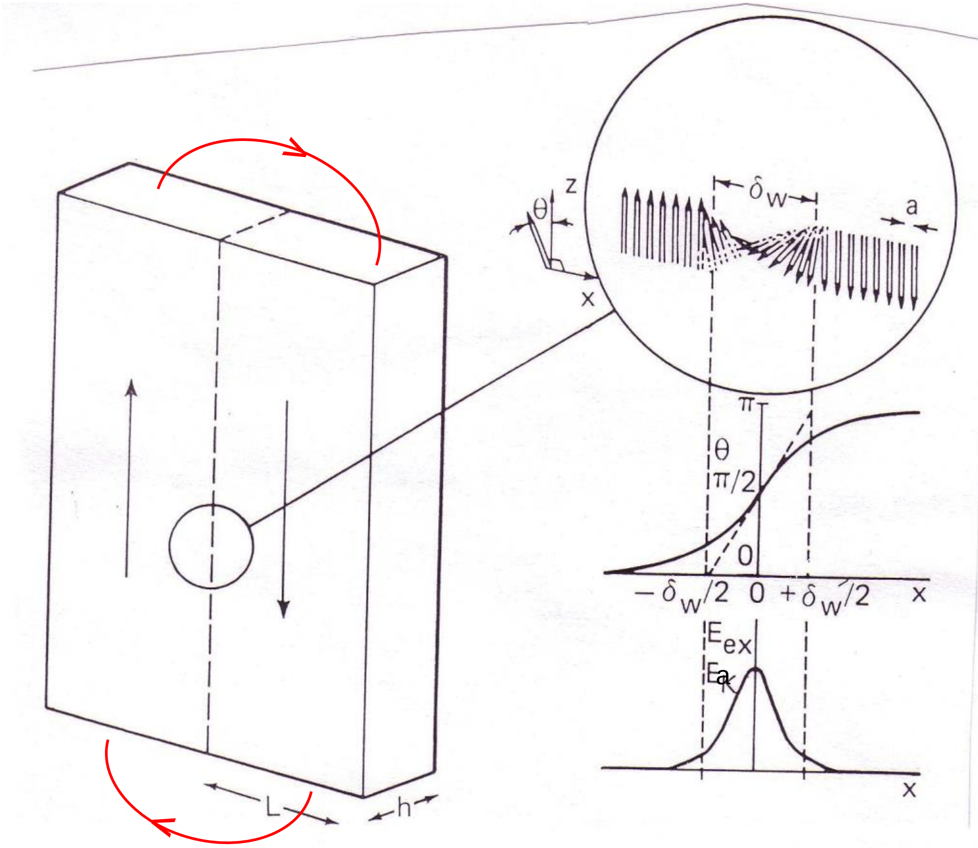
The region separating two oppositely-magnetized domains is a 180° domain wall, known as a *Bloch wall.* The structure is obtained by minimizing the energy

$$E_{tot} = E_{ex} + E_a + E_{ms}.$$

We give an approximate treatment which illustrates the physics.

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





A 180° Bloch wall between oppositely-magnetized domains in a sample with uniaxial anisotropy.

The wall width δ_w is related to a (atomic spacing) and φ (misalignment of adjacent spins), $\delta_w = (\pi/\varphi)a$

Exchange energy for a neighbouring pair of spins is

$$-2\mathcal{J}\mathbf{S}_i.\,\mathbf{S}_j. = -2\mathcal{J}S^2\cos\varphi \approx -2\mathcal{J}S^2(1 - \tfrac{1}{2}\varphi^2 + ...)$$

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

If this were the *only* term, φ 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 ½ K_1a^3 per spin or

$$E'_a = \tfrac{1}{2} K_1 a\pi/\varphi \quad \text{per unit area.}$$

The wall energy $\gamma_{wall} = E'_{ex} + E'_a$ is minimum with respect to φ when

$$\partial E_w/\partial\varphi = \mathcal{J}S^2\pi/a^2 - \tfrac{1}{2}K_1a/\varphi^2 = 0. \qquad \varphi^2 = \tfrac{1}{2}K_1a^3/JS^2$$

$$\boxed{\delta_w = \pi\sqrt{(2\mathcal{J}S^2/K_1a)}} \quad \text{units m}$$

$$\boxed{\gamma_w = \pi\sqrt{(2K_1\mathcal{J}S^2/a)}} \quad \text{units Jm}^{-2}$$

Taking the example of cobalt, K_1 = 500 kJ m^{-3}, J = S ≈ 1 and using T_C = 1390 K and Z = 12 to deduce $\mathcal{J}$ from the expression $T_C = 2Z\mathcal{J}J(J+1)/3k_B$ gives $\mathcal{J}$=1.2 10^{-21} J. $a \approx 0.2$ nm; hence $\delta_w \approx$ 15 nm, about 75 atomic spacings; γ_W = 8 mJ m^{-2}.

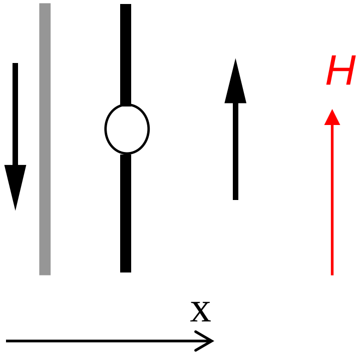
The wall is like a soap bubble — its area is minimized

Domain wall pinning

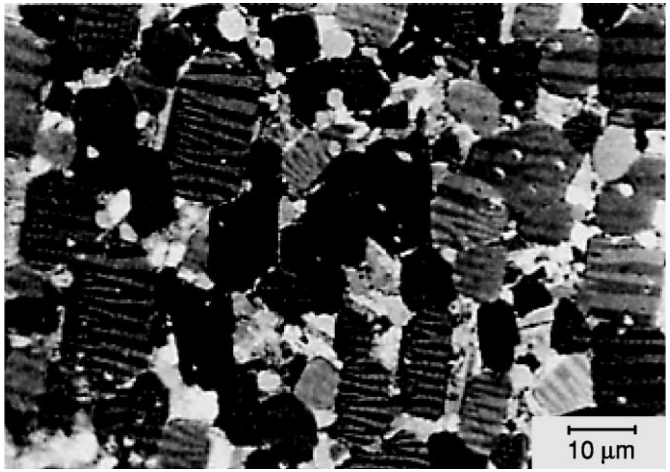
The domain wall acts like an elastic membrane with energy γ_w J m^{-2}. It will be strongly pinned at defects, especially planar defects, with different J or K_1 to the bulk, especially when these defects have dimension comparable to the domain wall width δ_w.

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



$$E_{tot} = f(x) - 2\mu_0 MHx$$



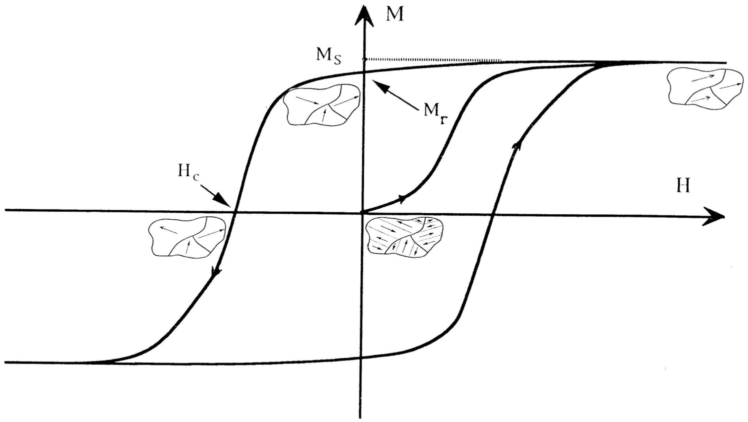
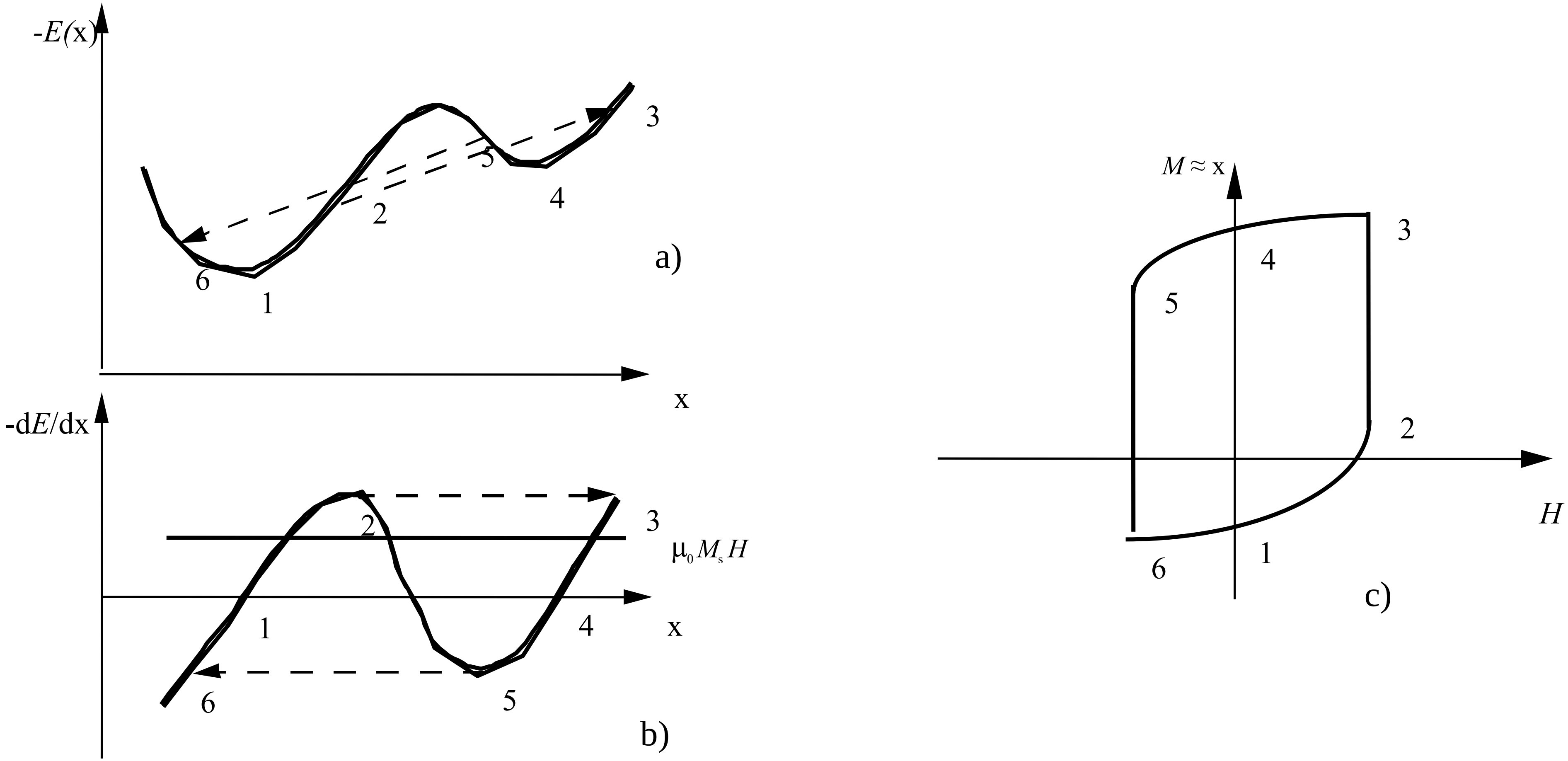


Image of the polished surface of a Nd–Fe–B sintered magnet in the Kerr microscope. The magnet is in the virgin state, and the oriented $Nd_2Fe_{14}B$ crystallites are unmagnetized multidomains. The domain contrast is due to Kerr rotation observed between crossed polarizers. Domain walls are trapped between the grains

We show how a hysteresis loop results from the energy landscape with several minima due to pinning. At local energy minimum $df(x)/dx = 2\mu_0 MH$. 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 in a magnetic field H . b) The equilibrium condition $df(x)/dx = 2\mu_0 MH$
c) a hysteresis loop due to field cycling.

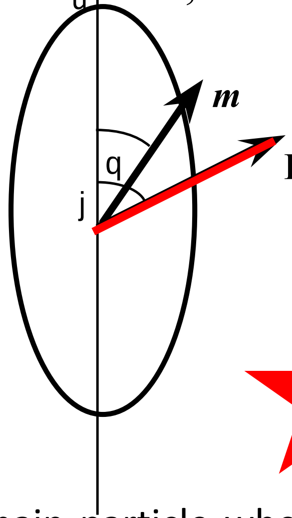
6.3.3 Single-domain particles.

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 $\frac{1}{2}\mu_0 M^2 V \sim \mu_0 M^2 r^3$, whereas the cost of forming the wall is $\gamma_w \pi r^2$. When the particle radius r is sufficiently small, $\sim \pi\gamma_w/\mu_0 M^2$ the latter outweighs the former.

When the particle is very small, reversal takes place by *coherent rotation* of the magnetic moment ***m***.

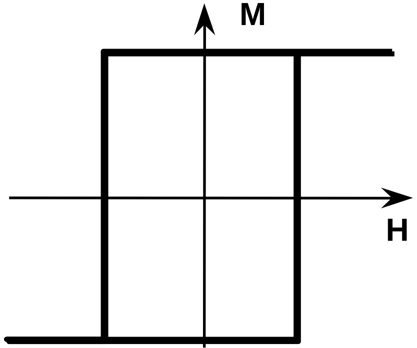
If an external field ***H*** is applied at an angle φ to the easy direction, and the magnetization is at an angle θ to the easy direction, the energy is $E_{tot} = E_{ms} + E_a + E_Z$ the sum of magnetostatic (shape anisotropy), magnetocrystalline and Zeeman terms. The first two are given by a term $K_u \sin^2\theta$, hence

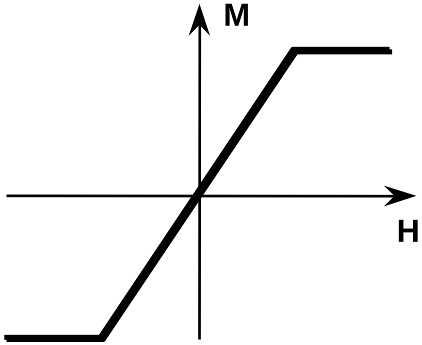
$$E_{tot} = K_u V \sin^2\theta - \mu_0 m H \cos(\varphi - \theta)$$



A single domain particle where the magnetization rotates coherently.

The energy can be minimized, and the hysteresis loop calculated numerically for a general angle φ. 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 π, 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

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 $\boldsymbol{F} = -\nabla \boldsymbol{m}.\boldsymbol{B}$,
or on Faraday's law $\varepsilon = -d\Phi/dt$, where Φ is the flux threading a circuit and ε is the induced emf.
We consider three examples:

Force method (Faraday balance)

Considering one component, the z-component, of the force equation; (***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 of susceptibility. Sensitivity may be improved by applying an alternating current to the gradient coils and using lock-in detection.

Extraction method.

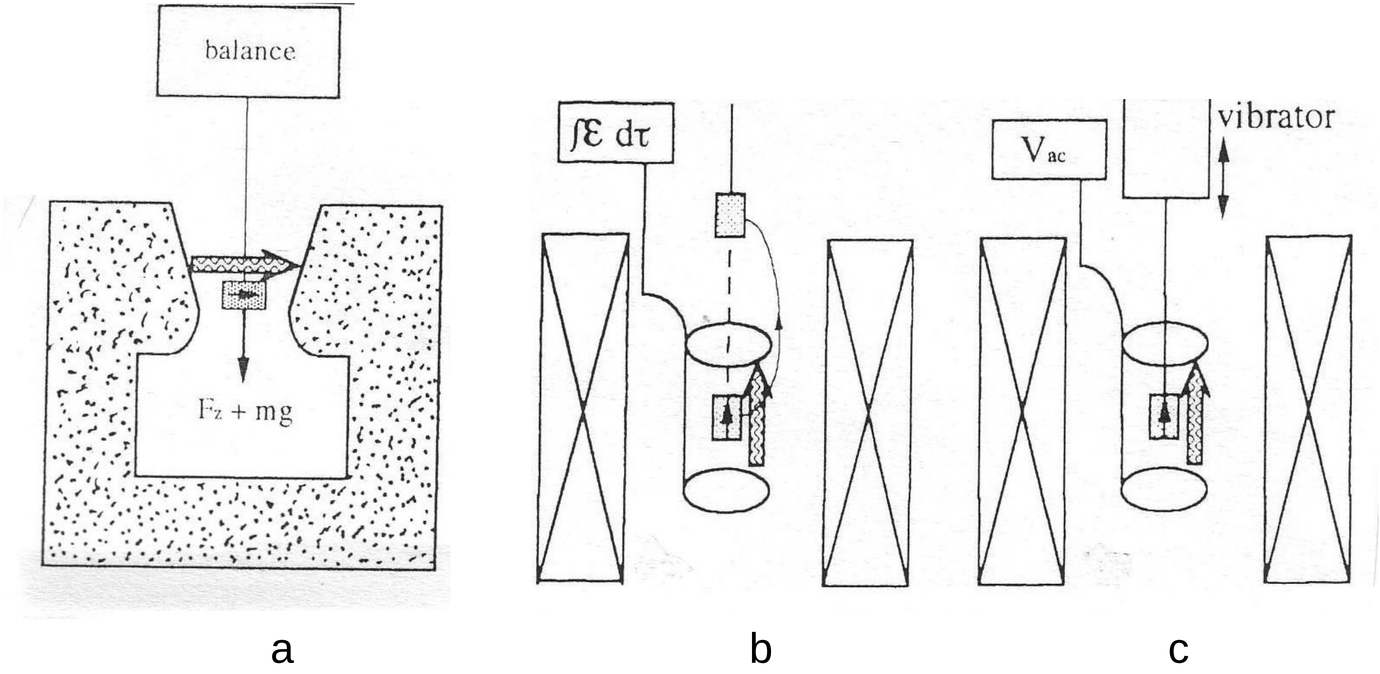
Here the sample is first located in a pickup coil in the field, and then removed to a distant point. An emf ε is induced in the coil, and

$$\int \varepsilon \, dt = \Phi$$

The flux Φ produced by the moment ***m*** is proportional to its magnetization. A SQUID detector can be used to achieve great sensitivity in the measurement of Φ. Sensitivity of 10^{-11} A m^2 for ***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}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	ρ (kg/m^3)	Structure	T_C (K)	$\mu_0 M$ (290 K) (T)	m_0 (μ_B/formula)	K_1 (kJ/m^3)
Soft						
Fe	7874	cubic	1044	2.15	2.2	50
Ni	8902	cubic	628	0.62	0.6	-5
$Fe_{65}Co_{35}$*	8110	cubic	1240	2.34	2.5	40
$Ni_{80}Fe_{20}$¶	8715	cubic	843	1.04	1.1	<1
Gd	7886	hexagonal	292	0.80	7.0	
CrO_2	4870	tetragonal	396	0.50	2.0	20
Hard						
Co	8836	hexagonal	1390	1.81	1.7	530
$SmCo_5$	8606	hexagonal	1020	1.08	7.8	17200
$Nd_2Fe_{14}B$	7760	tetragonal	588	1.61	37.3	4900

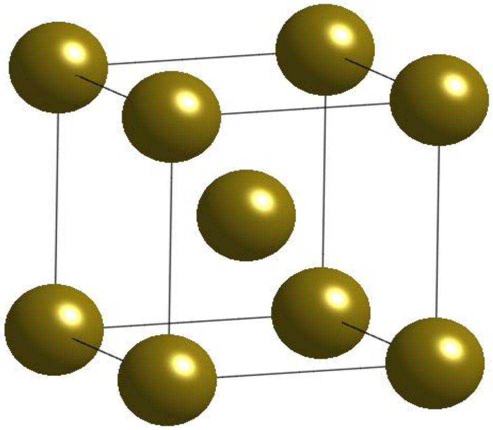
* permendur ¶ permalloy

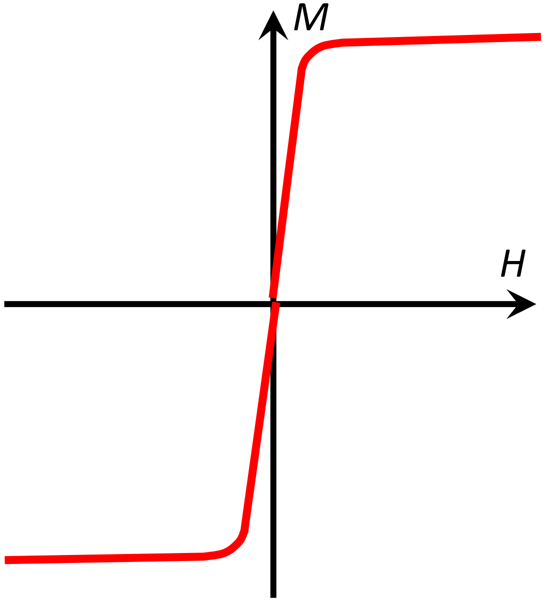
6.5 Hard and soft ferromagnets

Two categories of useful ferromagnets are distinguished by their hysteresis loops.

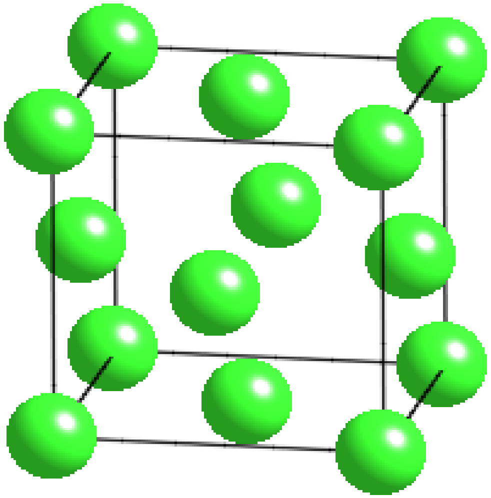
Soft ferromagnets have narrow loops with as little hysteresis as possible (Energy loss is proportional to the area of the loop). Good examples are bcc *iron* with 3% Si substitution, and '*permalloy*' — fcc $Fe_{20}Ni_{80}$

Iron





Permalloy

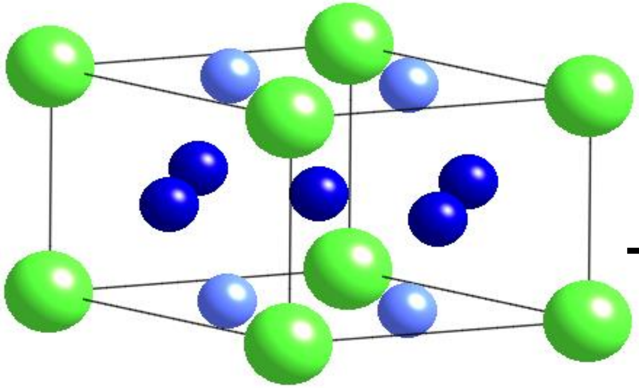


$\mu_0 M_s = 2.1$ T $M_s = 1.73$ MA m^{-1}
$K_{1c} \approx 48$ kJ m^{-3} ⟨100⟩ directions easy
$\lambda_s = -7\ 10^{-6}$ $T_C = 1044$ K

$\mu_0 M_s = 1.0$ T $M_s = 0.8$ MA m^{-1}
$K_1 \approx 1$ kJ m^{-3}
$\lambda_s = 2\ 10^{-6}$ $T_C = 843$ K

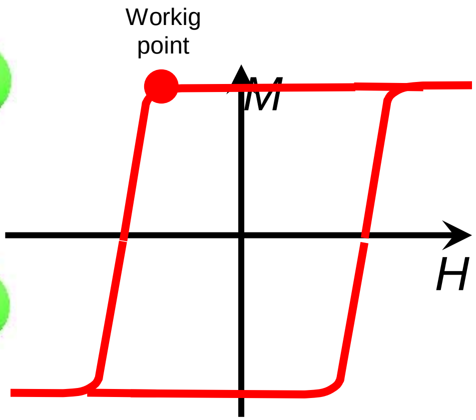
Hard ferromagnets have broad square loops with $H_c > ½\ M_s$. They *always* have a uniaxial crystal structure (hexagonal, tetragonal ...) with one *easy axis* of magnetization $K_1 > 0$
Once magnetized they remain in their metastable, fully magnetized state creating a stray field around them with no expenditure of energy.
Good examples are $SmCo_5$ and $Nd_2Fe_{14}B$.

$SmCo_5$

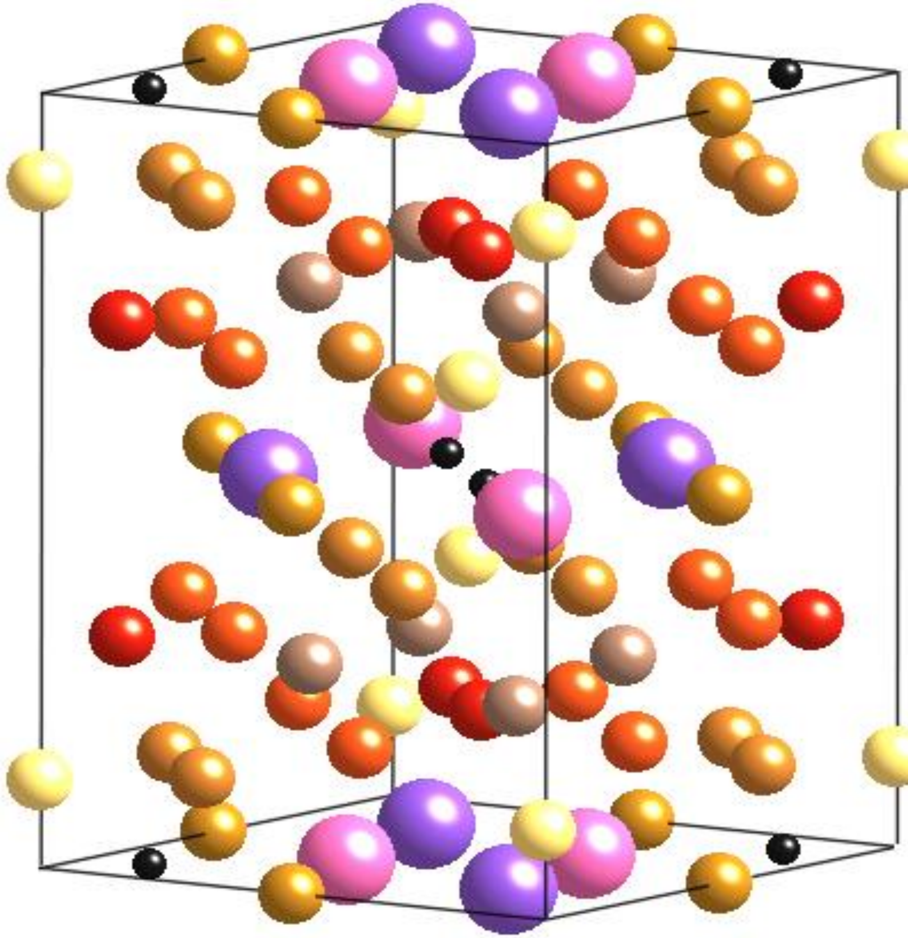


$\mu_0 M_r$ = 1.0 T; M_s = 0.8 MA m^{-1}
K_1 = 17 MJ m^{-3} (hexagonal)
T_C = 1020 K
$(BH)_{max}$ = 200 kJ/m^3

$Nd_2Fe_{14}B$



$\mu_0 M_r$ = 1.4 T; M_s = 1.1 MA m^{-1}
K_1 = 4.9 MJ m^{-3} (tetragonal)
T_C = 878 K
$(BH)_{max} \approx$ 400 kJ/m^3



MOOC 2.2.   10’

7. Miscellaneous Topics

Other types of magnetic order arise from antiferomagnetic 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 $E = D_{sw}q^2$ in the ferromagnetic case. Spin electronics is the new frontier in magnetism, where we consider not only the electron charge (which is conserved), but also its spin magnetic moment (which is not conserved) in thin-film electronic devices.

A

Introduction

E & M

Basic Ideas

M. B, H

Energy

Quantum theory

Magnetism of the electron

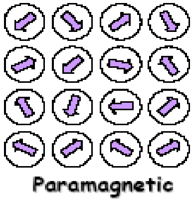
Molecular field theory

single electron magnetism.

Magnetism of the atom with one or more electrons

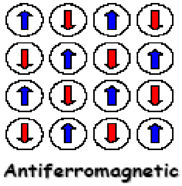
multi-electron atoms

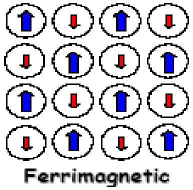
Paramagnetism



Disordered

Magnetism of interacting atoms Ferromgnetism





Ordered

Other topics

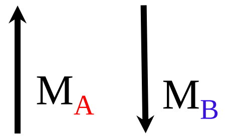
multi-atom solids

Applications

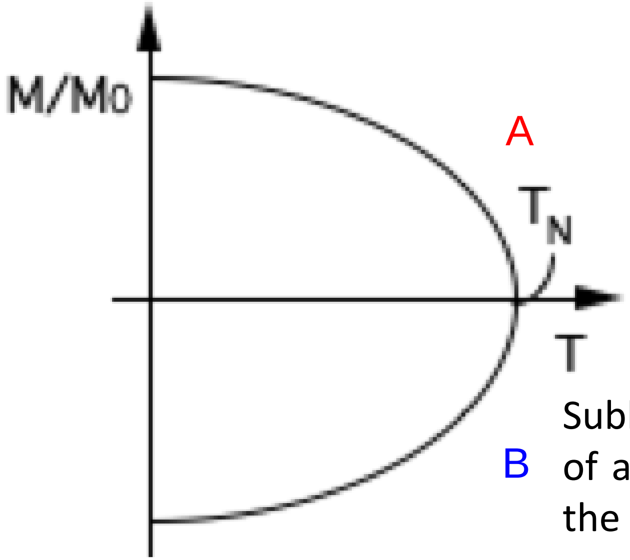
7.1 Antiferromagnetism

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; $\boldsymbol{M}_A = -\boldsymbol{M}_B$ when the coupling between them is negative. Two Weiss coefficients n_W and n_W' represent the inter- and intrasublattice interactions. Here n_W is negative.

$$\boldsymbol{H}_A^i = n_W' \boldsymbol{M}_A + n_W \boldsymbol{M}_B + \boldsymbol{H}$$
$$\boldsymbol{H}_B^i = n_W' \boldsymbol{M}_B + n_W \boldsymbol{M}_A + \boldsymbol{H}$$

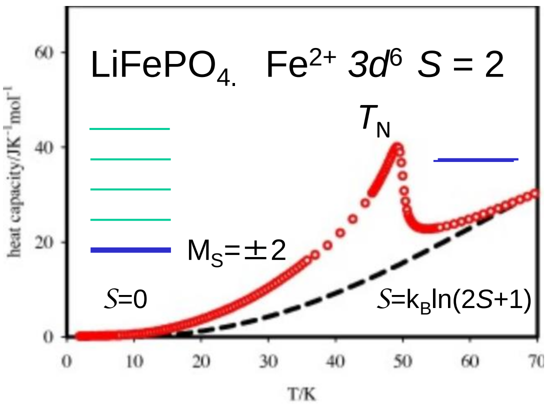


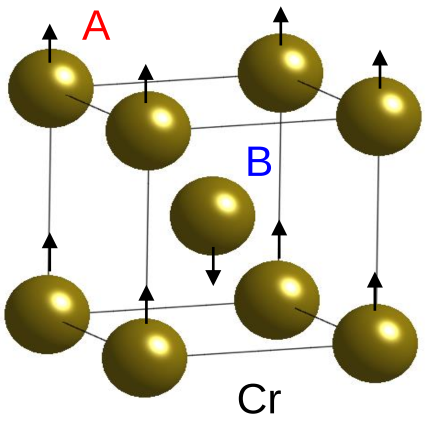
The net magnetization $\boldsymbol{M} = \boldsymbol{M}_A + \boldsymbol{M}_B$ is zero when $\boldsymbol{H} = 0$. The magnetization of each sublattice is represented by a Brillouin function, and each falls to zero at a critical temperature, the Néel temperature T_N. The sublattice magnetization $\langle M_\alpha \rangle = M_0 \mathcal{B}_J(x_\alpha)$ where α = A,B and $x_\alpha = \mu_0 m H_\alpha^i / k_B T$.



Sublattice magnetizations of an antiferromgnet. T_N is the Néel temperature

Q How could you ever tell that a substance is antiferromagnetic? What could you measure ?

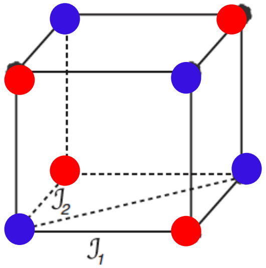




Susceptibility Calculation

Above T_N $M_\alpha = \chi H_\alpha^{i}$ where $\chi = C'/T$ with $C' = \frac{1}{2}\mu_0 N m_{eff}^2/3k_B$. $m_{eff} = g\mu_B\surd(S(S+1)$

Here ½N is the number of atoms per m^3 of each sublattice. Hence



Magnetic interactions in a simple cubic lattice.

$$M_A = (C'/T)(n_W' M_A + n_W M_B + H)$$
$$M_B = (C'/T)(n_W M_A + n_W' M_B + H)$$

The condition for the appearance of spontaneous sublattice magnetization is that these equations have a nonzero solution in zero applied field H. The determinant of the coefficients is zero, hence $[(C'/T)n_W' - 1]^2 - [(C'/T)n_W]^2 = 0$, which yields

$$\boxed{T_N = C'(n_W' - n_W)}$$

To calculate the susceptibility above T_N we evaluate $\chi = (M_A + M_B)/H$. Adding the equations for M_A and M_B, we find the Curie-Weiss law

$$\boxed{\chi = C/(T - \theta_p)}$$

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 θ_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_{eff} from C, and θ_P.

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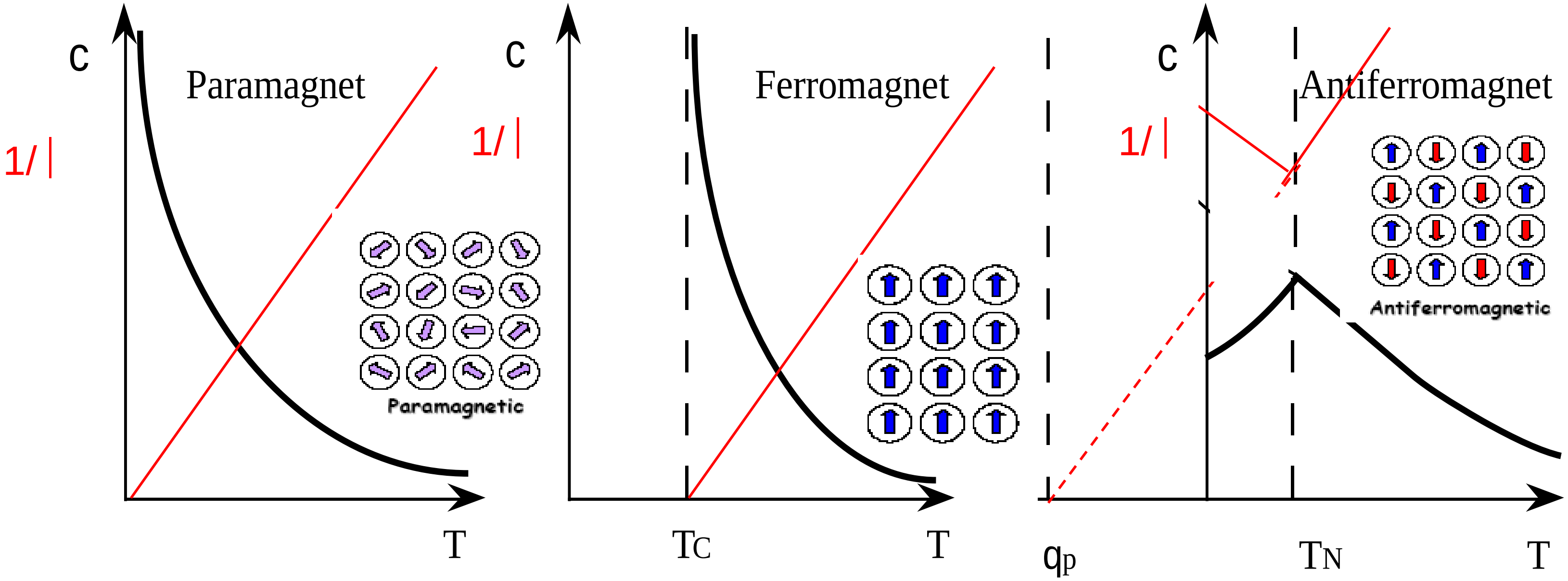
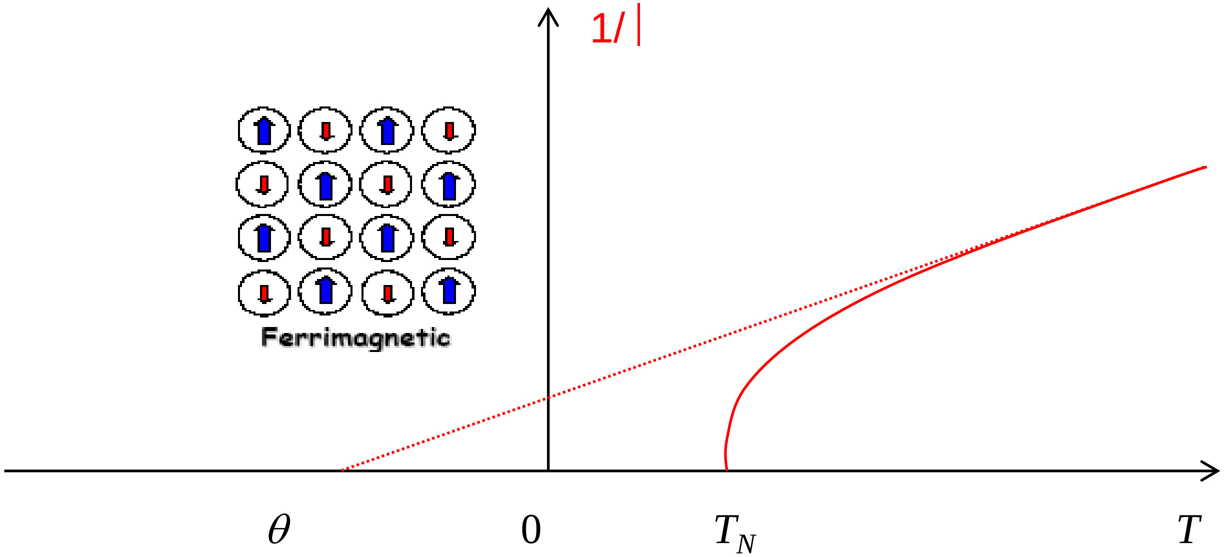
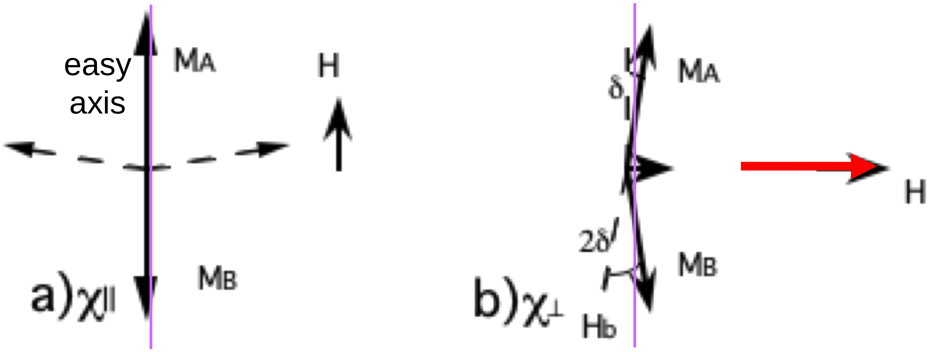


Comparison of the susceptibility of a paramagnet, a ferromagnet and an antiferromagnet



Inverse susceptibility of a ferrimagnet above its Néel point T_N

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 ***H*** relative to this easy 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 $\chi_{\parallel}$ 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 $\chi_{\parallel} = [M_A(H) + M_B(H)]/H$ is

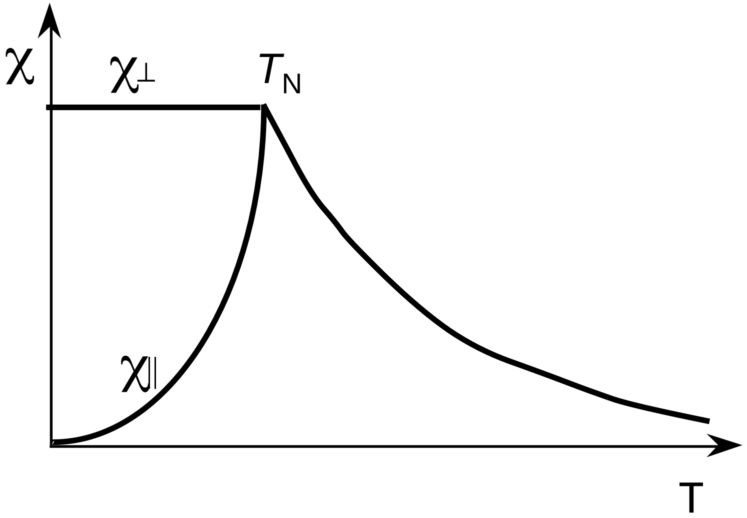
$$\chi_{\parallel} = 2C'[3J(J+1)\mathcal{B}'_J(x_0)]/[T - n_W C'[3J(J+1)\mathcal{B}'_J(x_0)] \text{ where } \mathcal{B}'_J(x) = \partial\mathcal{B}'_J(x)/\partial x$$

This rises from 0 at $T = 0$ to $C/(T - \theta_p)$ at T_N. 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 δ. In equilibrium the torque on each one is zero, hence $M_\alpha H = M_\alpha n_W M_\beta \sin 2\delta$. Since $M = 2M_\alpha \sin\delta$,

$$\boxed{\chi_{\perp} = -1/n_W}$$

$$\boxed{\chi_\perp = -1/n_W}$$



The perpendicular susceptibility is therefore constant and independent of temperature up to T_N.

For a powder, the average is $\frac{1}{3}\chi_\parallel + \frac{2}{3}\chi_\perp$, or $(2/3)(-1/n_W)$ at low temperature.

Parallel and perpendicular susceptibility of an antiferromagnet.

Since $\chi_\perp > \chi_\parallel$ for all $T < T_N$, we might think that an antiferromagnet will always adopt the transverse, flopped configuration. It doesn't because of the magnetocrystalline 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_α the *spin flop* occurs when the energies of the parallel and perpendicular configurations are equal;

$$-2M_aH_K - \tfrac{1}{2}\chi_\parallel H_{sf}^2 = -\tfrac{1}{2}\chi_\perp H_{sf}^2$$

$$\boxed{H_{sf} = [4M_\alpha H_K/(\chi_\perp - \chi_\parallel]^{1/2}}$$

When $T \ll T_N$, this reduces to $H_{sf} = 2\sqrt{(H_kH^i)}$. 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.

Antiferromagnet

$$\boldsymbol{H}_A^i = n_{AA}\boldsymbol{M}_A + n_{AB}\boldsymbol{M}_B + \boldsymbol{H}$$
$$\boldsymbol{H}_B^i = n_{AB}\boldsymbol{M}_A + n_{BB}\boldsymbol{M}_B + \boldsymbol{H}$$

Two Weiss coefficients to account for inter- and intra-sublattice interactions.

$n_{AA} = n_{BB} = n_W'$. $n_{AB} = n_W$

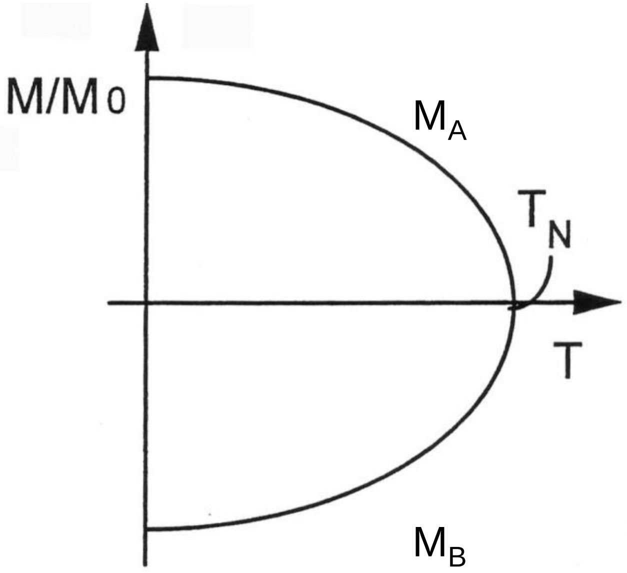
Ferrimagnet

$$\boldsymbol{H}_A^i = n_{AA}\boldsymbol{M}_A + n_{AB}\boldsymbol{M}_B + \boldsymbol{H}$$
$$\boldsymbol{H}_B^i = n_{AB}\boldsymbol{M}_A + n_{BB}\boldsymbol{M}_B + \boldsymbol{H}$$

Three Weiss coefficients account for inter- and intra-sublattice interactions.

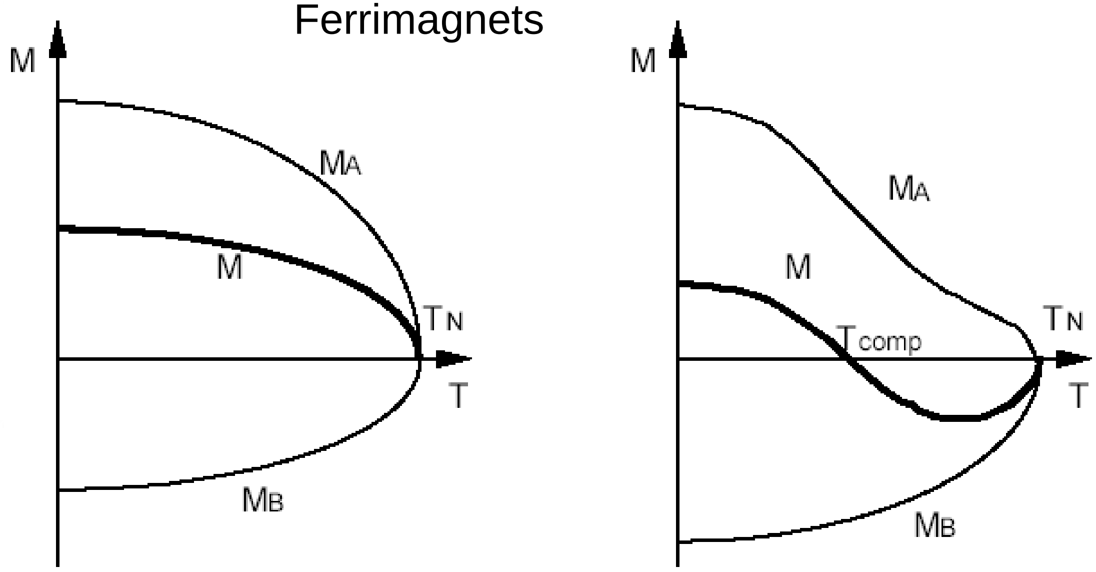
$n_{AA} \neq n_{BB}$

Antiferromagnet



Sublattice magnetization of an antiferromagnet

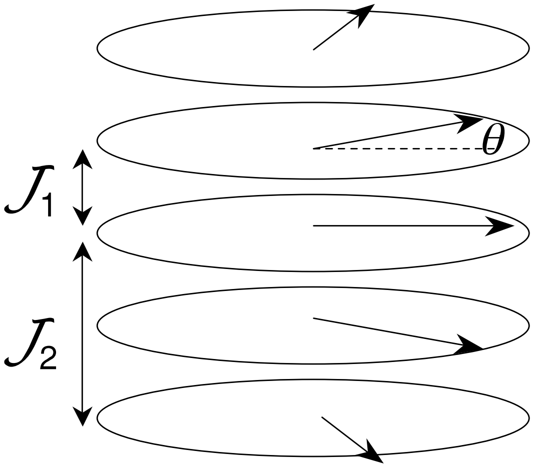
Ferrimagnets



$|n_{AB}| >> |n_{AA}|, |n_{BB}|$ $|n_{BB}| >> |n_{AA}|, |n_{AB}|$

Sublattice magnetizations for two ferrimagnets

7.2 Other forms of magnetic order

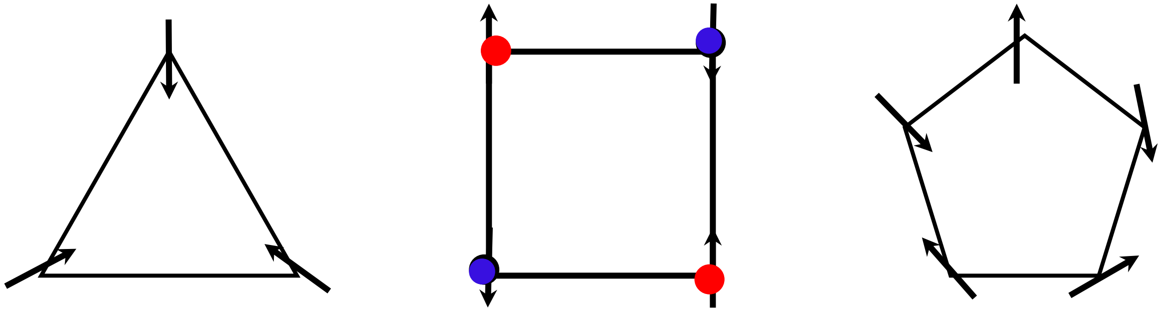


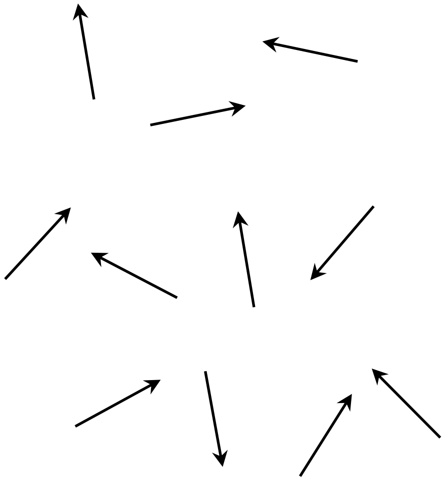
A planar helimagnet

Many 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 noncolinear spin structure may then arise, such as a helimagnetic structure where there are ferromagnetic planes, but the ferromagnetic axis turns by an angle θ from one plane to the next.

$J_1 > 0$; $-J_2 > ¼ J_1$

Frustration may also arise with purely antiferromagnetic interactions, when there are odd-membered rings. Some examples are shown below.





A spin glass

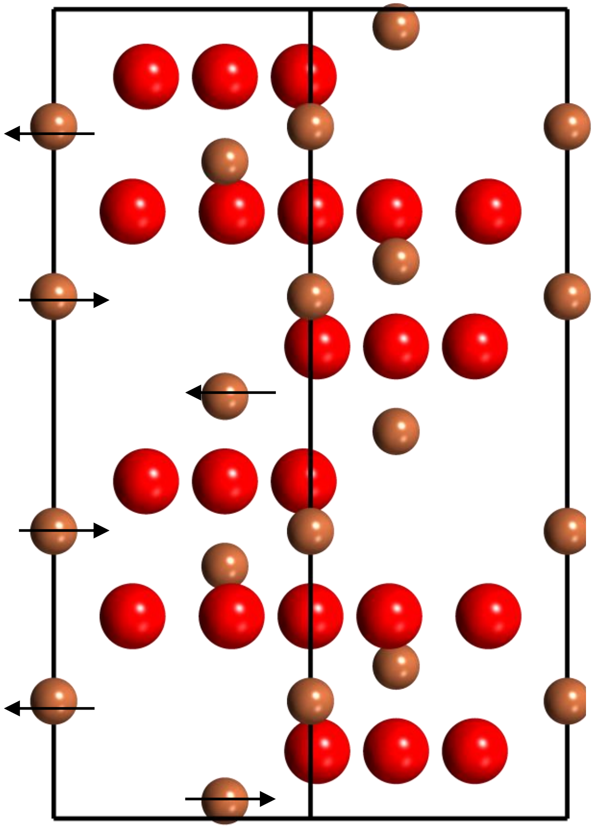
In disordered and amorphous solids, frustrated antiferromagnetic interactions, or competing ferromagnetic and antiferromagnetic interactions may give rise to spin freezing in random directions. Such materials are known as *spin glasses*.

7.3 Antiferromagnets and Ferrimagnets

Antiferromagnets

Hematite; αFe_2O_3

Most common iron oxide mineral on Earth. hcp oxygen array with Fe^{3+} 3*d*^{5} in 2/3 of the octahedral sites. Hexagonal; *a* = 504 pm, *c* = 1375 pm



T_N = 960 K.

$J_s = 2.8\ 10^{-3}$ T

$m_s = 0.002\ \mu_B$/fu

$K_1 = 23$ kJ m^{-3}

$B_a = 2\mu_0 K_1/J_s = 20$ T

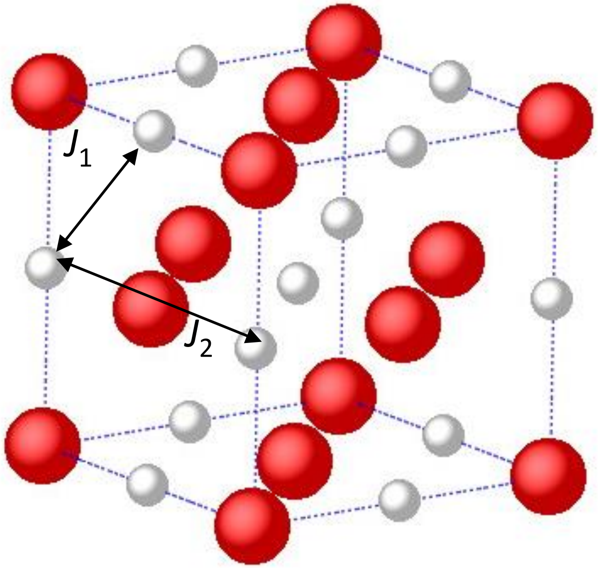
Antiferromagnetic with slightly canted sublattices above 260 K due to weak additional antisymmetric exchange $\boldsymbol{D}.\boldsymbol{S}_i \times \boldsymbol{S}_j$

Nickel oxide NiO

Cubic NaCl structure with antiferromagnetic nearest- and next-nearest neighbour 'superexchange interactions. Forms for divalent 3*d* cations

T_N = 525 K.

m = $2\mu_B$/atom



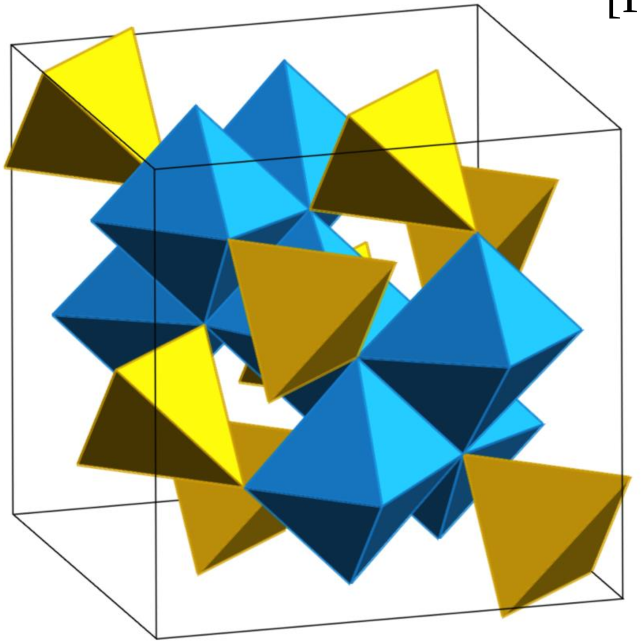
		a_0 (pm)	S	T_N (K)	θ_p (K)	J_1(K)	J_2(K)
MnO	**3d^5**	**445**	**5/2**	**117**	**-610**	**-7.2**	**-3.5**
FeO	**3d^6**	**431**	**2**	**198**	**-570**	**-7.8**	**-8.2**
CoO	**3d^7**	**426**	**3/2**	**291**	**-330**	**-6.9**	**-22**
NiO	**3d^8**	**418**	**1**	**525**	**-1310**	**-50**	**-85**

Ferrimagnets

Magnetite Fe_3O_4

Most common magnetic mineral; magnetized by lightning; main constituent of lodestone. Oxygen array with Fe^{3+} $3d^5$ in tetrahedral sites and Fe^{3+}& Fe^{2+} on octahedral sites. Cubic a_0 =839 pm.

$[Fe^{3+}]\{Fe^{2+}Fe^{3+}\}O_4$

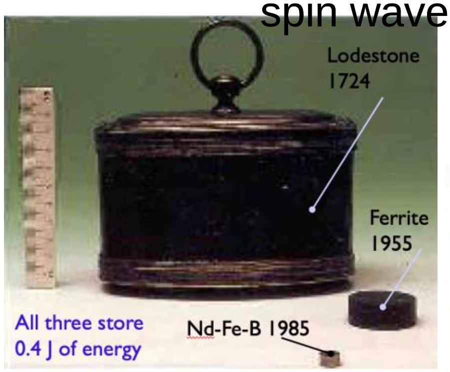


T_c = 843 K

J_s = 0.60 T

m_0 = 4μ_B/fu

spin waves

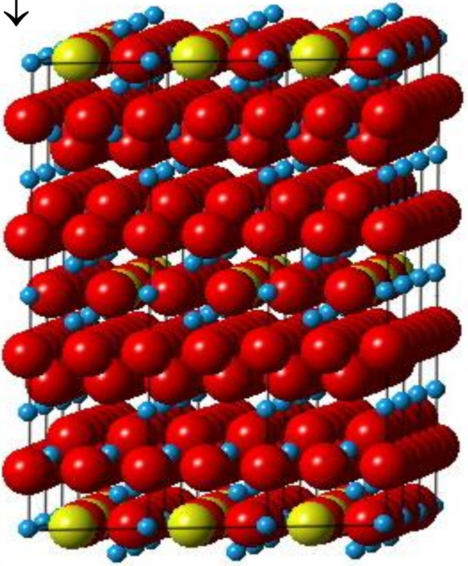


All three store 0.4 J of energy

Tetrahedral A $[Fe^{3+}]\downarrow$ & octahedral B$\{Fe^{2+}Fe^{3+}\}\uparrow$ sublattices coupled antiparallel by negative A-B exchange. The iron sites are represented by blue and yellow oxygen polyhedra. A conductor with the single ↓ Fe^{2+} d electron hopping among B sites.

Barium ferrite $BaFe_{12}O_{19}$

All low-cost permanent magnets are made of Ba (or Sr) ferrite discovered in 1952. 1 MT is produced annually. Big hexagonal unit cell with a = 589 pm, c = 2319 pm and five sites occupied by Fe^{3+} . The ferrimagnetic structure is $12k\uparrow 2a\uparrow 2b\uparrow 4f_1\downarrow 4f_2\downarrow$



T_c = 740 K

J_s = 0.48 T

m_0 = 20μ_B/fu

K_1 = 330 kJ/m^3

$(BH)_{max}$= 45kJ/m^3

Polymer bonded magnets

Sintered magnets

Powder is oriented and sintered, or else mixed with polymer and moulded into desired shapes.

7.4 Spin waves (magnons).

The exchange energy in the ferromagnetic ground state is $-2Z\mathcal{J}S^2$ 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 ↑↑↑↑↓↑↑↑↑ costs $8\mathcal{J}S^2$ ($2\mathcal{J}$ for $S = ½$), which is greater than k_BT_C for a chain where $T_C = 2Z\mathcal{J}S(S+1)/3$ (for $S = 1/2$, $Z = 2$). Such expensive excitations cannot occur at low temperature; instead, all the atoms share the reversal, with periodic oscillation of spin orientation.

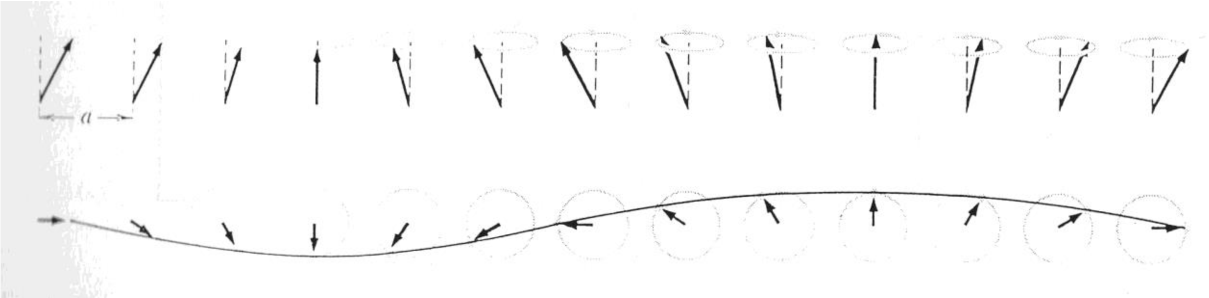


Illustration of a spin wave.

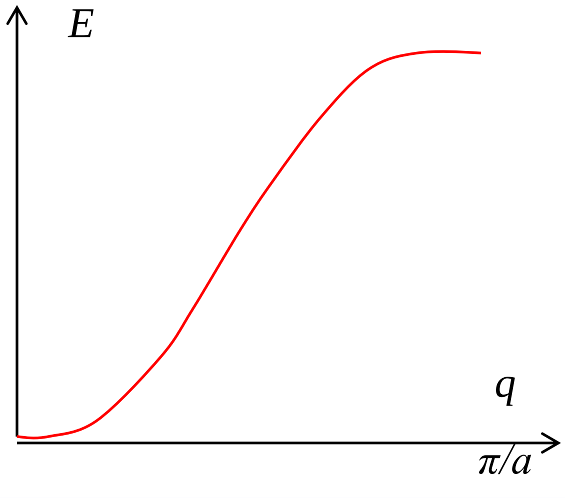
In one dimension, the relation between the frequency and wave-vector of a wave-like excitation of the spin system can be calculated classically

$$\omega_q = 4\mathcal{J}S(1 - \cos qa)$$

In the limit of small wave vectors, the dispersion relation becomes

$$E_q \approx D_{sw}q^2$$

where $E_q = \hbar\omega_q$, $D_{sw} = 2\mathcal{J}Sa^2$; a is the interatomic spacing.
The expression for any of the three basic cubic lattices is the same, where a is the lattice parameter.



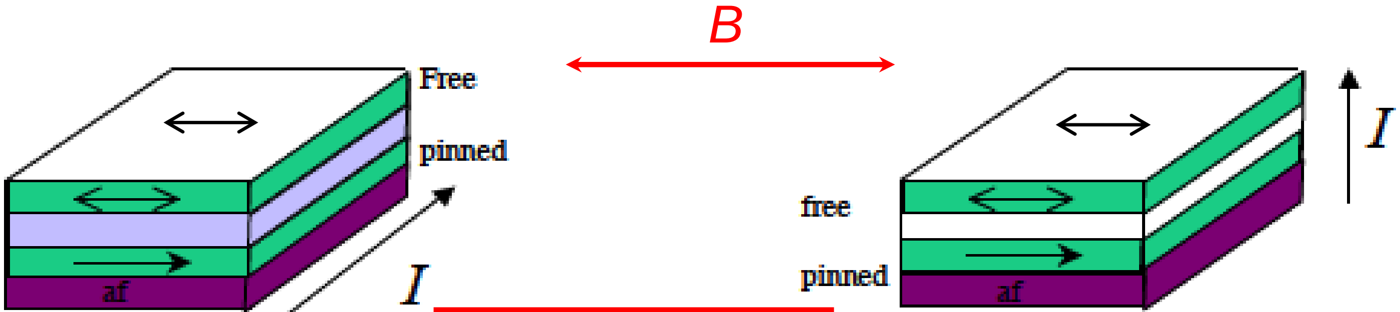
The spin-wave dispersion relation for a chain of atoms.

7.4 Spin Electronics

Look at MOOC 2.2

First-generation spin electronics has been built on *spin-valves* – sandwich structures using GMR or TMR with a pinned layer and a free layer.

They can serve as bistable memory elements:



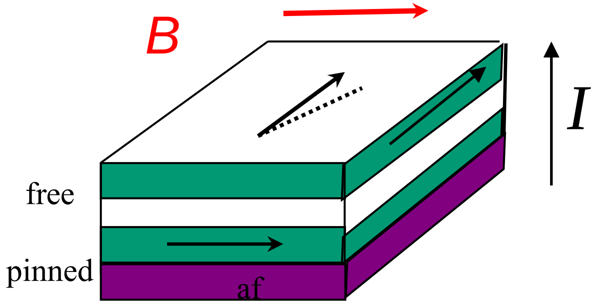
GMR spin valve

$MR = (R_{\uparrow\downarrow}-R_{\uparrow\uparrow})/R_{\uparrow\uparrow}$

planar magnetic tunnel junction

One layer in the sandwich has its magnetization direction pinned by exchange coupling with an antiferromagnet – *exchange bias.*

They can also serve as sensitive magnetic field sensors:

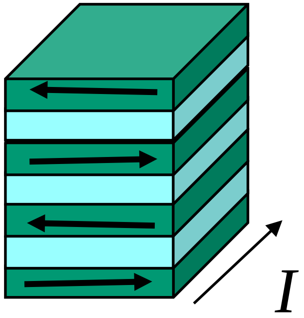


planar magnetic tunnel junction

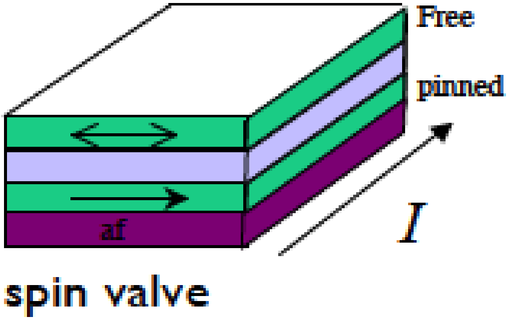
GMR – Giant magnetoresistance
TMR – Tunneling magnetoresistance

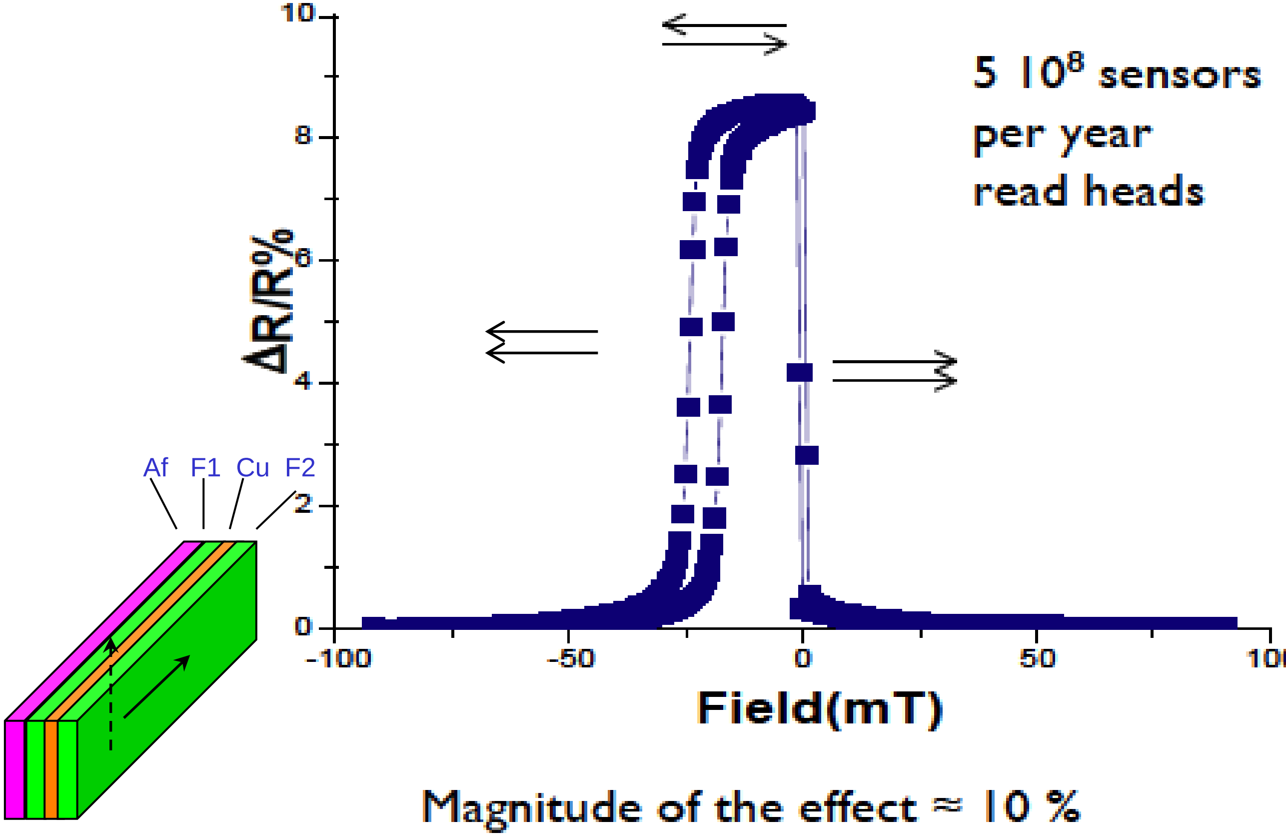
Giant magnetorsistance spin valve

Peter Grunberg, Albert Fert;



Fe/Cr multilayer stack





Magnitude of the effect ≈ 10 %

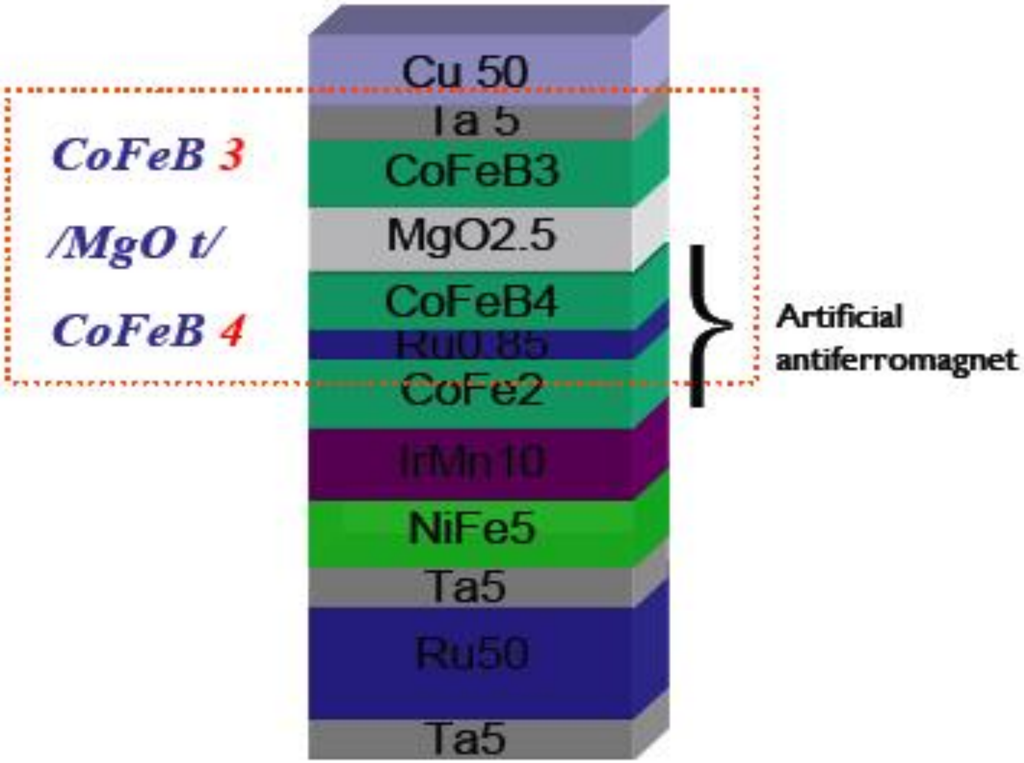
Discovery of GMR 1988

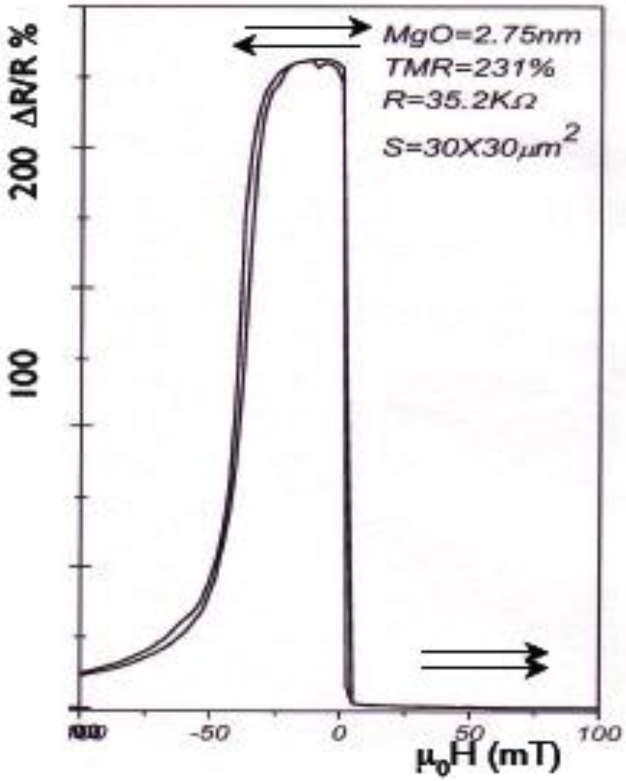
Implementation in hard disk drive 1998

Nobel Prize 2007

MgO-barrier magnetic tunnel junctions

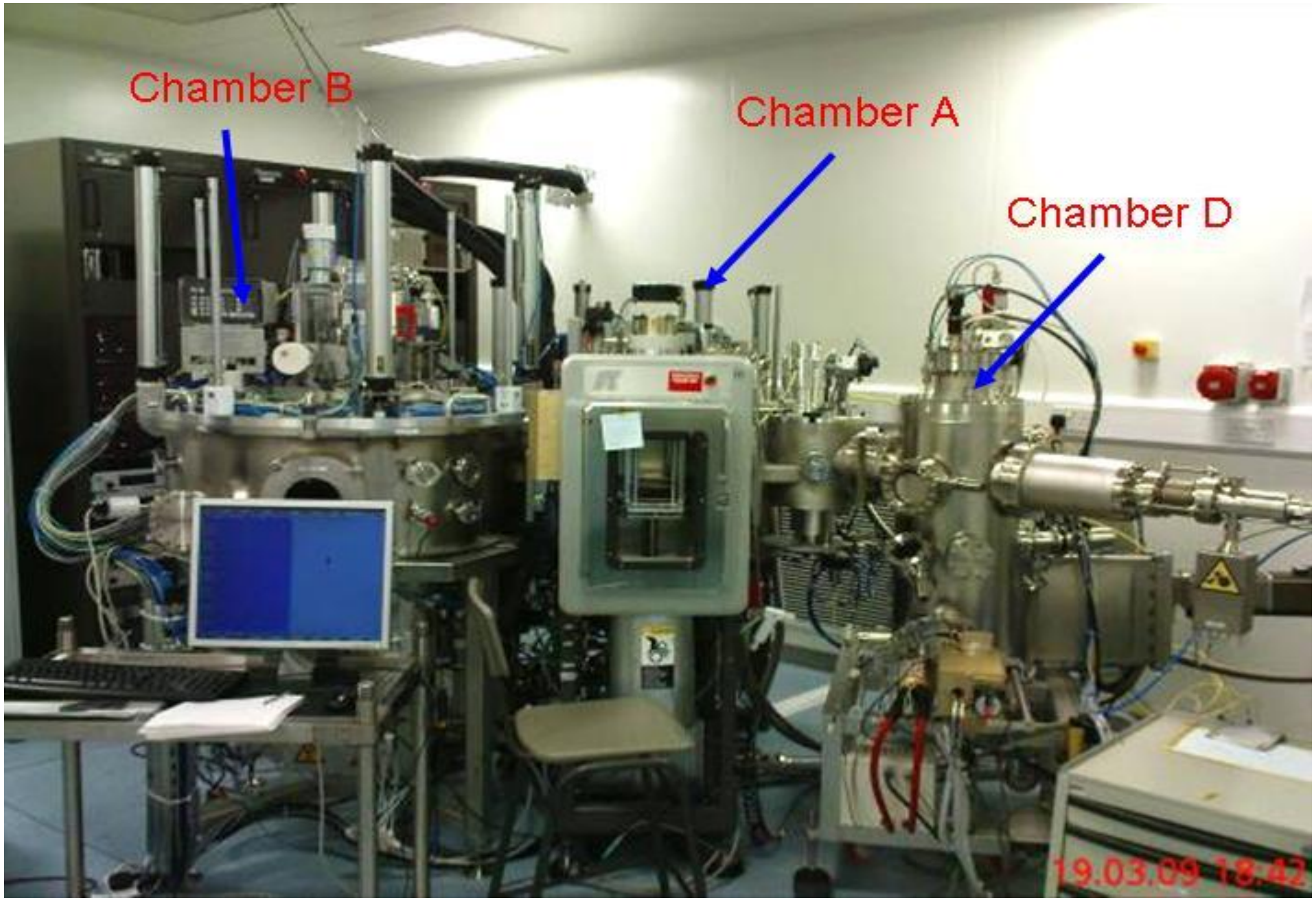
Discovered in 2003
Implemented in 2005





Magnitude of the effect > 200%:

Shamrock sputtering tool; For producing complex thin film (~ nm) stacks. TCD 2002 -2018. Superseded by *Trifolium Dubium* in CRANN in 2019.



Chamber A: Metal Sputtering (6 guns + 1 ion gun)
Chamber B: Oxide Sputtering (8 guns + 1ion gun)
Chamber C: Wafer flip
Chamber D: UHV E-beam (4 pockets) + Sputtering (1 gun)

The End

Magnetite, Fe_3O_4

spinel; $a_0 = 839$ pm

Most common magnetic mineral, source of rock magnetism, main constituent of lodestones..

A ferrimagnet. with Fe^{2+} and Fe^{3+} disordered on B -sites above the Verwey transition at $T_v = 120$ K, ordered below; A-B superexchange is the main magnetic interaction

$$\underset{\downarrow}{[Fe^{3+}]_{tett}}\ \{\underset{\uparrow}{Fe^{2+}}\ \underset{\uparrow}{Fe^{3+}}\}_{oct}\ O_4$$

$$-5\ \mu_B \quad +4\ \mu_B \quad +5\ \mu_B \quad = \quad 4\ \mu_B$$

A half-metal. Fe(B); ↓ electrons hop in a t_{2g} band

Used as toner, and in ferrofluids.

Potential for spin electronics..

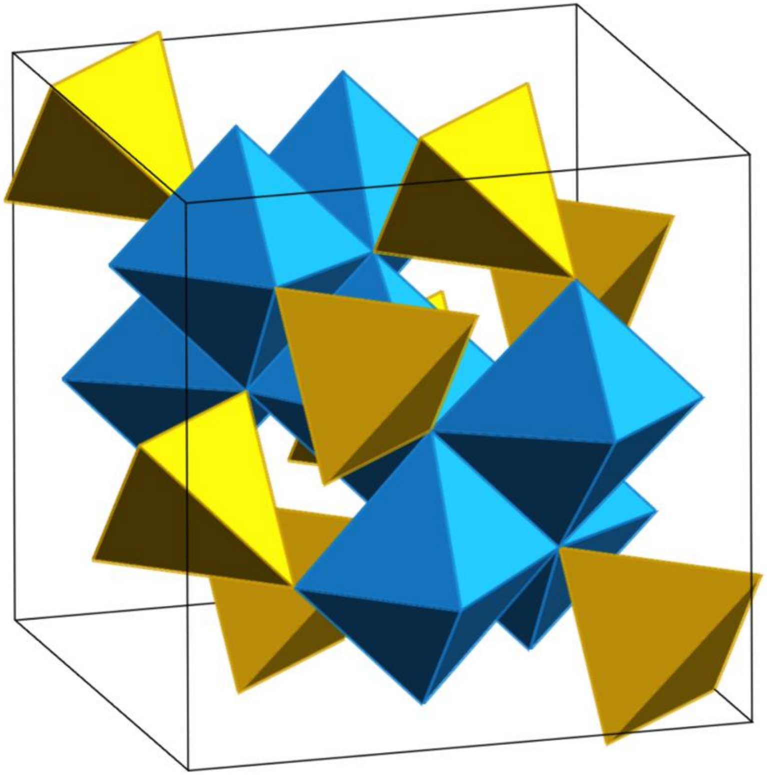
$J_s = 0.60$ T

$K_1 = -13$ kJ m^{-3}

$T_C = 843$ K

$m_0 = 4.0\ \mu_B$ / fu

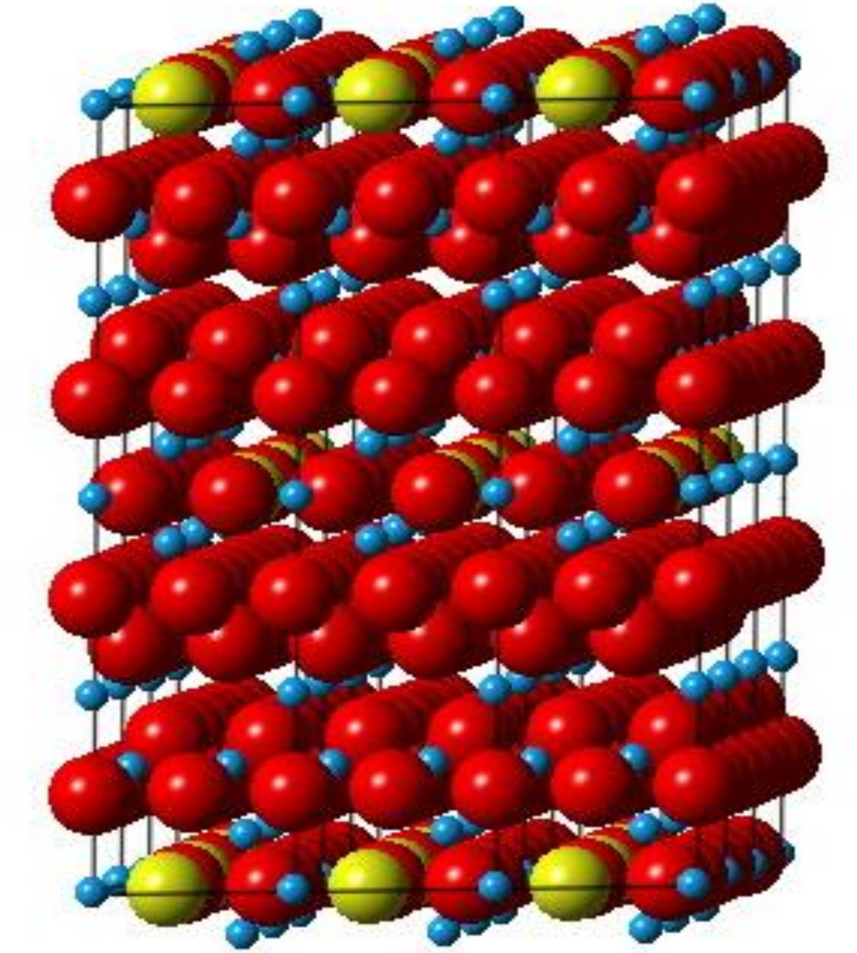
$\lambda_s = 40\ 10^{-6}$



$[A]\{B_2\}O_4$

$SrFe_{12}O_{19}$ - Hexagonal ferrite; also $BaFe_{12}O_{19}$

hexagonal; a = 589 pm, c = 2319 pm



A brown ferrimagnetic oxide, with an hcp lattice composed of oxygen and strontium (or barium), with iron in five different interstital sites, three octahedral 12k,2a,$4f_2$ one tetrahedral $4f_1$ one trigonal 2b. All magnetic ions are Fe^{3+}.

Structure is 12k↑2a↑2b↑$4f_1$↓$4f_2$↓

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 T , M_r = 0.33 MAm^{-1}

K_1 = 330 kJ m^{-3} (hexagonal)

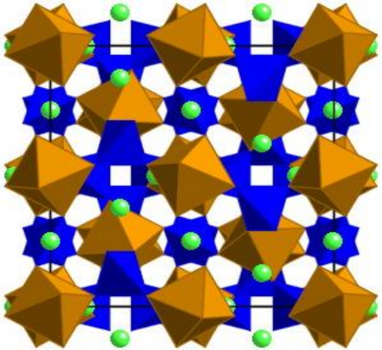
B_a = 1.7 T

T_C = 467 °C.

A ferrimagnet may be regarded as an antiferromagnet with two unequal sublattices.

An example is yttrium-iron garnet (YIG) $Y_3Fe_5O_{12}$. 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

$$\underset{a}{\uparrow\uparrow}\quad\underset{d}{\downarrow\downarrow\downarrow}$$



leading to a moment of 5 μ_B/formula at T= 0, due to a single uncompensated 3 .

Ferrimagnets have two unequal and oppositely-directed magnetic sublattices $M_B|$.

The net magnetization $\boldsymbol{M} = \boldsymbol{M}_A + \boldsymbol{M}_B$ 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

$$\boldsymbol{H}_A^i = n_{AA}\boldsymbol{M}_A + n_{AB}\boldsymbol{M}_B + \boldsymbol{H}$$
$$\boldsymbol{H}_B^i = n_{AB}\boldsymbol{M}_A + n_{BB}\boldsymbol{M}_B + \boldsymbol{H}$$

when $\boldsymbol{H} = 0$. The magnetization of each sublattice is represented by a Brillouin function, and each falls to zero at a critical temperature, the ferrimagnetic Néel temperatute T_N. The sublattice magnetization $\langle M_\alpha \rangle = M_{\alpha 0}\mathcal{B}_J(x_\alpha)$ where α = A,B and $x_\alpha = \mu_0 m_\alpha H_\alpha^i/k_B T$,

7.4 Spin waves (magnons).

The exchange energy in the ferromagnetic ground state is $-2Z\mathcal{J}S^2$ 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 ↑↑↑↑↓↑↑↑↑ costs $8\mathcal{J}S^2$ ($2\mathcal{J}$ for S = ½), which is greater than k_BT_C for a chain. $T_C = 2Z\mathcal{J}S(S+1)/3$ (for 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.

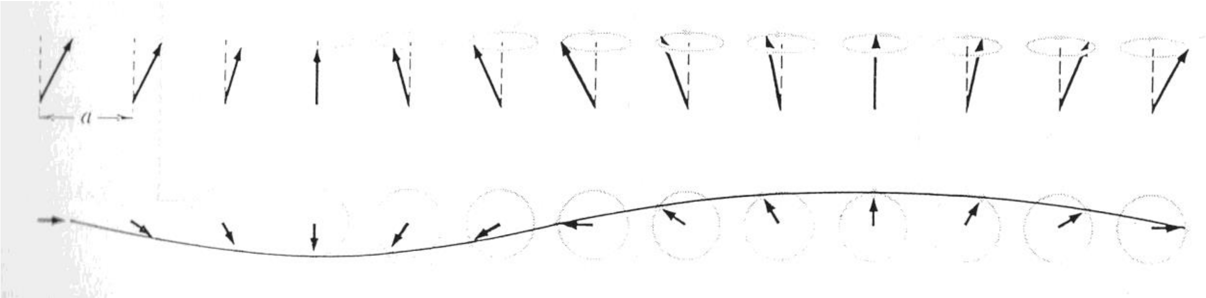


Illustration of a spin wave.

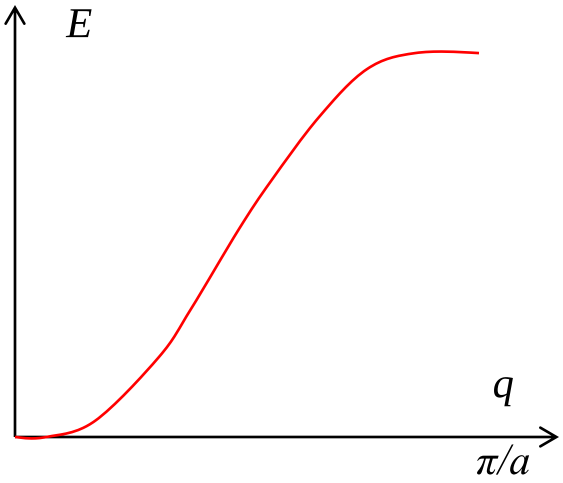
In one dimension, the relation between the frequency and wave-vector of a wave-like excitation of the spin system can be calculated classically

$$\hbar\omega_q = 4\mathcal{J}S(1 - \cos qa)$$

In the limit of small wave vectors, the dispersion relation becomes

$$E_q \approx D_{sw}q^2$$

where $E_q = \hbar\omega_q$, $D_{sw} = 2\mathcal{J}Sa^2$; 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.

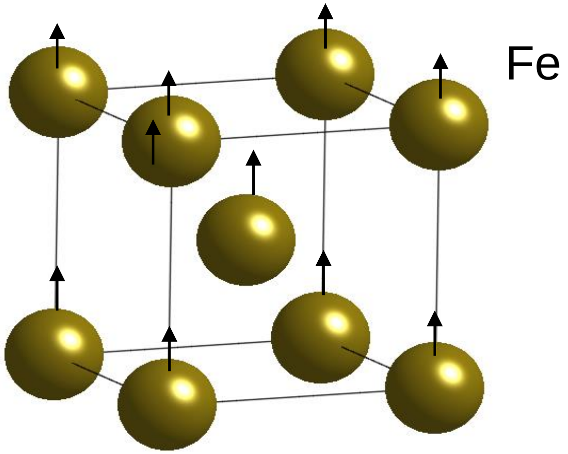
Data on some antiferromagnets and ferrimagnets

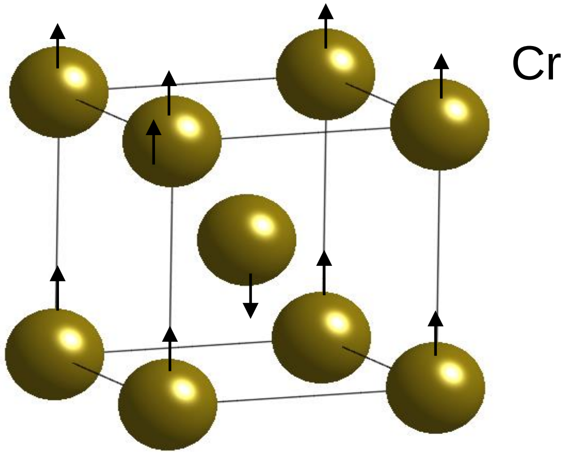
Material	**Density (kg m^{-3})**	**Structure**	**T_N (K)**	**$\mu_0 M$ (T)**	***m* A/B (μ_B/formula)**	**K_1 (kJm^{-3})**
Antiferromagnets						
Cr	7190	cubic	310	–	0.7	
NiO	6793	cubic	525	–	2	
Fe_2O_3	5260	hexagonal	960	0.003	5	9
Ferrimagnets						
Fe_2O_4	5195	cubic	860	0.60	9/5	
$Y_3Fe_5O_{12}$	5166	cubic	560	0.18	15/10	
$BaFe_{12}O_{19}$	5290	hexagonal	740	0.48	40/20	330

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 inetron, with incident wavevctor $\boldsymbol{K}$ is scattered into a state $\boldsymbol{K}'$, the Bragg condition is that the scattering vector $\boldsymbol{\kappa} = \boldsymbol{K} - \boldsymbol{K}'$ should be a reciprocal lattice vector $\boldsymbol{G}_{hkl.}$

For example, magnetic Bragg scattering can be used to detect antiferromagnetic order



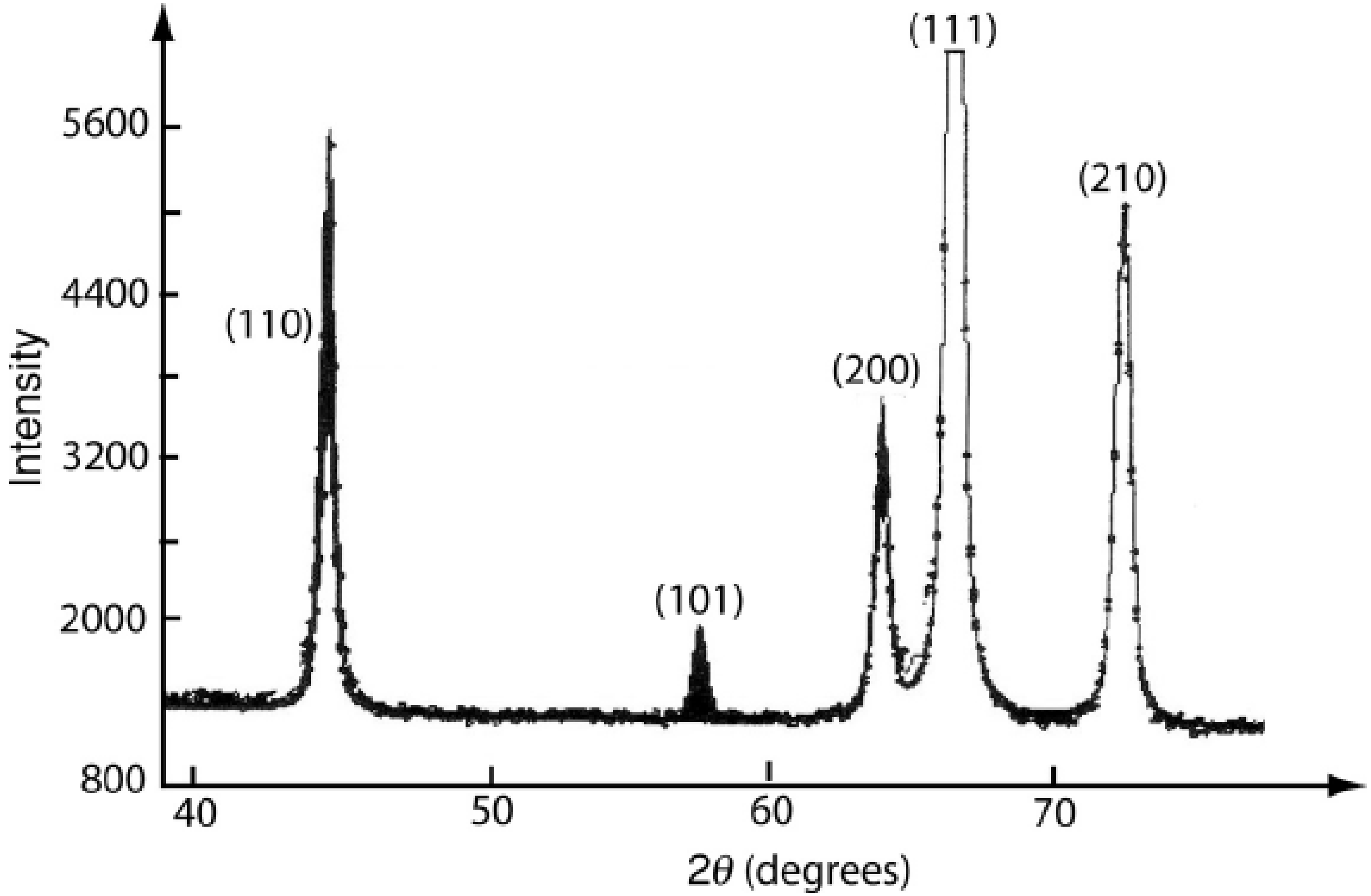


For iron, the magnetic Bragg reflections coincide with the nuclear reflection. The unit cell is body-centred, so there are no extra peak. The structure factor is zero when h + k + l is odd.

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 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 ***q***, can be used to map spin wave dispersion relations.

For Fe, $E = D_{sw}q^2$, where $D_{sw} = 8\ \mathrm{Jm}^{-2}$.

The energy in a mode of frequency ω_q containing n_q magnons is $(n_q + 1/2)\hbar\omega_q$

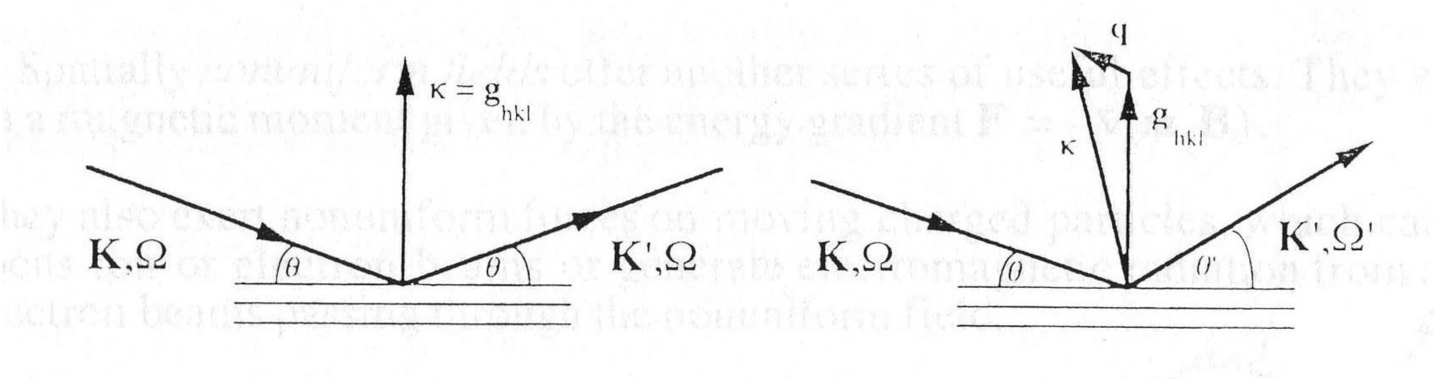


Illustration of elastic| scattering, |**K**| = |**K**‘| (left) and inelastic scattering. **K** = **K**’ + **q** + $\mathbf{g}_{hkl}$. (right)

Data on some antiferromagnets.

Material	T_N(K)	θ(K)
Mn	96	-200
CoO	291	-330
NiO	525	-1300
MnF_2	85	-113
αFe_2O_3	950	-2000

Data on some ferrimagnets.

Material	T_C(K)	m_0 (μ_B/*formula*)	$\mu_0 M$ at 290 K (T)
Fe_3O_4	840	4.0	0.63
γFe_2O_3	1020	3.3	0.54
$Y_3Fe_5O_{12}$	560	5.0	0.18
$BaFe_{12}O_{19}$	742	20.0	0.48

More information on some magnetic materials

Hematite; Fe_2O_3

corundum; a = 504 pm, c = 1375 pm

Most common iron oxide mineral.

hcp oxygen array with 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 K.

J_1 = 6.0 K, J_2 = 1.6K

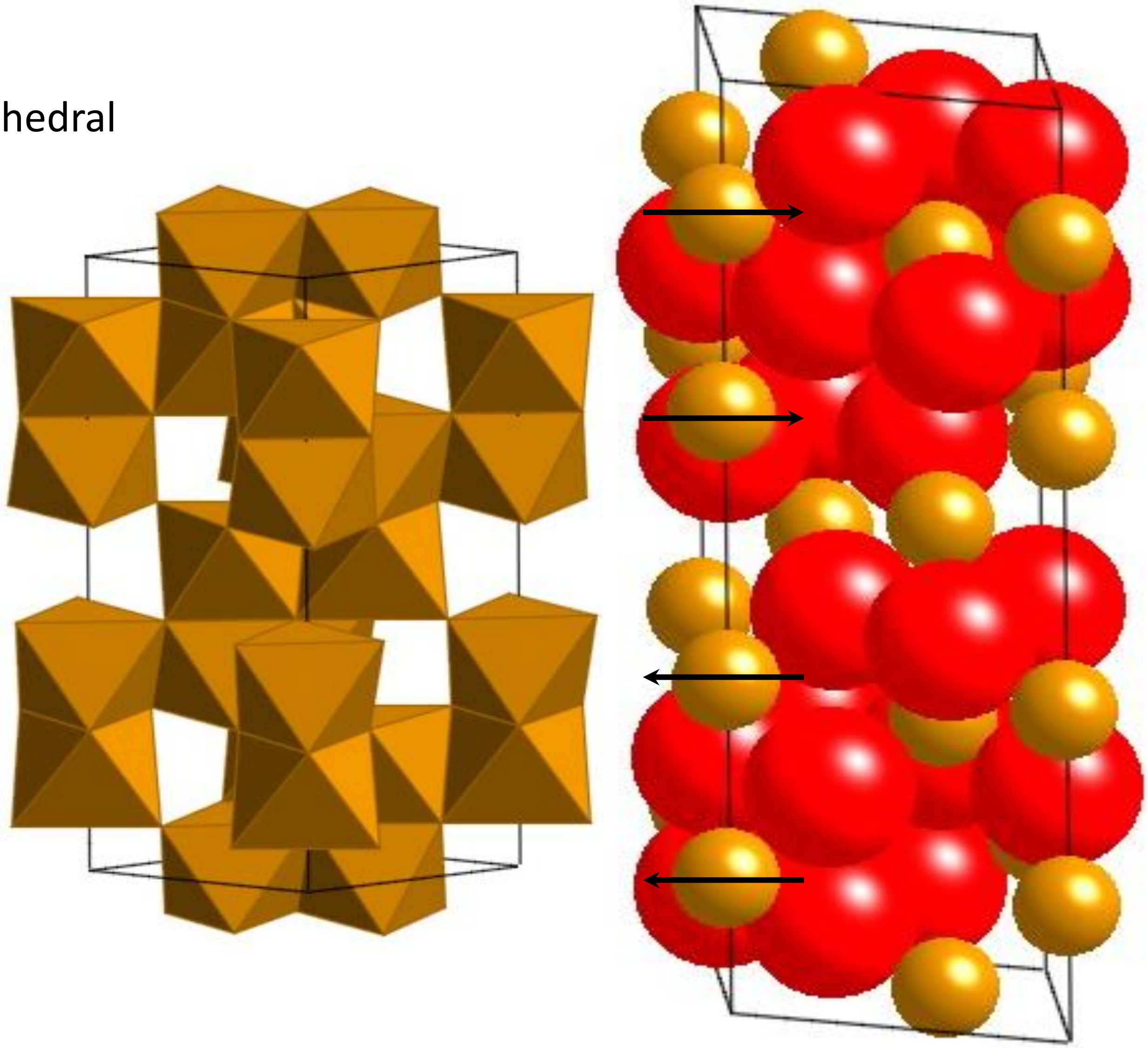
J_3 = -29.7 K, J_4 = -23.2 K.

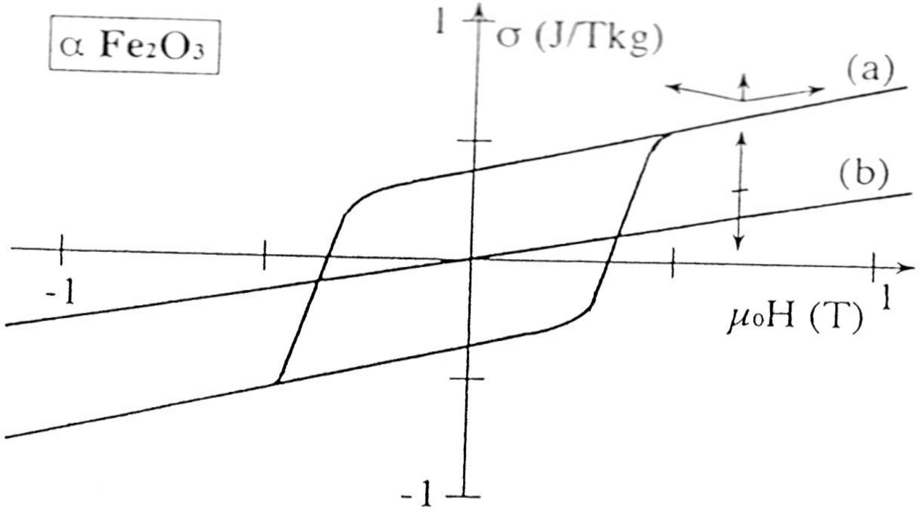
$J_s = 2.8\ 10^{=3}$ T

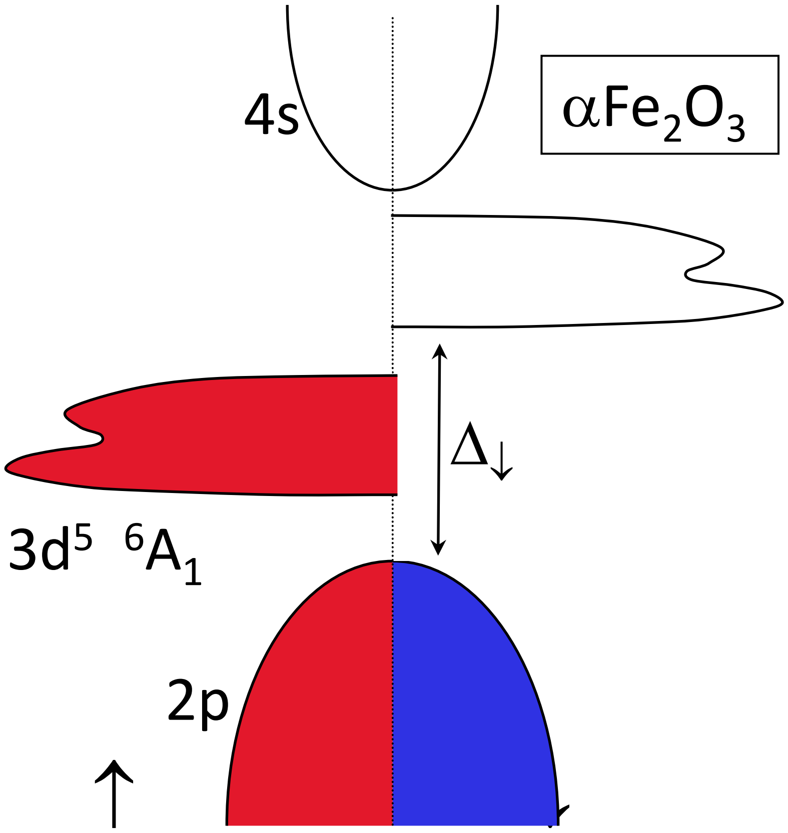
K_1 = 23 kJ m^{-3}

$m_0 = 0.002\ \mu_B$ / fu

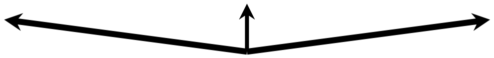
$B_a = 2\mu_0K_1/J_s$ = 20 T







Ar room temperature there is a weak ferromagnetic moment caused by canting of the sublattice magnetizations by the Dzialoshinski- Moria (D-M) interaction $\mathcal{H}_{\mathrm{DM}} = \boldsymbol{\mathcal{D}}\cdot\boldsymbol{S}_i \times \boldsymbol{S}_i$.



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 ?

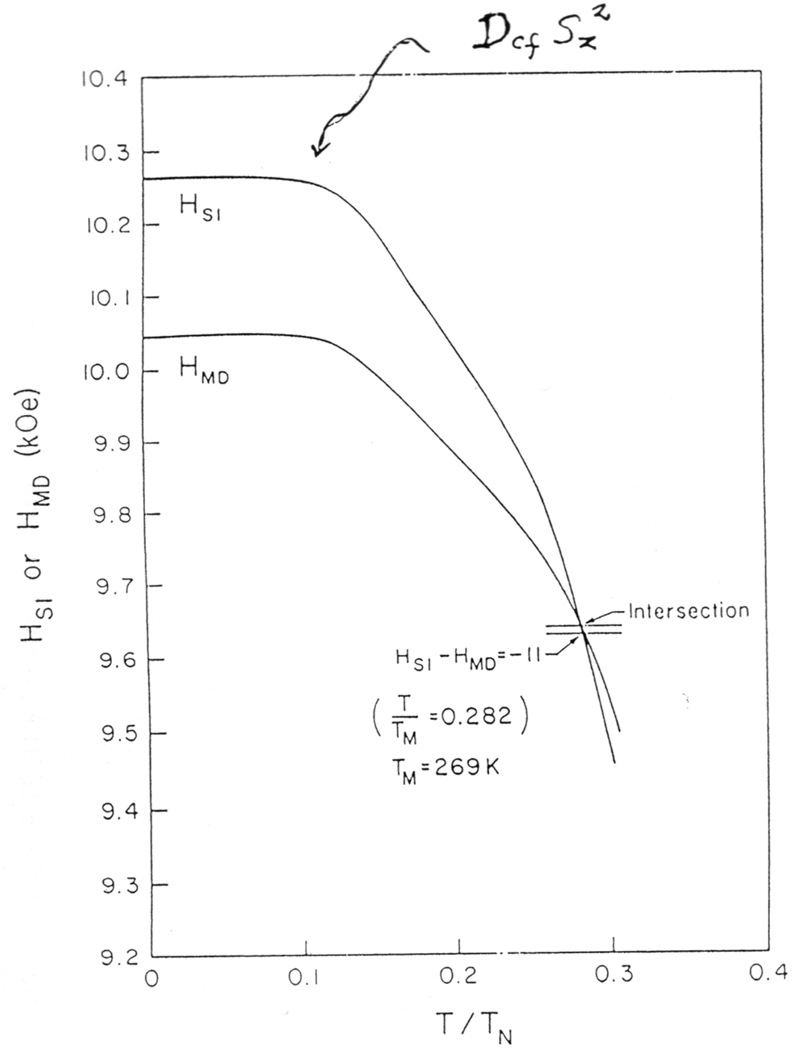


Figure 4.6: The temperature dependence of single-ion and magnetic-dipole fields to illustrate the prediction of the Morin temperature.

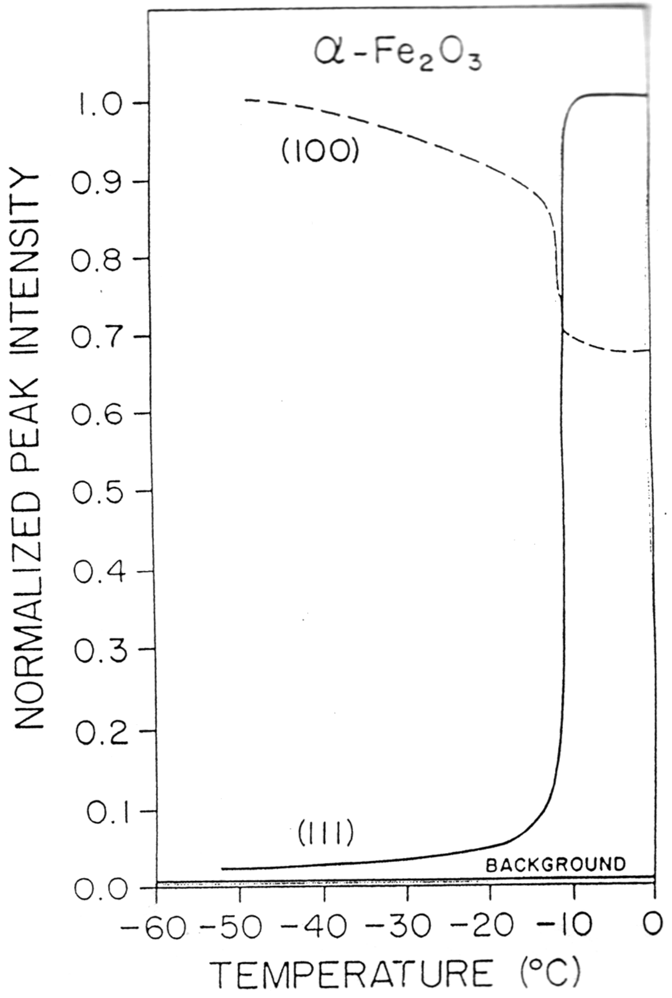


Figure 2.8: Neutron-diffraction intensities of the (111) and (100) lines as a funct of temperature. The background intensity is also shown.

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. $B_{dip} = \mu_0/4\pi[3(\boldsymbol{m}.\mathbf{r})\mathbf{r}/r^5 - \boldsymbol{m}/r^3]$

Magnetite, Fe_3O_4

spinel; a_0 = 839 pm

Most common magnetic mineral, source of rock magnetism, main constituent of lodestones..

A ferrimagnet. with Fe^{2+} and Fe^{3+} disordered on B -sites above the Verwey transition at T_v = 120 K, ordered below; A-B superexchange is the main magnetic interaction

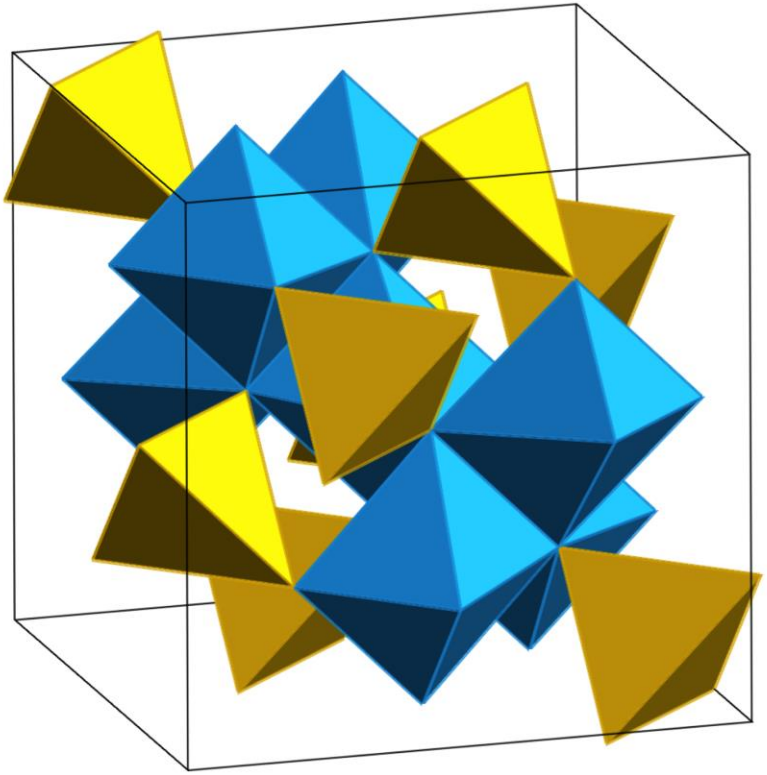
$$\underset{\downarrow}{[Fe^{3+}]}_{tett}\ \{\underset{\uparrow}{Fe^{2+}}\ \underset{\uparrow}{Fe^{3+}}\}_{oct}\ O_4$$

$$-5\ \mu_B\ \ +4\ \mu_B\ \ +5\ \mu_B\ =\ 4\ \mu_B$$

A half-metal. Fe(B); ↓ electrons hop in a t_{2g} band

Used as toner, and in ferrofluids.

Potential for spin electronics..



$[A]\{B_2\}O_4$

J_s = 0.60 T

K_1 = -13 kJ m^{-3}

T_C = 843 K

m_0 = 4.0 μ_B / fu

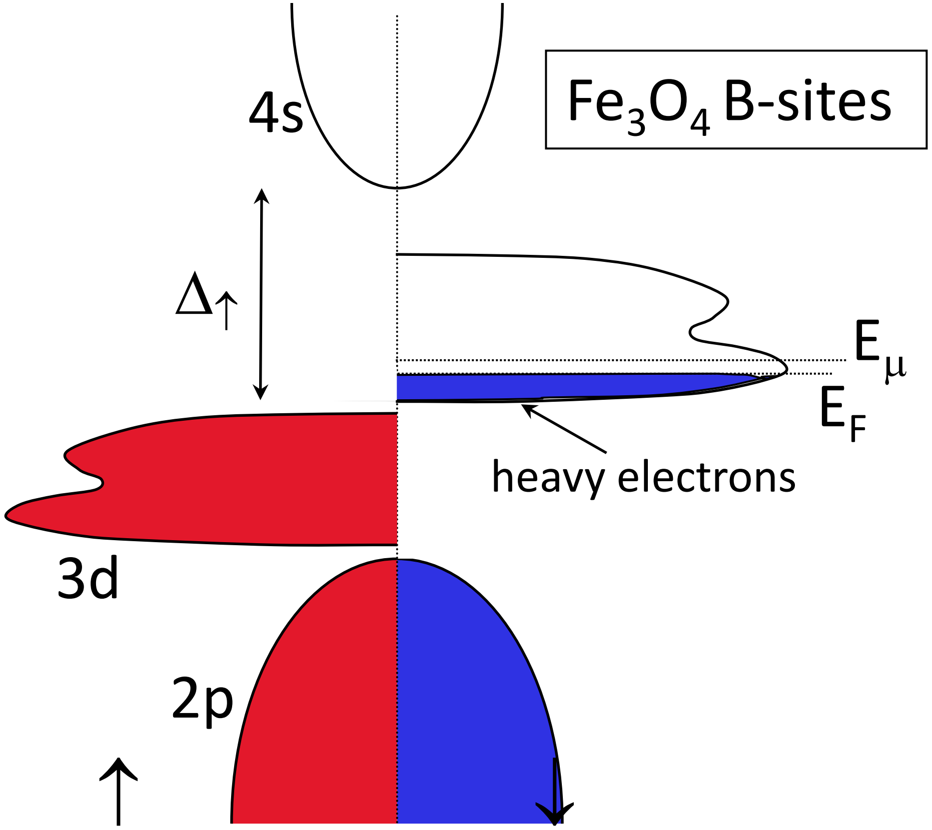
λ_s = 40 10^{-6}

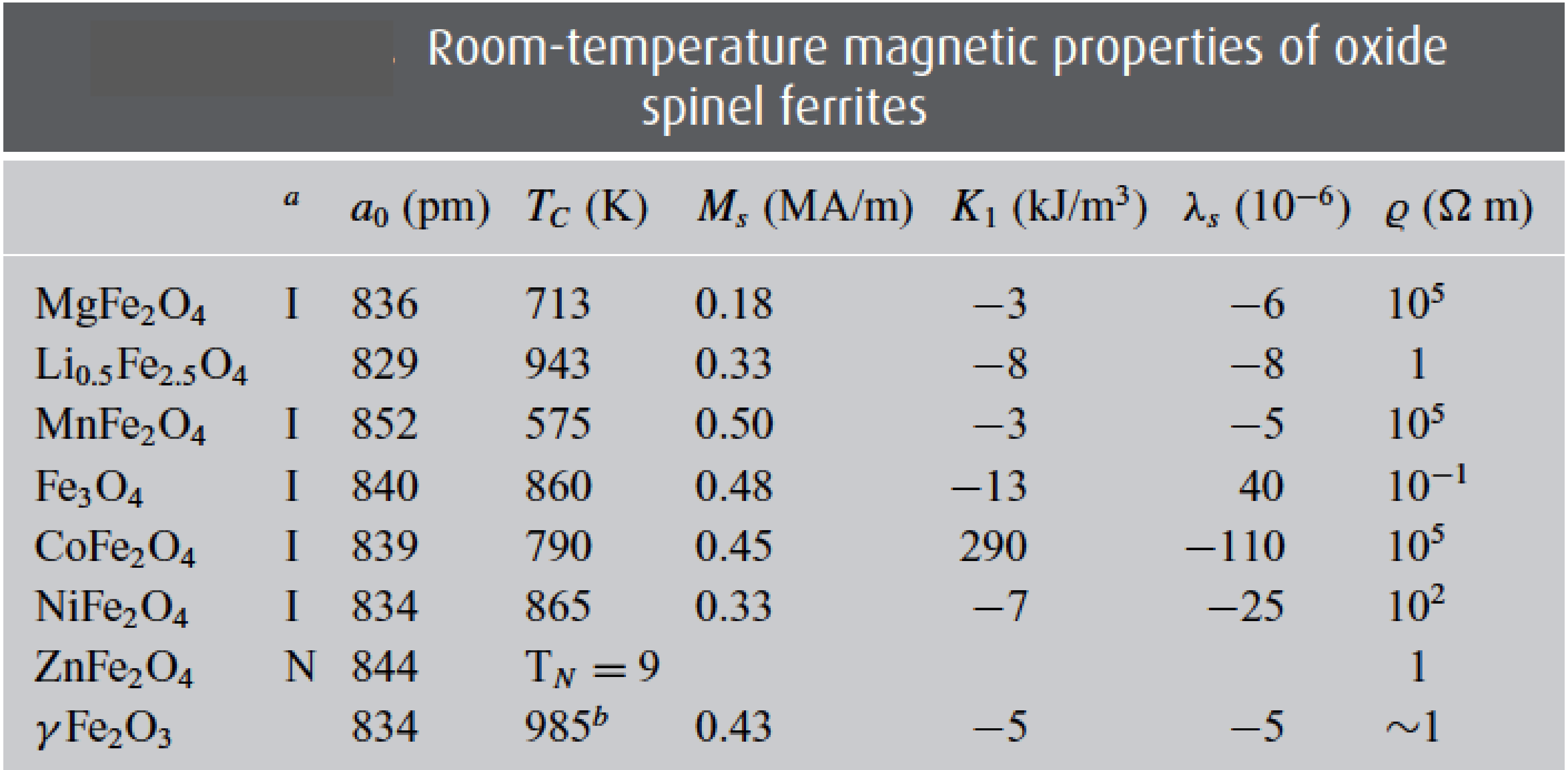
The B sites are populated by a mixture of $Fe^{3+}(3d^5)$ and $Fe^{2+}(3d^6)$ ions. At RT the $t_{2g}\downarrow$ electrons hop in a narrow polaron band. Resistivity is ≈ 50 μΩ m.

At the Verwey transition T_V = 119 K, the interatomic Coulomb interactions lead to charge ordering – 'Wigner crystallization' Resistivity increases by 100 x. Symmetry is reduced to monoclinic; details of charge order are still controversial

J_{AB} = -28 K J_{AA} = -18 K J_{BB} = +3 K

Magnetite is the prototype for a family of spinel ferrites, which includes Ni-Zn ferrite for rf applications and γFe_2O_3 $[Fe]\{Fe_{5/3}v_{1/3}\}O_4$ that was used for particulate magnetic recording.



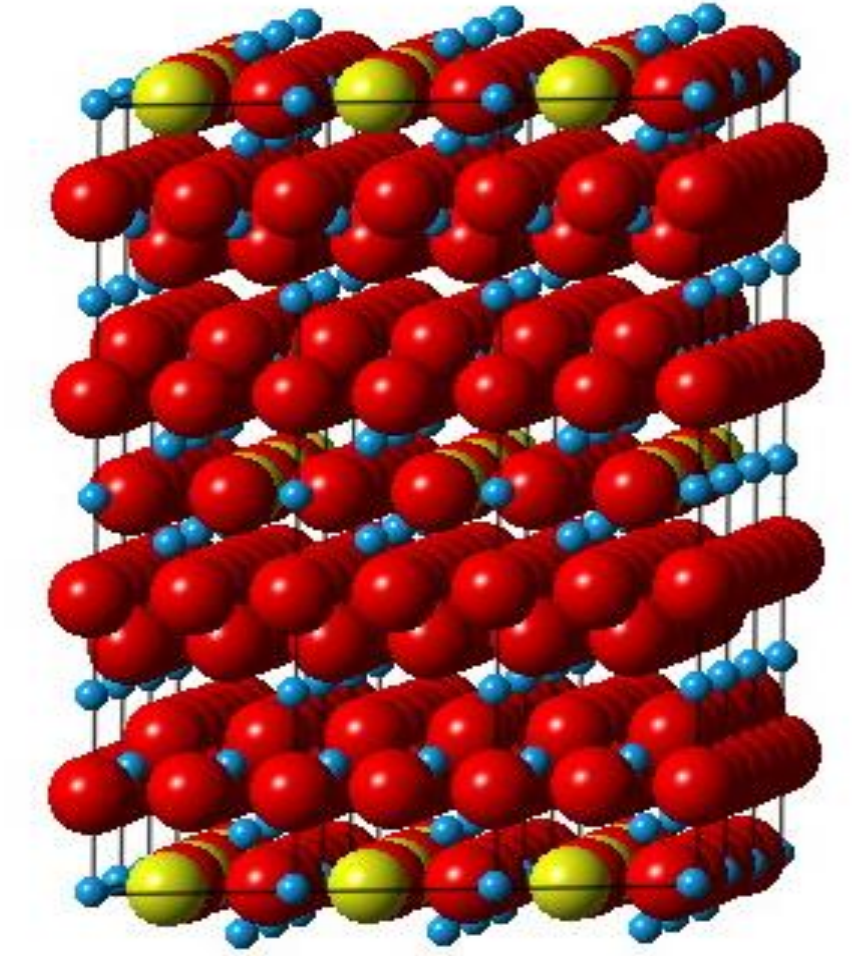


[redacted] Room-temperature magnetic properties of oxide spinel ferrites

	^{a}	a_0 (pm)	T_C (K)	M_s (MA/m)	K_1 (kJ/m^3)	λ_s (10^{-6})	ϱ (Ω m)
$MgFe_2O_4$	I	836	713	0.18	−3	−6	10^5
$Li_{0.5}Fe_{2.5}O_4$		829	943	0.33	−8	−8	1
$MnFe_2O_4$	I	852	575	0.50	−3	−5	10^5
Fe_3O_4	I	840	860	0.48	−13	40	10^{-1}
$CoFe_2O_4$	I	839	790	0.45	290	−110	10^5
$NiFe_2O_4$	I	834	865	0.33	−7	−25	10^2
$ZnFe_2O_4$	N	844	$T_N = 9$				1
γFe_2O_3		834	985^b	0.43	−5	−5	~1

$SrFe_{12}O_{19}$ - Hexagonal ferrite; also $BaFe_{12}O_{19}$

hexagonal; a = 589 pm, c = 2319 pm



A brown ferrimagnetic oxide, with an hcp lattice composed of oxygen and strontium (or barium), with iron in five different interstital sites, three octahedral 12k,2a,$4f_2$ one tetrahedral $4f_1$ one trigonal 2b. All magnetic ions are 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 T , M_r = 0.33 $\mathrm{MAm^{-1}}$

K_1 = 330 kJ $\mathrm{m^{-3}}$ (hexagonal)

B_a = 1.7 T

T_C = 467 °C.

Ferrite magnets

	J_r (T)	$(BH)_{max}$ (kJ/m^3)
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

Ferrite magnets are made from powder platelets, with a particle size of about 2 μm.

The powder may be sintered or bonded in plastic or rubber, with or without prior orientation of the hexagonal crystallites.

Sintered magnets

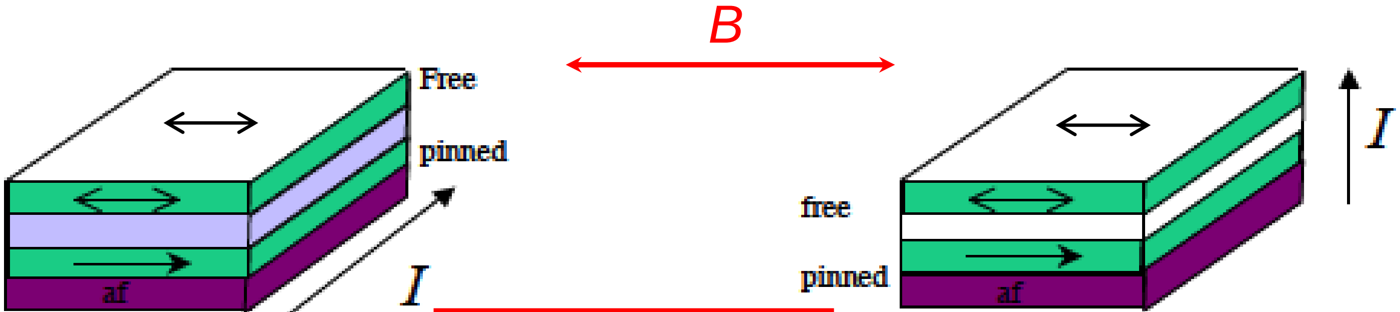
Bonded magnets

7.4 Spin Electronics

Look at MOOC 2.2

First-generation spin electronics has been built on *spin-valves* – sandwich structures using GMR or TMR with a pinned layer and a free layer.

They can serve as bistable memory elements:



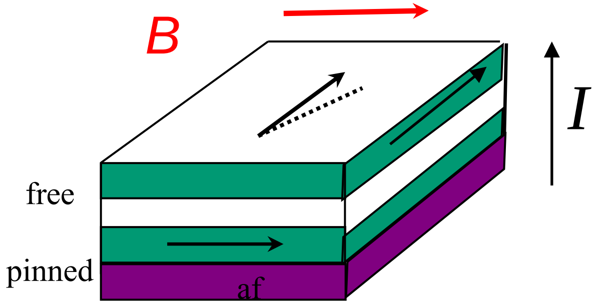
GMR spin valve

$MR = (R_{\uparrow\downarrow}-R_{\uparrow\uparrow})/R_{\uparrow\uparrow}$

planar magnetic tunnel junction

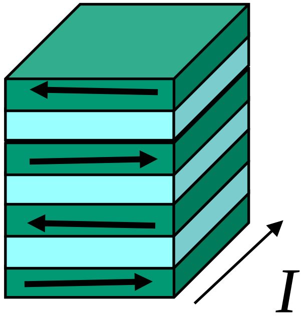
One layer in the sandwich has its magnetization direction pinned by exchange coupling with an antiferromagnet – *exchange bias*.

They can also serve as sensitive magnetic field sensors:



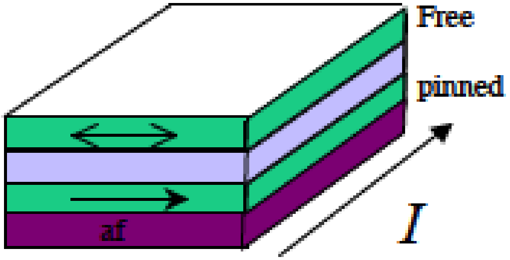
planar magnetic tunnel junction

Giant magnetorsistance spin valve

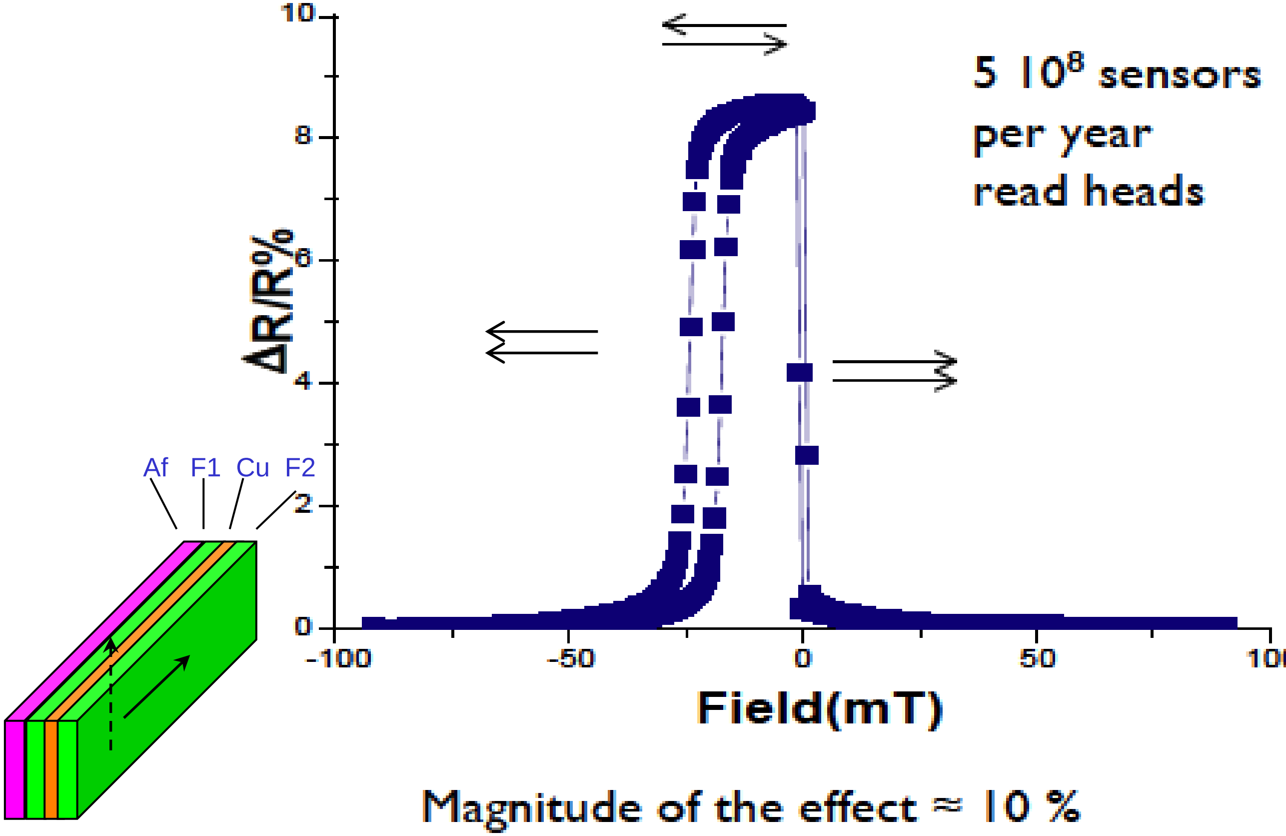


Fe/Cr multilayer stack

Peter Grunberg, Albert Fert;



spin valve



5 10^8 sensors

per year

read heads

Magnitude of the effect ≈ 10 %

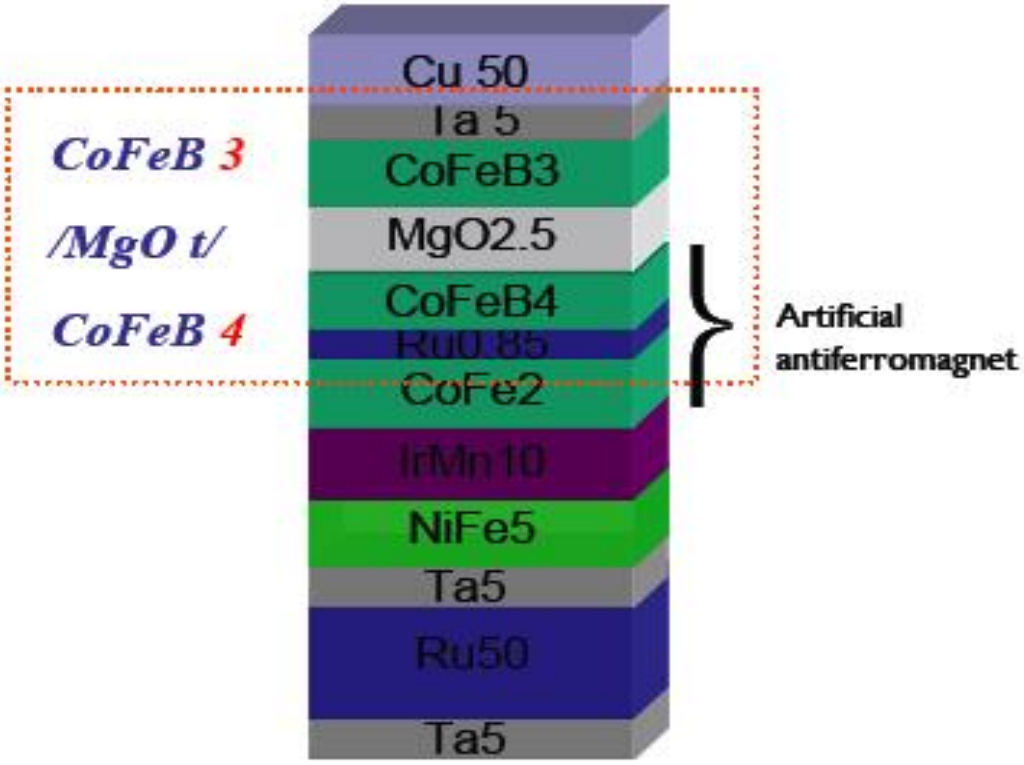
Discovery of GMR 1988

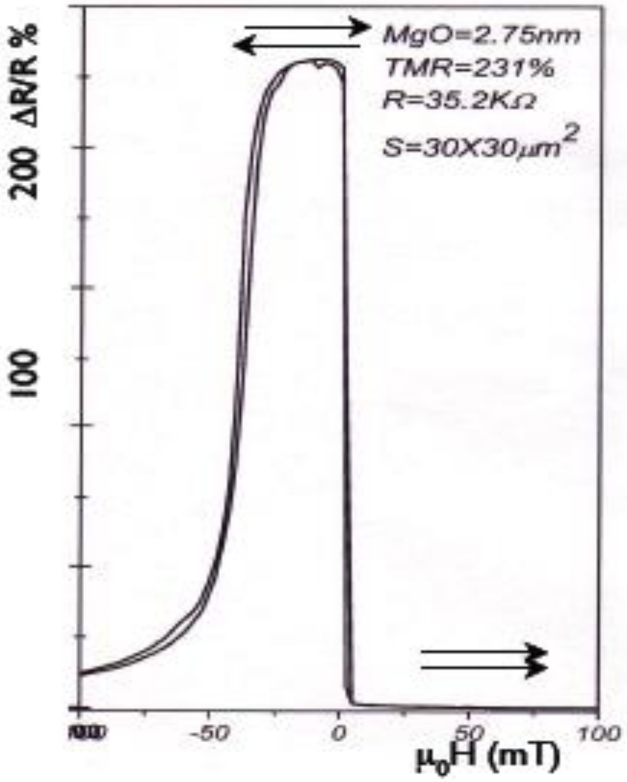
Implementation in hard disk drive 1998

Nobel Prize 2007

MgO-barrier magnetic tunnel junctions

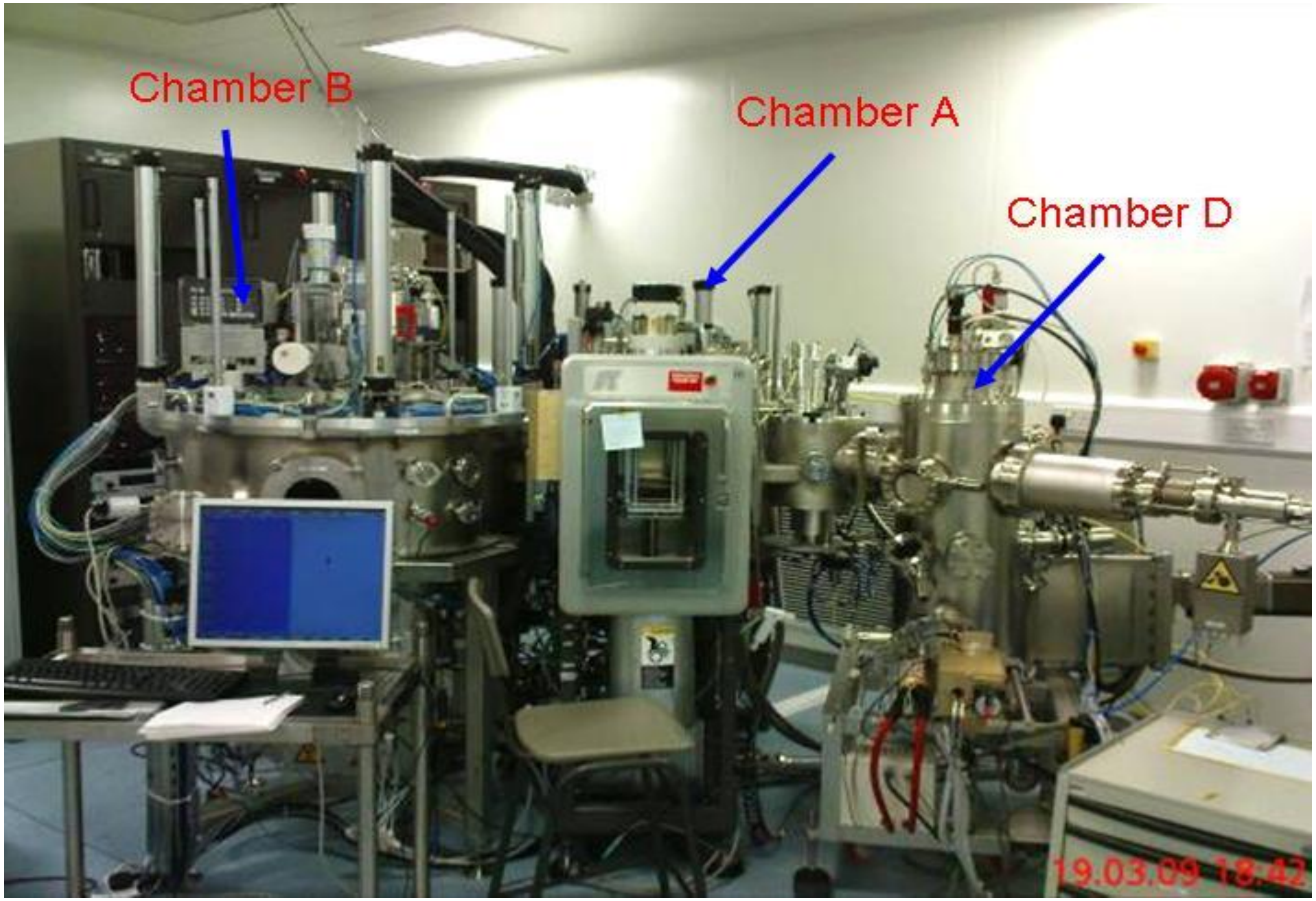
Discovered in 2003
Implemented in 2005





Magnitude of the effect > 200%:

Shamrock sputtering tool; For producing complex thin film (~ nm) stacks. TCD 2002 -2018. Superseded by *Trifolium Dubium* in CRANN in 2019.

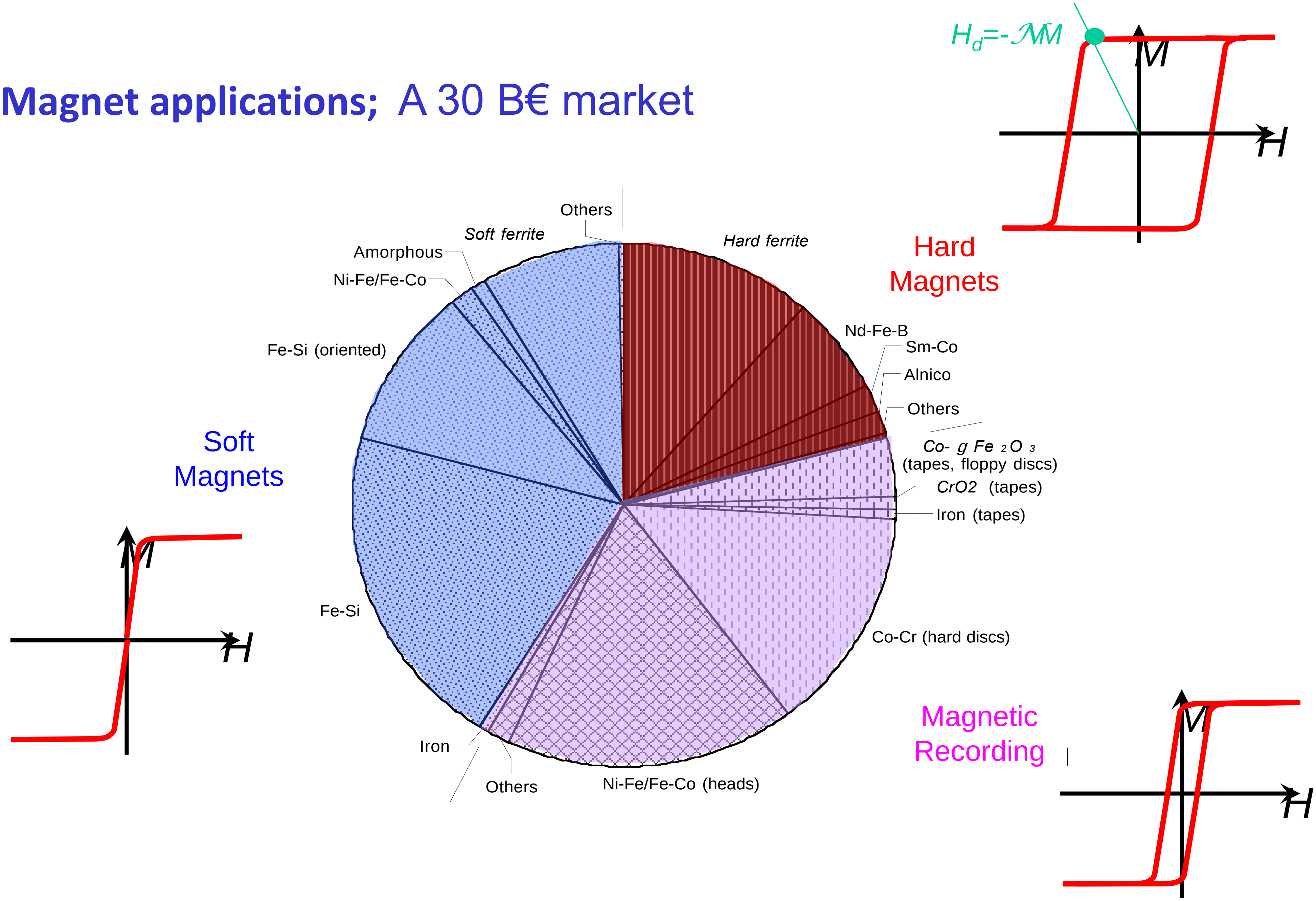


Chamber A: Metal Sputtering (6 guns + 1 ion gun)
Chamber B: Oxide Sputtering (8 guns + 1ion gun)
Chamber C: Wafer flip
Chamber D: UHV E-beam (4 pockets) + Sputtering (1 gun)

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. The new field of spin electronics has underpinned magnetic recording and data storage, which have been the key to the information revolution and the advent of big data.

Magnet applications; A 30 B€ market

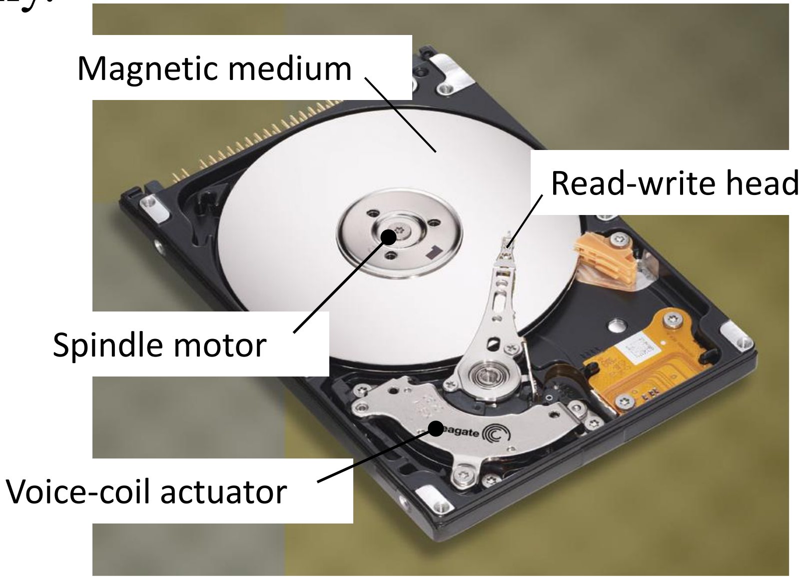


8.1 Magnetic recording; Driving the technology

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

A

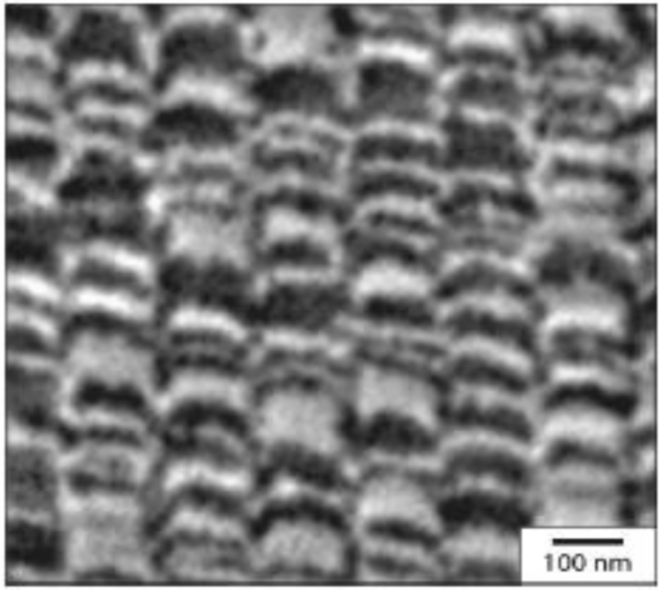


160 Gbit 2.5” perpendicular drive for laptops

8.1 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.

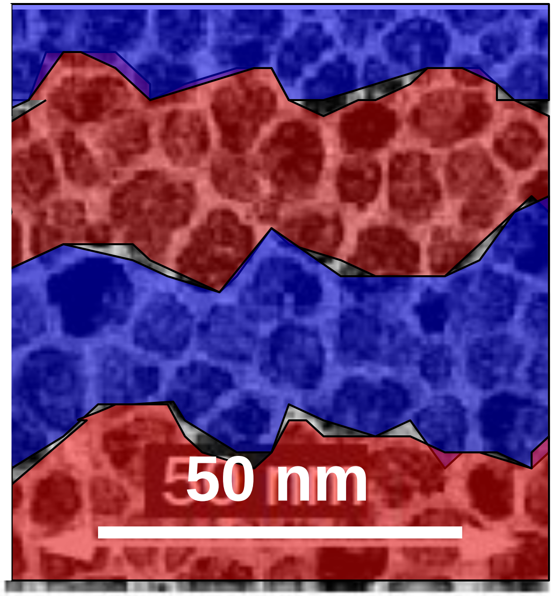


Perpendicular tracks on a hard-disc imaged by high-resolution magnetic force microscopy. The width of the tracks is determined by the width of the write head. The density is 1200 bits/μm or 1 Tbit/square inch.

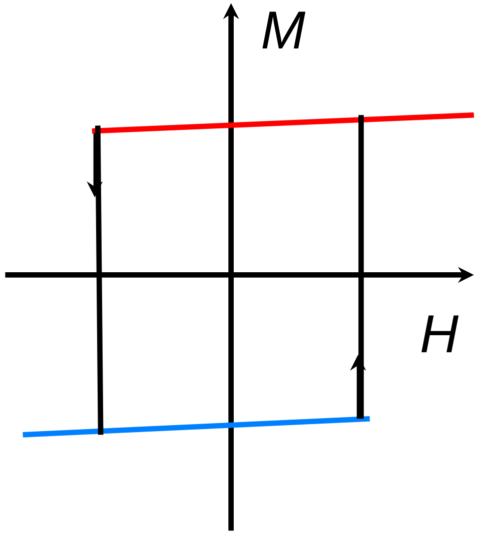
Miniaturization ←

A personal stereo, ca 1935. (Courtesy Orphée Cugat.)

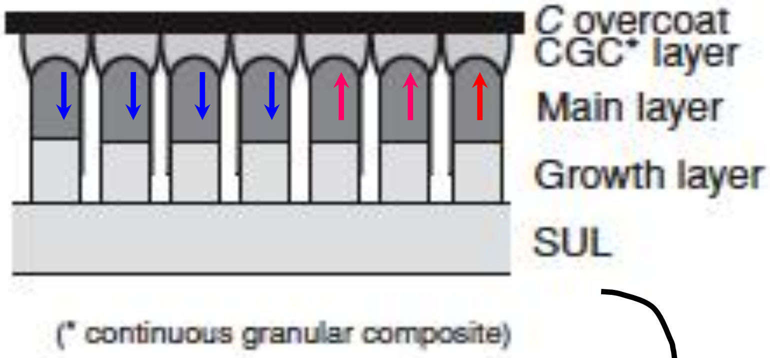
Magnetic media



CoPtCr alloy

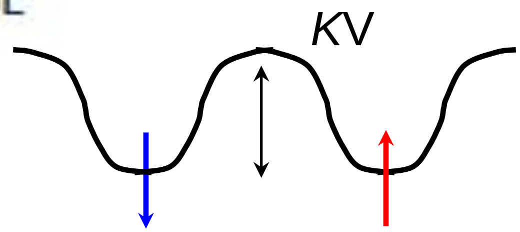


Magnetic recording medium consisting of sub-10-nm metallic grains with oxide-rich grain boundaries. The bit is recorded on a patch of grains along the track. The cross section shows the layer structure of the recording layer.



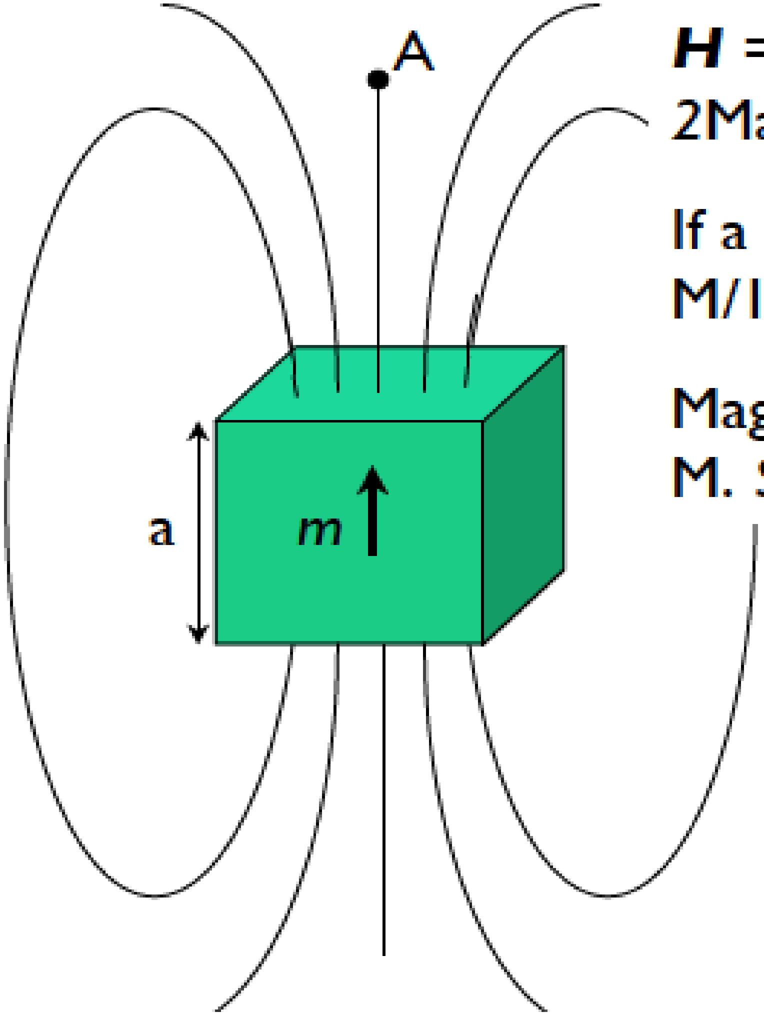
$\boxed{KV/kT > 50}$

Stability condition



Scaling

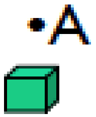
Why does magnetism lend itself to miniaturization ?



$\boldsymbol{H} = (m/4\pi r^3)[2\cos\theta\,\mathbf{e}_r + \sin\theta\,\mathbf{e}_\theta]$ $H_A = 2Ma^3/4\pi r^3$;

If a = 0.1m, r = 2a, M = 1 MAm^{-1} $H_A = M/16\pi =$ 20 kAm^{-1} (~25 mT)

Magnet-generated fields are limited by M. *Scale-independent*

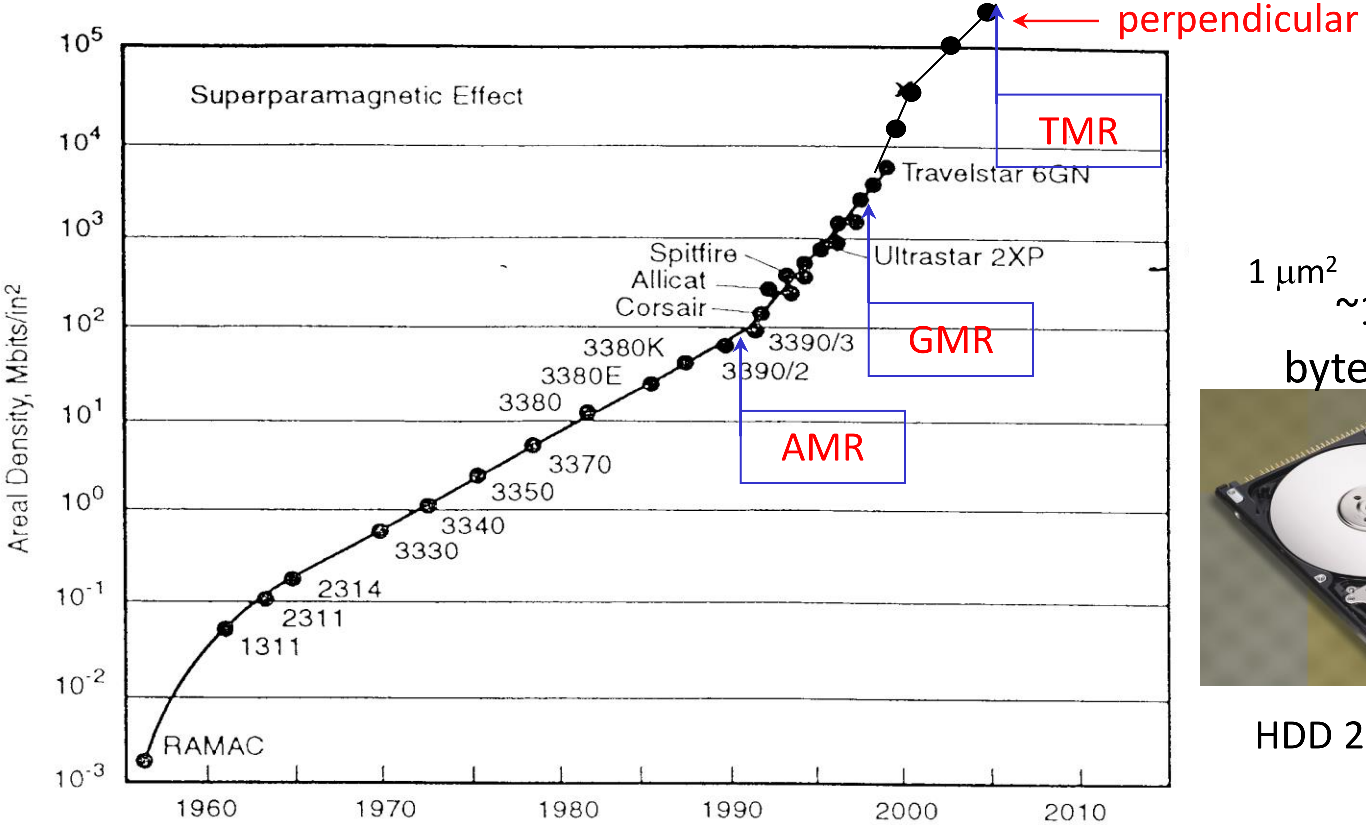


$H = I/2\pi r = 8jr$ $\quad H \sim r$

Current-generated fields are limited by j. Scaling is *poor*

~10^{10} bytes/year

RAMAC 1955 40 Mb

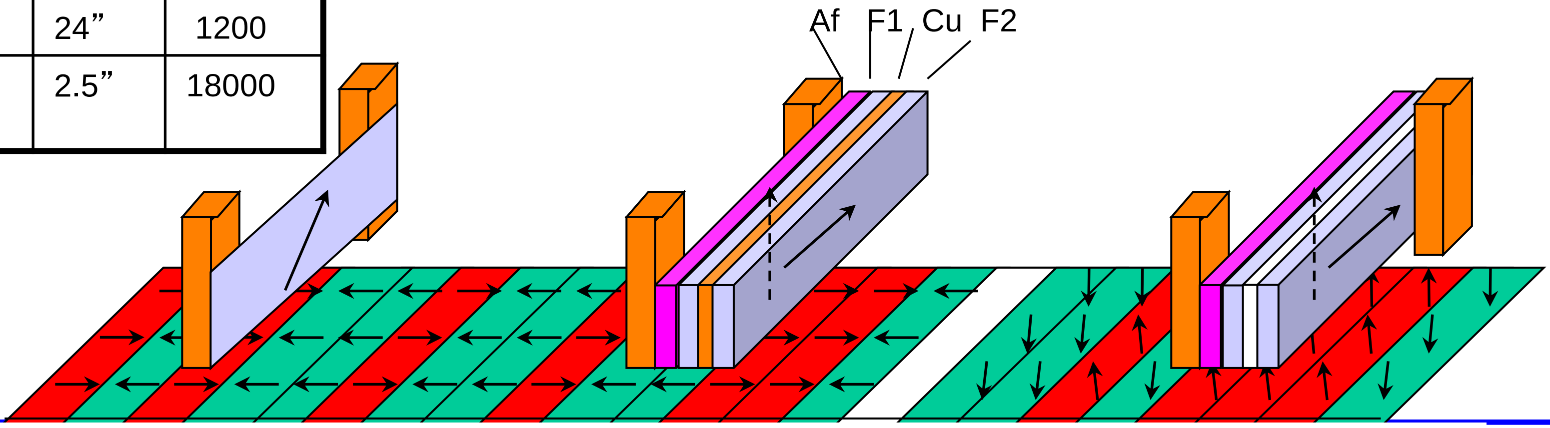


1 μm^2

~10^{21} bytes/year

HDD 2005 160 Gb

year	caapcity	platters	size	rpm
1955	40 Mb	50x2	24”	1200
2005	160 Gb	1	2.5”	18000



read head

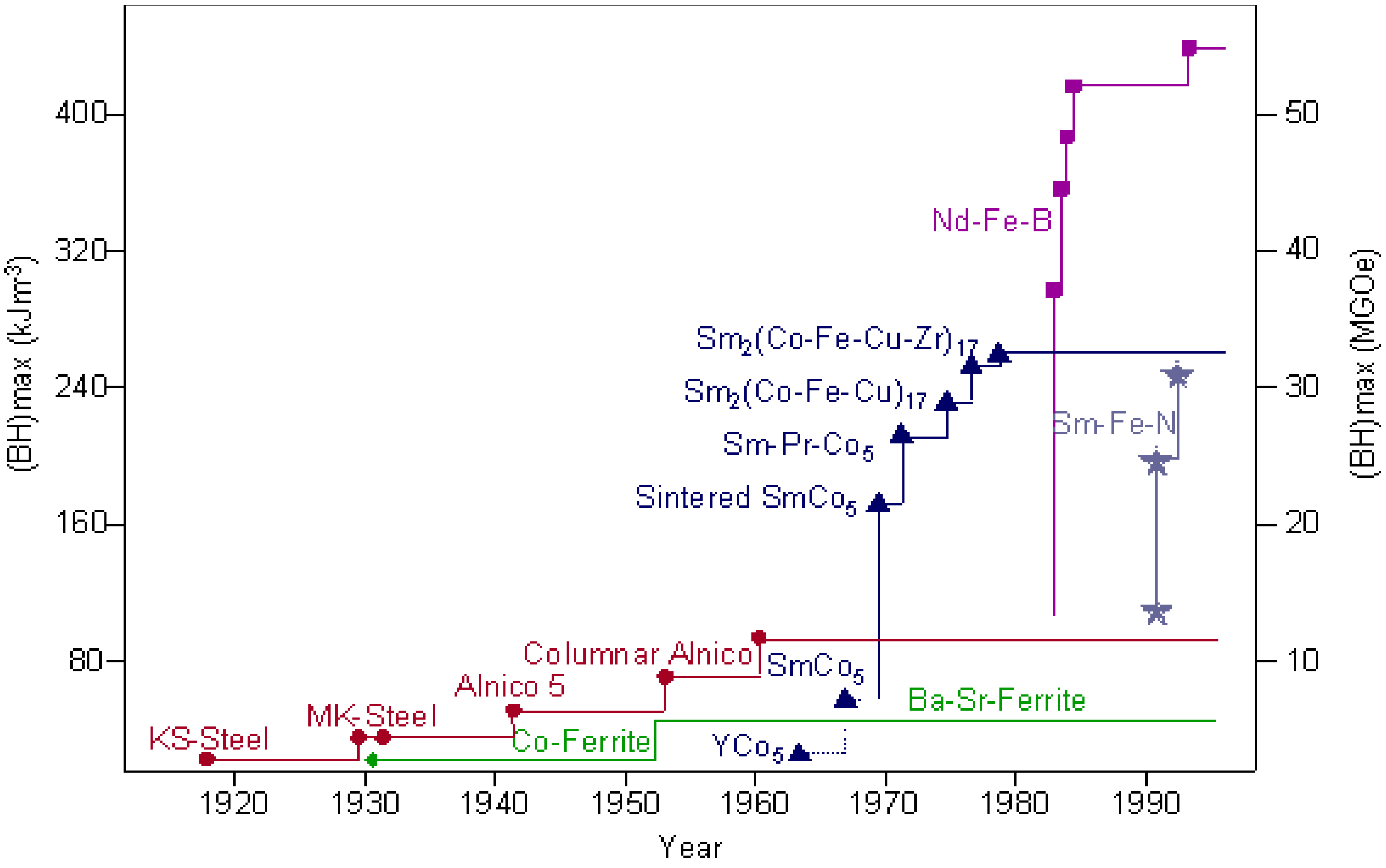
Anisotropic MR

Giant MR

Tunnel MR

8.2 Hard magnets

All three store
0.4 J of energy



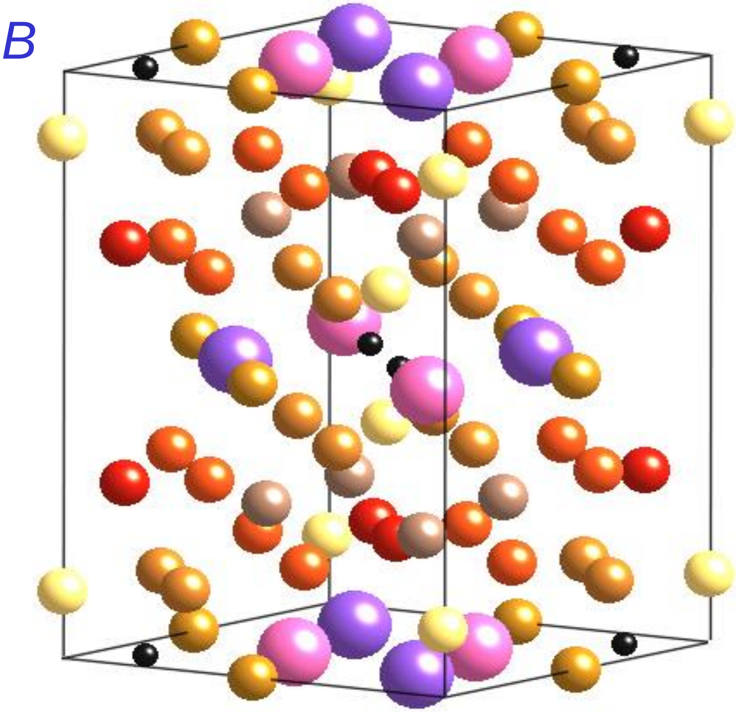
Energy product increased exponentially during the 20th century but it has now almost reached the physical limit $(BH)_{max} < \frac{1}{4}\mu_0 M_s^2$ for a perfect square hysteresis loop.

Hard ferromagnets have broad square loops with $H_c > \frac{1}{2}M_s$. They always have a uniaxial crystal structure (hexagonal, tetragonal ...) with one *easy axis* of magnetization.

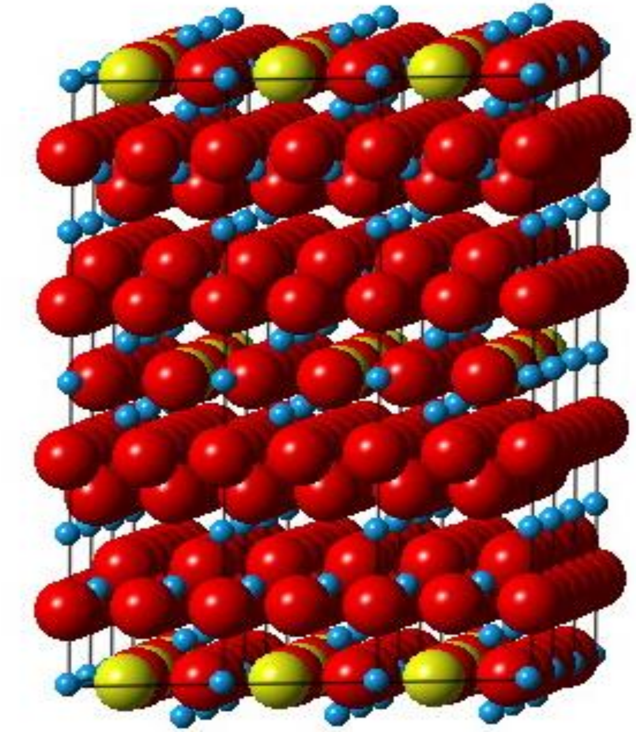
Once magnetized they remain in their metastable, fully magnetized state creating a stray field around them with no expenditure of energy.

Main examples are $Nd_2Fe_{14}B$ and $SrFe_{12}O_{19}$

$Nd_2Fe_{14}B$



$SrFe_{12}O_{19}$



J_r = 1.6 T; M_s = 1.3 MA m^{-1} Ferromagnetic

K_1 = 4.9 MJ m^{-3} (tetragonal)

T_C = 588 K

$(BH)_{max} \approx 400$ kJ/m^3

15 g per year for everyone on Earth

J_r = 0.41 T , M_r = 0.33 MAm^{-1} Ferrimagnetic

K_1 = 330 kJ m^{-3} (hexagonal)

T_C = 740 K.

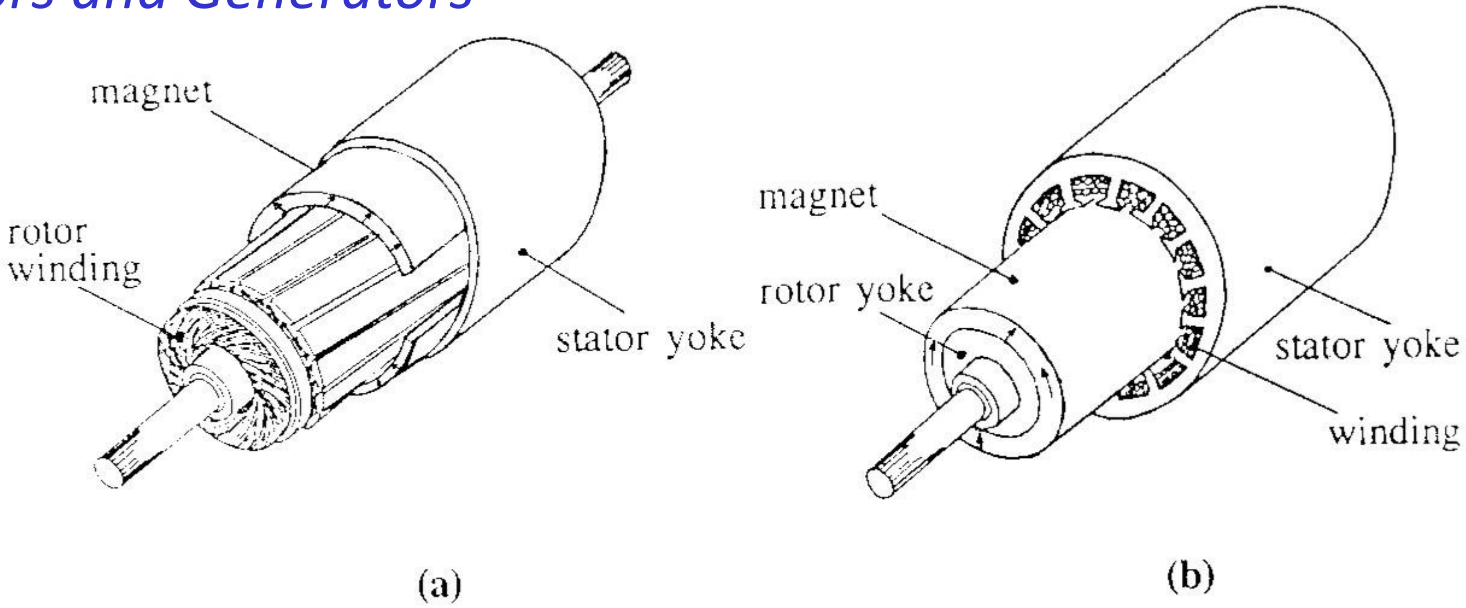
$(BH)_{max} < 40$ kJ/m^3

150 g per year for everyone on Earth

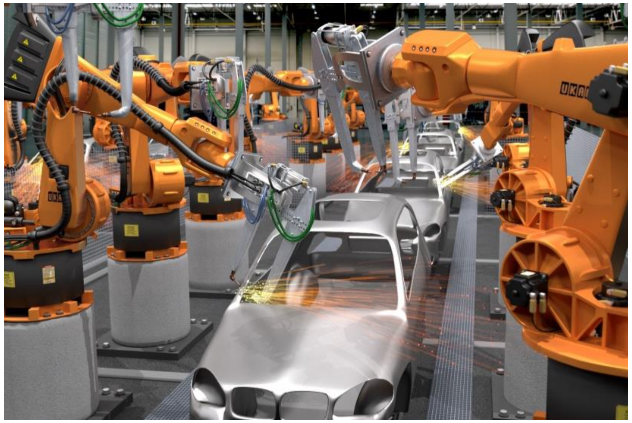
Examples of permanent magnet applications.

Field	Magnetic effect	Application
Uniform	Zeeman splitting	magnetic resonance imaging
	Torque	magnetic powder alignment
	Hall effect, Magnetoresistance	sensors
	Force on conductor	motors, actuators, loudspeakers
	Induced emf	generators, microphones
Nonuniform	Forces on charged particles	beam control, radiation sources (microwave, uv, X-ray)
	Force on paramagnet	mineral separation
	Force on iron	holding magnets
	Force on magnet	bearings, couplings, maglev
Time-varying	Variable field	magnetometery
	Force on iron	switchable clamps
	Eddy currents	brakes, metal separation

Motors and Generators



DC motor designs: (a) brush motor with magnets on the stator and (b) brushless motor with magnets on the rotor.



Electric vehicles

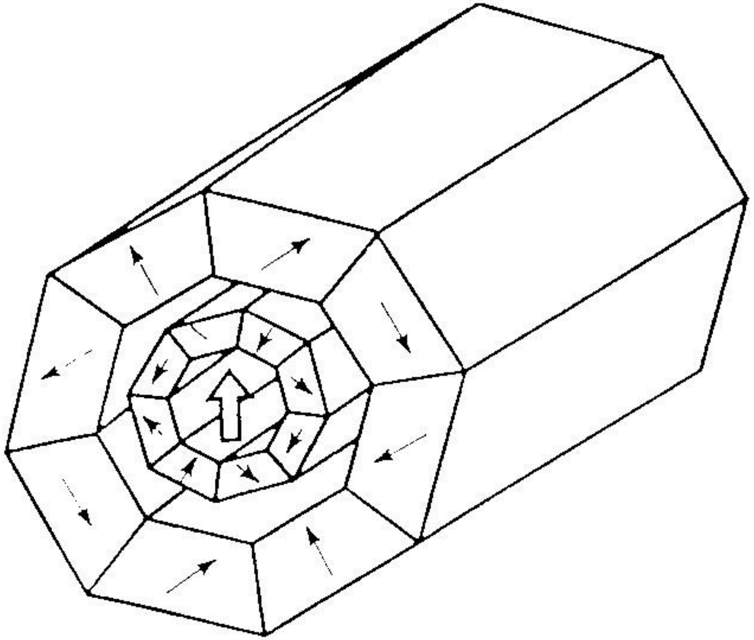
Robots

Direct drive wind turbines

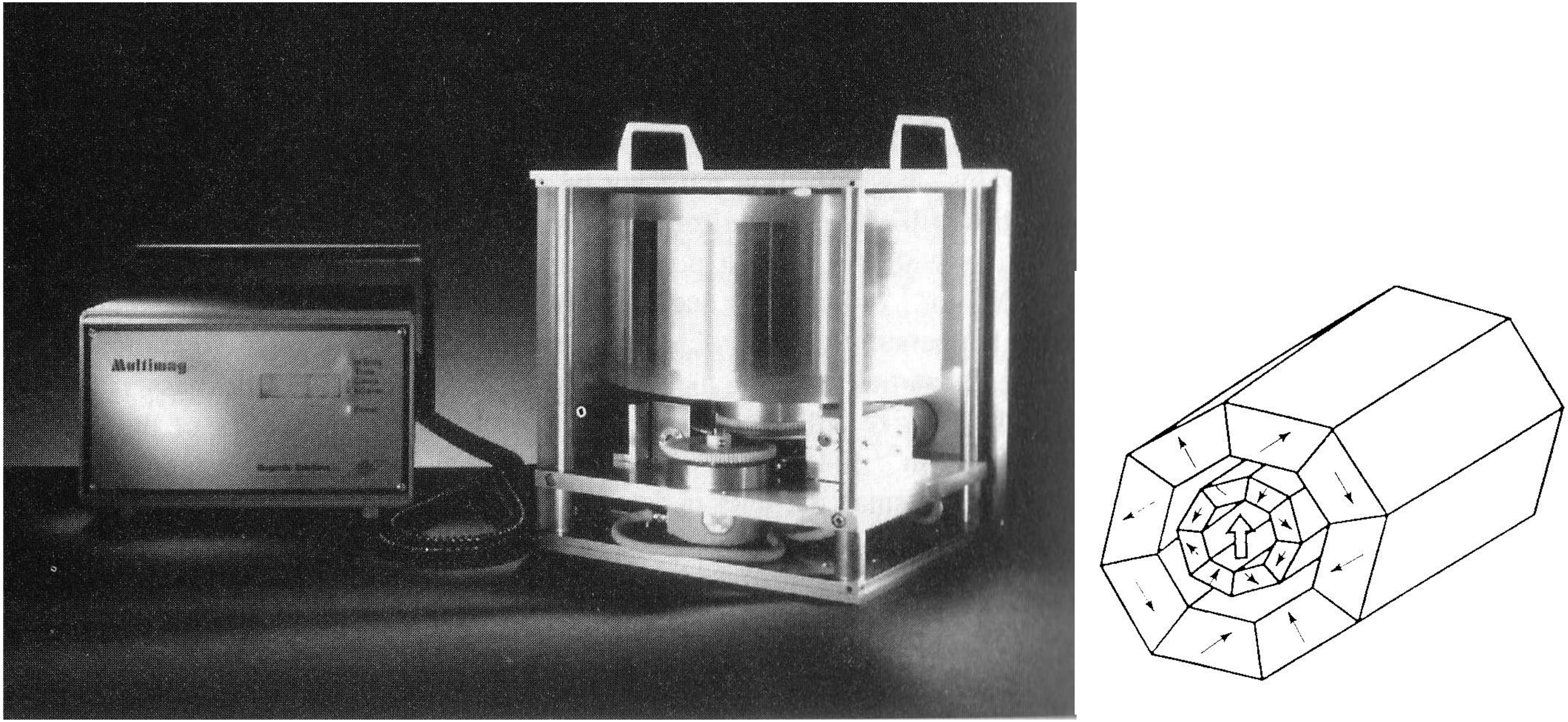
There is no limit in principle to the magnitude of the field that can be produced in a Halbach cylinder, but in practice the coercivity and anisotropy field of the magnets limit the ultimate performance. Because of the logarithmic dependence in (8.5) and the high cost of rare earth magnets, it becomes 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 ± α 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 ± 1.8 T in a 25 mm bore. These devices are ideal for compact instrumentation such as benchtop vibrating-sample magnetometer or a magnetoresistance measurment. 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 abut their common axis.

8.3 Soft magnets

A soft magnetic material should have minimal hysteresis and high permeability. In some range of field, the $B(H')$ characteristic is linear

$$\boldsymbol{B} = \mu \boldsymbol{H}' \quad \text{or} \quad \boldsymbol{B} = \mu_0 \mu_r \boldsymbol{H}'$$

where the relative permeability μ_r is a pure number. The value depends on sample shape, due to the demagnetizing field.
Values of μ_{max} can exceed 10^6 in toroids og 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 $\boldsymbol{B} = \mu_0(\boldsymbol{H}' + \boldsymbol{M})$; dividing by $\boldsymbol{H}'$, 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.

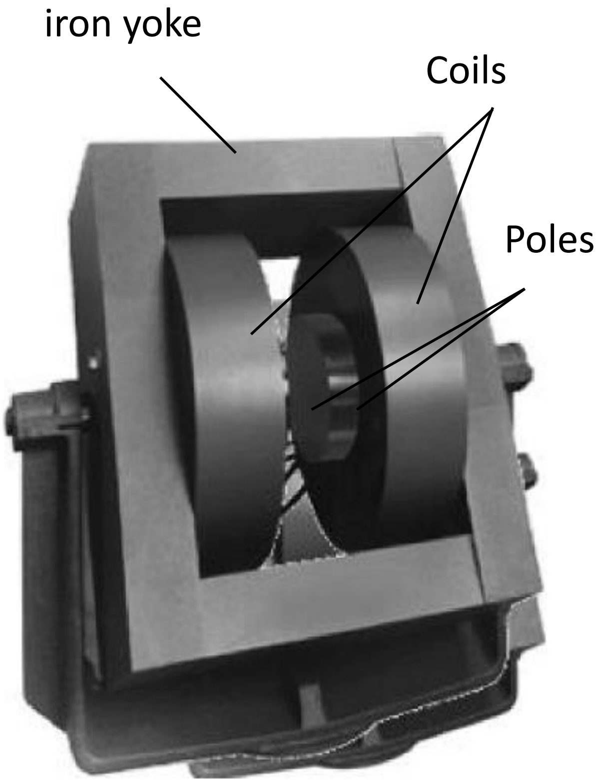
Major ac applications include cores for transformers and inductors.

8.2.1 *Magnetic circuits*

Transformers, motors and *generators* include soft iron cores to generate and guide flux. Eddy-current loses 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 $Fe_{65}Co_{35}$ is used. For best results, tapered pole pieces with an angle of 55° are used.



An electromagnet

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 $B_g^2/2\mu_0$

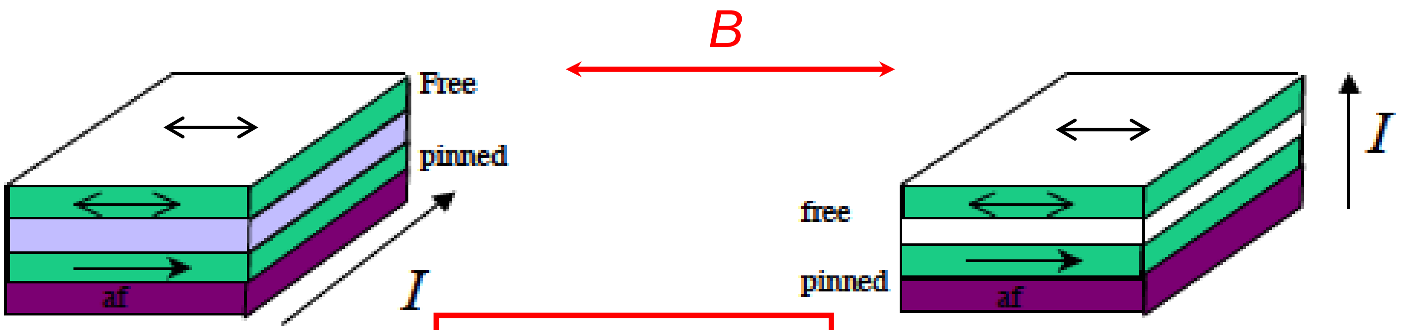
Magnetic shielding uses soft magnetic material to divert the flux.

8.4 Spin Electronics

Look at MOOC 2.2

First-generation spin electronics has been built on *spin-valves* – sandwich structures using GMR or TMR with a pinned layer and a free layer.

They can serve as bistable memory elements:



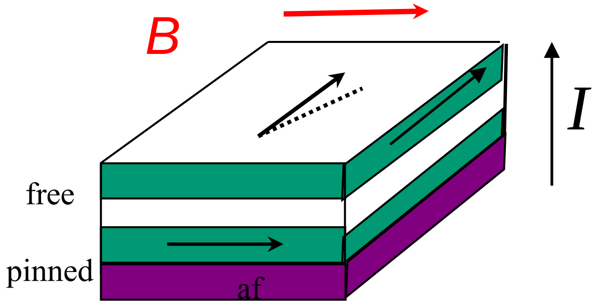
GMR spin valve

$MR = (R_{\uparrow\downarrow}-R_{\uparrow\uparrow})/R_{\uparrow\uparrow}$

planar magnetic tunnel junction

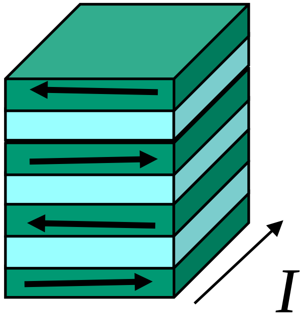
One layer in the sandwich has its magnetization direction pinned by exchange coupling with an antiferromagnet – *exchange bias.*

They can also serve as sensitive magnetic field sensors:



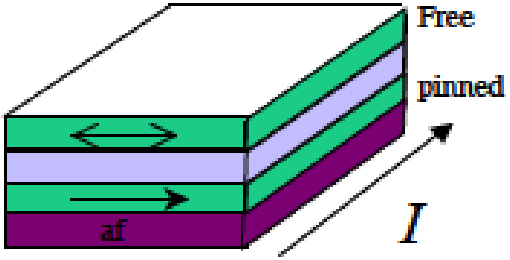
planar magnetic tunnel junction

Giant magnetorsistance spin valve

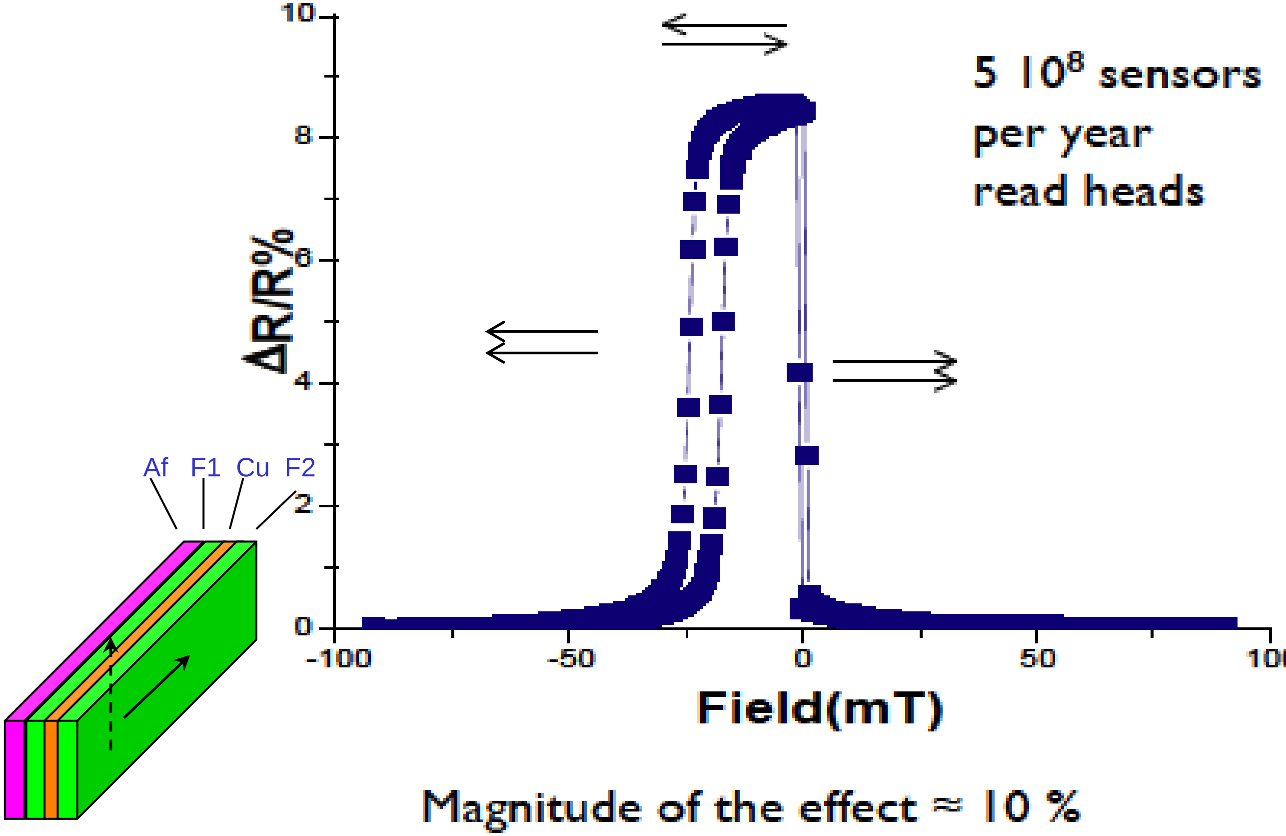


Fe/Cr multilayer stack

Peter Grunberg, Albert Fert;



spin valve



5 10^8 sensors per year read heads

Magnitude of the effect ≈ 10 %

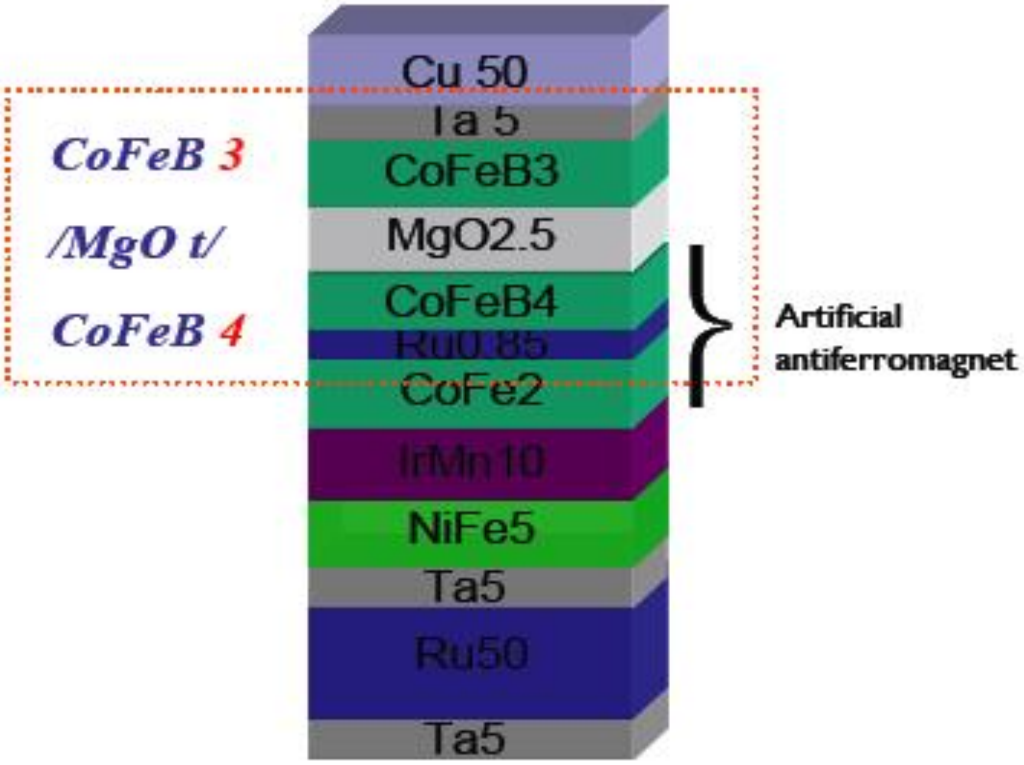
Discovery of GMR 1988

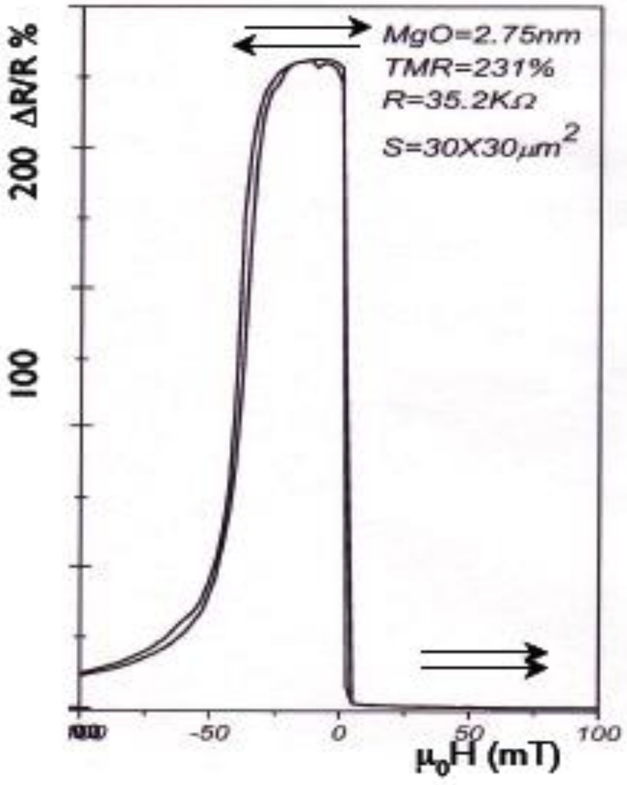
Implementation in hard disk drive 1998

Nobel Prize 2007

MgO-barrier magnetic tunnel junctions

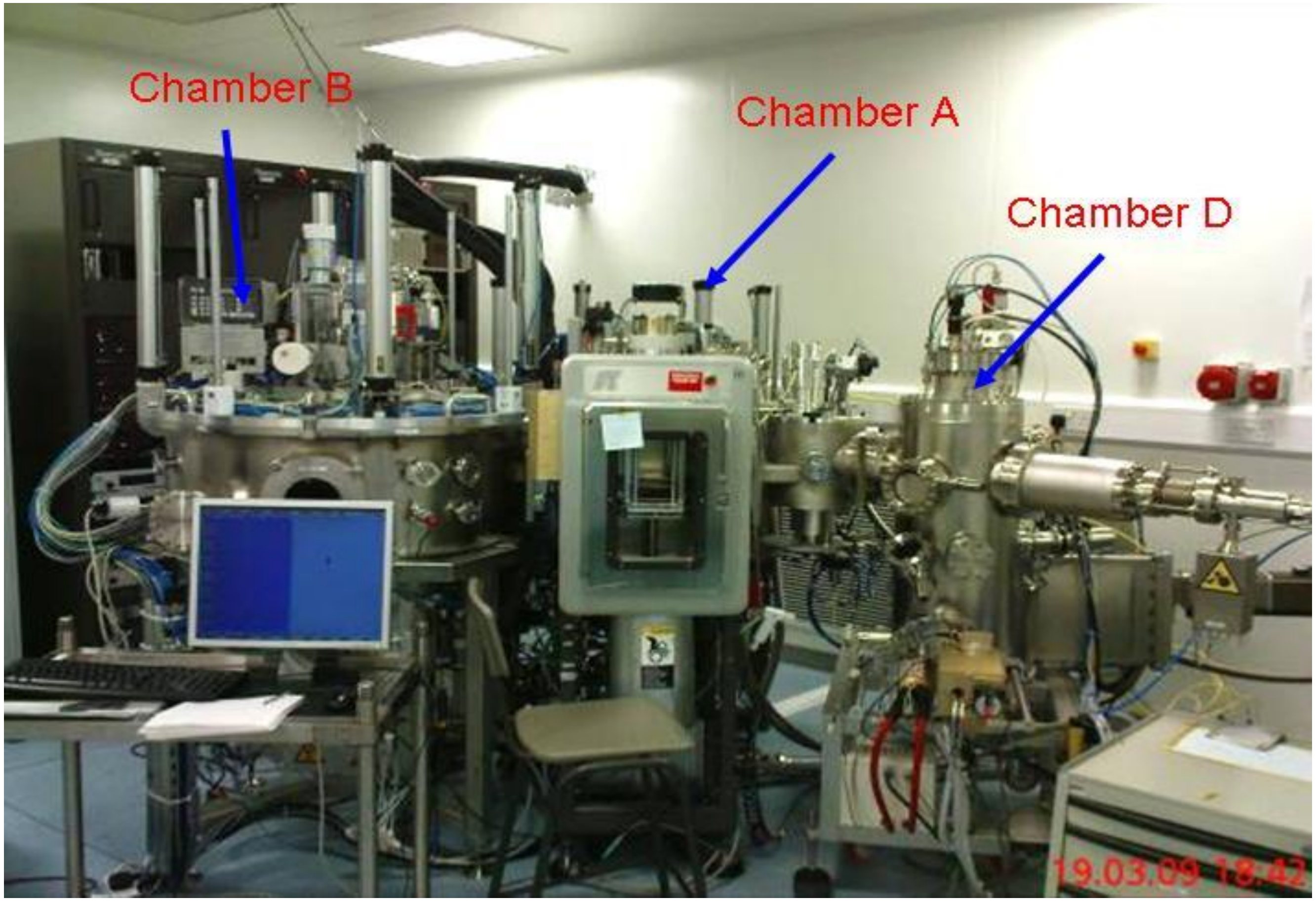
Discovered in 2003
Implemented in 2005





Magnitude of the effect > 200%:

Shamrock sputtering tool; For producing complex thin film (~ nm) stacks. TCD 2002 -2018. Superseded by *Trifolium Dubium* in CRANN in 2019.



Chamber A: Metal Sputtering (6 guns + 1 ion gun)
Chamber B: Oxide Sputtering (8 guns + 1ion gun)
Chamber C: Wafer flip
Chamber D: UHV E-beam (4 pockets) + Sputtering (1 gun)

8.4.4 *New directions in spin electronics*.

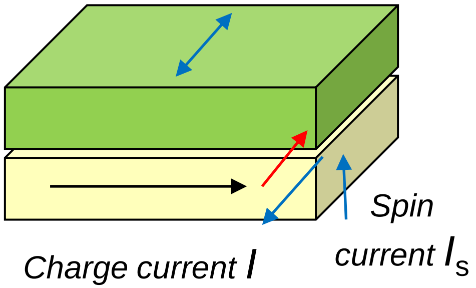
An aim for some years has been to develop nonvolatile magnetic random-access memory.

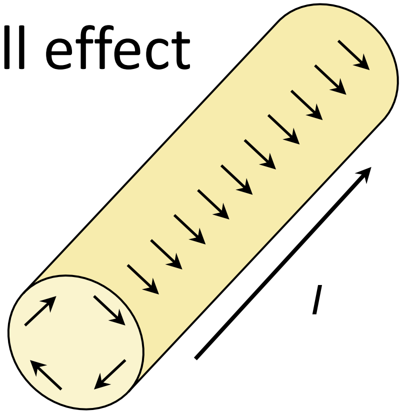
First generation MRAM used magnetic field switching; It was not scalable!

Second generation MRAM used 'spin transfer torque', The spin angular momentum of a spin-polarized electron current absorbed in the free layer switches the TMR memory element. Very high current densities needed

New approach uses spin-orbit torque resulting from spin Hall effect

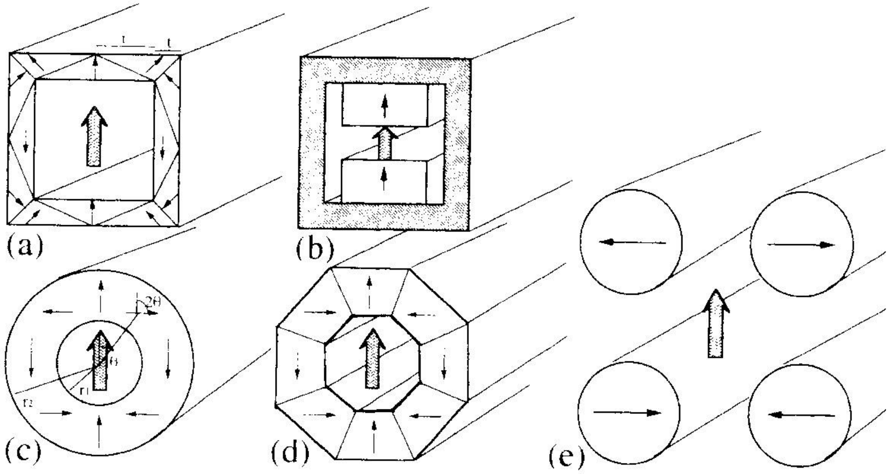
Next challenge: reduce enormously the Power consumption. Electric field Switching using ferroelectrics.





End of Part 1

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.



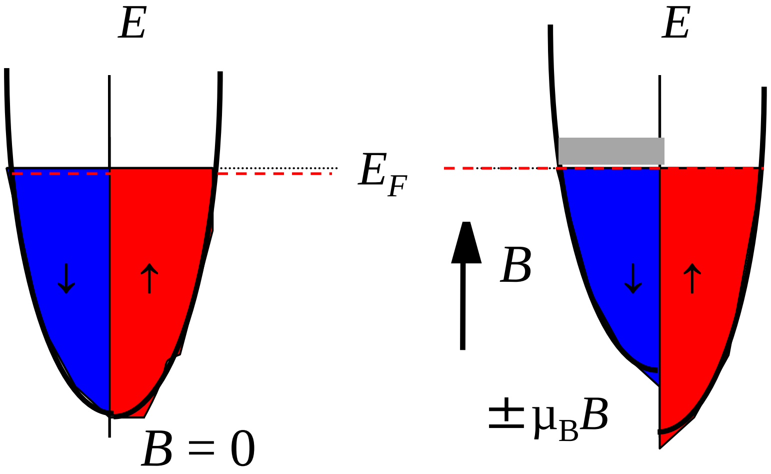
Designs for magnetic cylinders which produce a uniform transverse field.

Figure (c) shows a design where the direction of magnetization of any segment at angular position ϑ in the cylinder is at 2ϑ 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 ingeneous device is known as a *Halbach cylinder*, The field in the airgap is

$$\boxed{B_0 = B_r \ln(r_2/r_1)}$$

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 $s = ½$, $m = 1\mu_B$. They partly-fill an energy band up to the Fermi level E_F.



A rough calculation gives the susceptibility as follows:

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

$\approx 2[D(E_F)\mu_0\mu_B H]\mu_B/H$ where $D\,(E_F)$ is the density of states at the Fermi level for one spin direction.

$$\boxed{\chi_{\text{Pauli}} \approx 2\mu_0 D(E_F)\mu_B^2}$$

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

The density of states $D(E_F)$ 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 $\chi_{curie} = \mu_0 N\mu_B^2/k_BT$, we see that the Pauli susceptibility is a factor k_BT/W smaller than the Curie susceptibility. The factor is of order 100 at room temperature. χ_{Pauli} is of order 10^{-5}.

6.2.1 Exchange in Metals

The Heisenberg theory describes the exchange coupling of electrons in *localized* orbitals on adjacent atoms. 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 $\Delta p \Delta x \approx \hbar$.

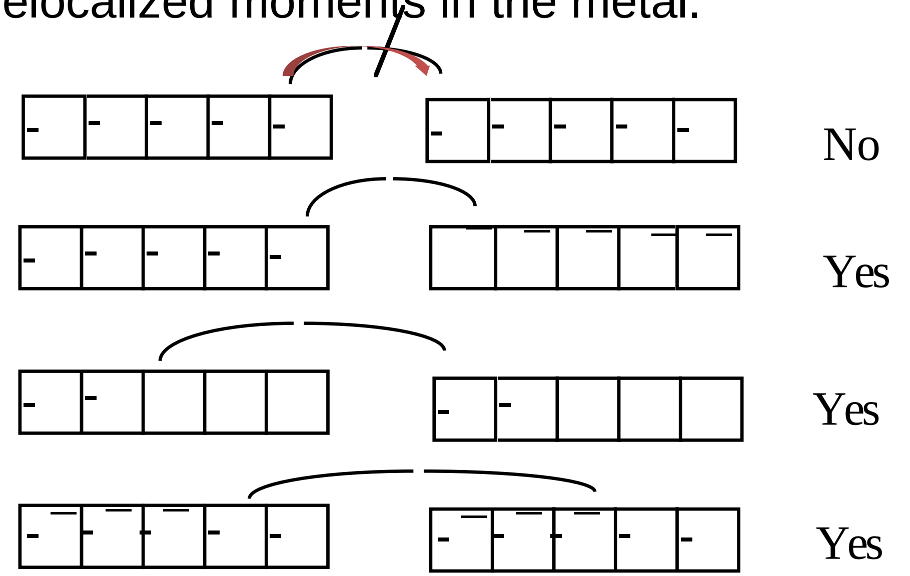
When many more-or-less delocalized electrons are present in different orbitals, the calculation of interatomic exchange is a delicate matter. Energies involved are only ≈ 0.01 eV, compared with bandwidths W of order 1 - 10eV. There are competing exchange mechanisms with different signs of coupling.

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.

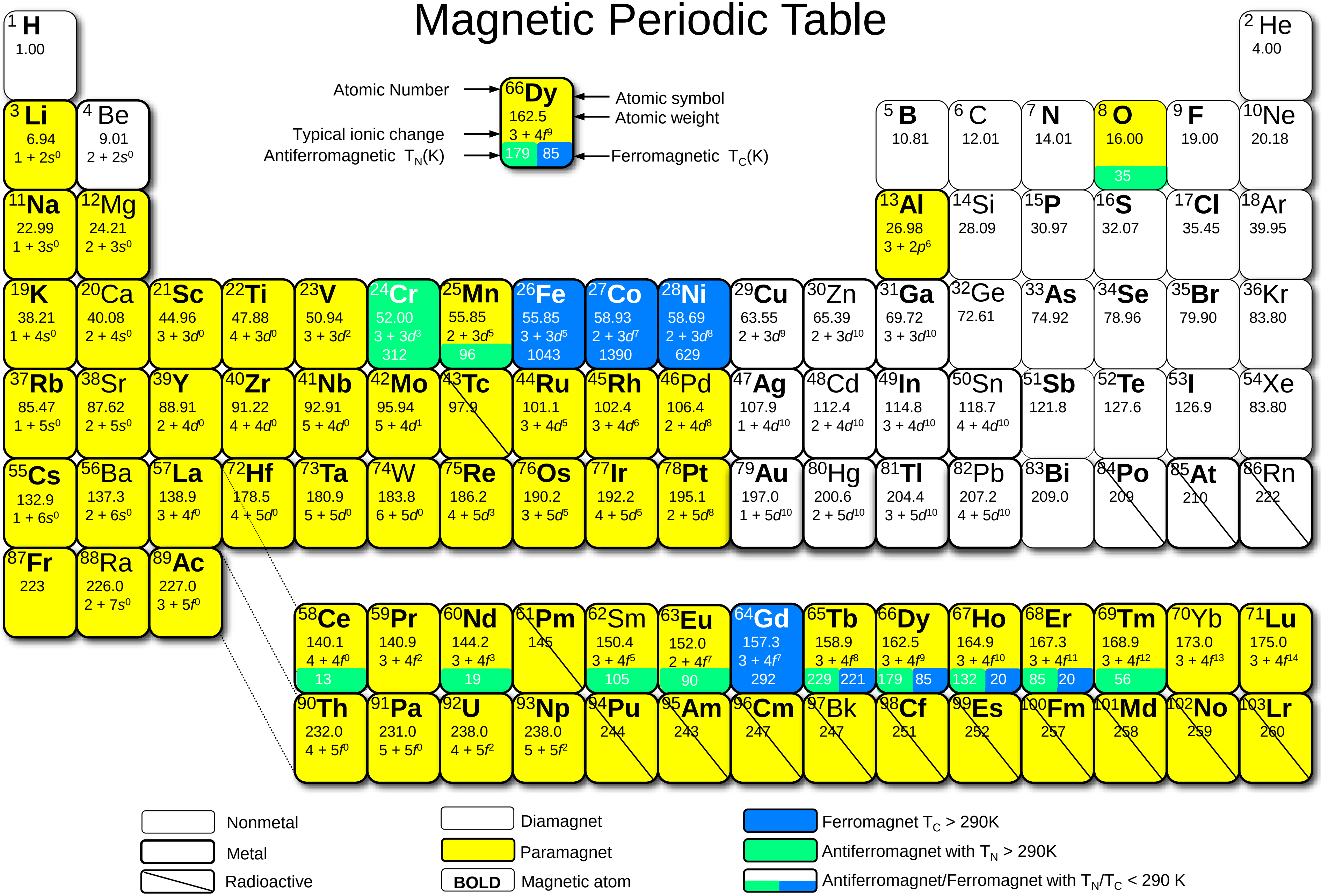
Electrons in 3d metals are described by extended wave functions and spin-polarized density of states

The bandwidth is 2 - 3 eV. In a ~ 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



Atomic Number → **66 Dy** ← Atomic symbol

162.5 ← Atomic weight

Typical ionic change → $3 + 4f^9$

Antiferromagnetic T_N(K) → 179 | 85 ← Ferromagnetic T_C(K)

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

▭	Nonmetal	▭	Diamagnet	🟦	Ferromagnet T_C > 290K
▭	Metal	🟨	Paramagnet	🟩	Antiferromagnet with T_N > 290K
⧄	Radioactive	**BOLD**	Magnetic atom	🟩🟦	Antiferromagnet/Ferromagnet with T_N/T_C < 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;

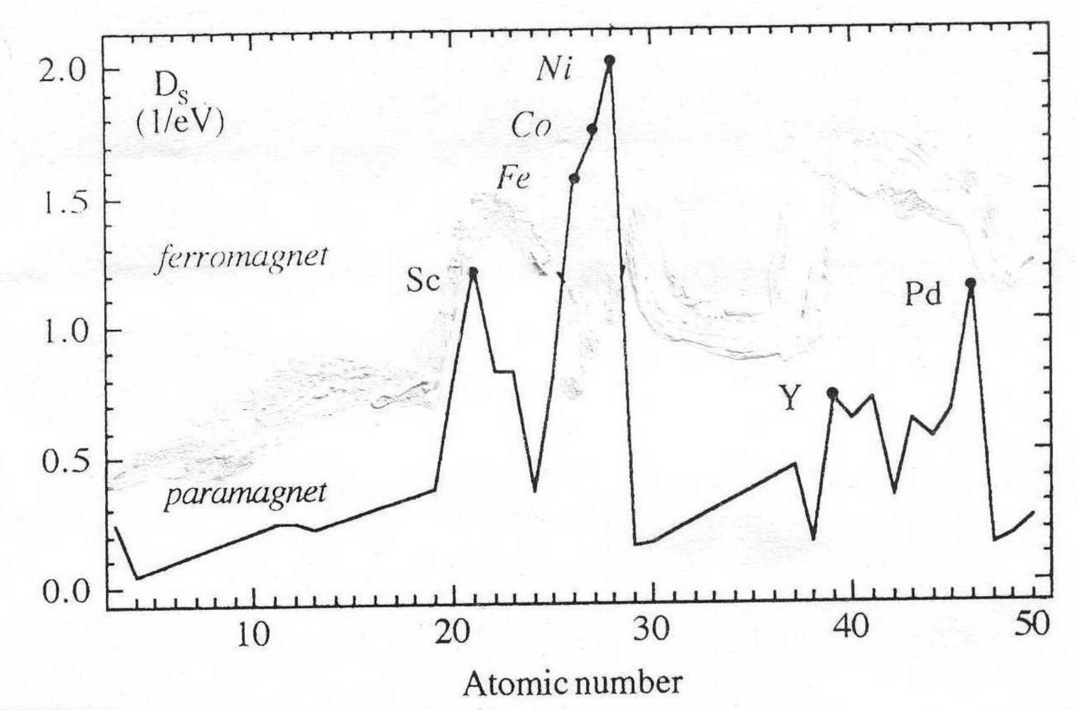
Bare Pauli susceptibility $\chi_p = M/(H + n_S M)$

enhanced:

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

Hence the susceptibility diverges when

$$\boxed{n_S\,\chi_p = 1}$$

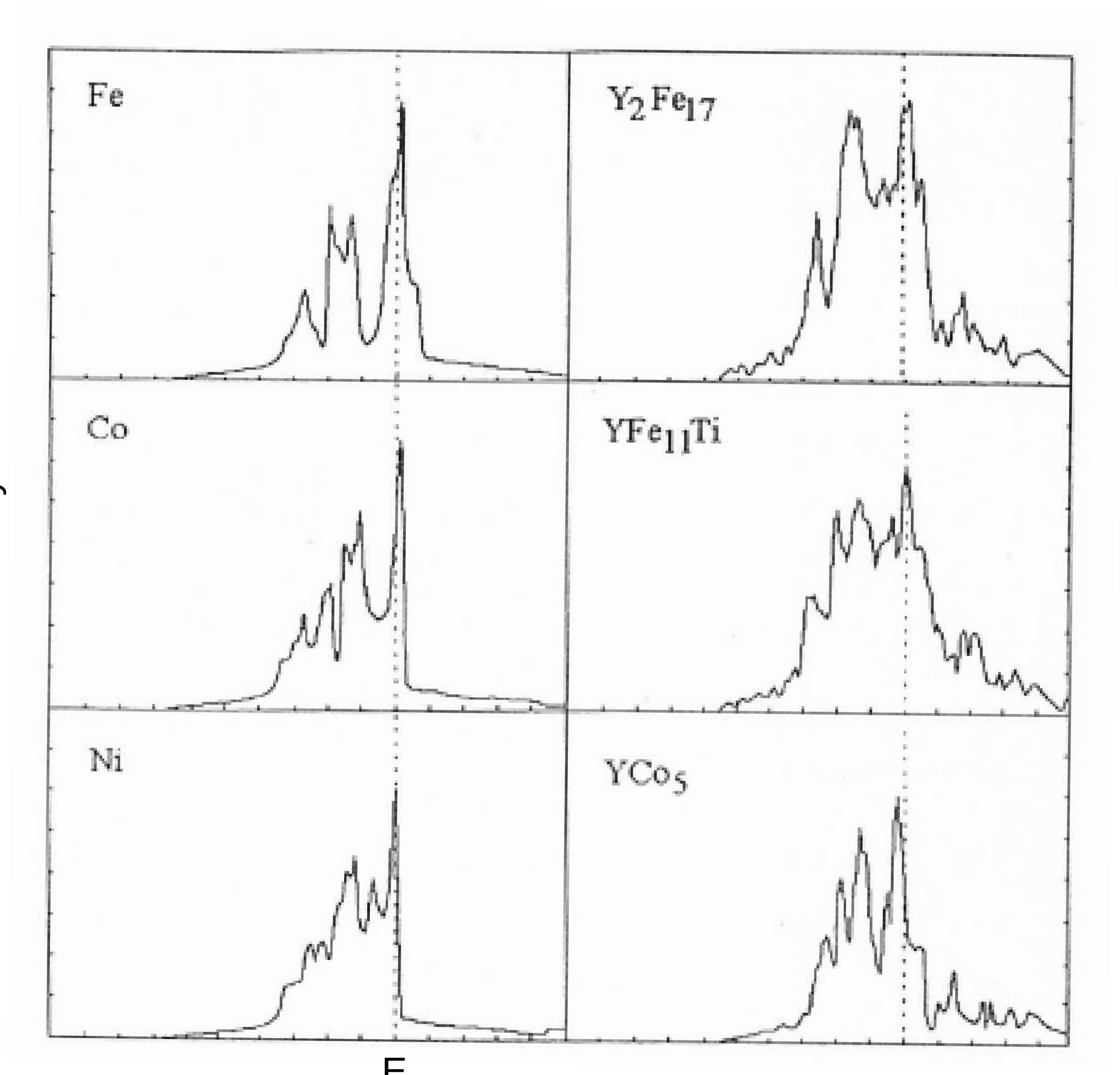


The value of n_S is about 10,000 in 3*d* metals.

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 ↑ and ↓ bands split spontaneously.



Density of states

E_F Energy (eV)

Q 4.

Measure the field perpendicular to the surface of one magnet with a Hall probe.

(only 2 out of 6 create a perpendicular field)

For Nd-F e-B it will be 400 mT. (theB-field)

If we imagine seperating then by a small distance d, the work done is Fd.

The change of energy is associated with the 400 mT field that has now been created in the airgap. The associated energy is ½ VB^2/μ_0 *(V is the volume of the airgap)* $E = 0.5x(10x10^{-3})^2d(0.4)^2/4\pi10^{-7}=Fd$

$F \approx 100N.$

An area of only ~ 3x3 cm^2 *would be enough to support your own weight*