Magnetism

1 Paramagnetism

2 Magnetic order

Introduction magnetism is nothing new........

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History of Magnetism and Electricity

600 BC - Lodestone

The magnetic properties of natural ferric ferrite (Fe_3O_4) stones (lodestones) were described by Greek philosophers.

600 BC - Electric Charge

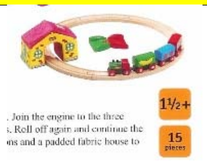
Amber is a yellowish, translucent mineral. As early as 600 BC the Greek philosopher, Aristophanes was aware of its peculiar property: when rubbed with a piece of fur, amber develops the ability to attract small pieces of material such as feathers. For centuries this strange, inexplicable property was thought to be unique to amber. This strange effect remained a mystery for over 2000 years, until, around AD 1600, Dr William Gilbert investigated the reactions of amber and magnets and first recorded the word 'Electric' in a report on the theory of magnetism.

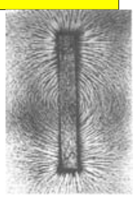
Later in, in 1895, H.A. Lorentz developed the Electron Theory. We now know that there are three ways to generate electricity: Static, Electrochemical and Electromagnetic Induction.

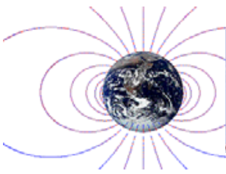
1175 - First Reference to a Compass

Alexander Neckem an English monk of St. Albans describes the workings of a compass.

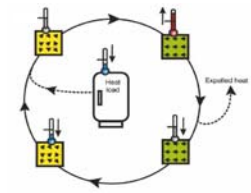
Our first contact with magnetism…







Technology



Magnetic Resonance Imaging

Plasma spectroscopy, Zeeman effect

Quizzzz

1. What are the three sources of atomic magnetism and sort them by size

?

2. What is Lenz's law?

?

3. How large is the magnetic field you can generate with:
   a)A refrigerator magnet
   b)An iron horseshoe magnet
   c)A superconducting magnet
4. Which material reacts strongest on an applied magnetic field?
   a)Argon
   b)Na
   c)O_2
   d)Fe_3O_4

Ferromagnetism of the elements

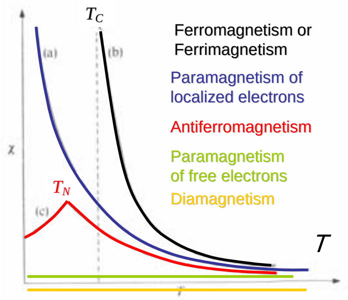
Room-temperature magnets

All other elements are:
Paramagnetic
or
Diamagnetic

5 different types of magnetic materials

Temperature dependence of magnetic susceptibility $\chi_m(T)$

$$\mathbf{M}(H,T) = \chi_m(T)\mathbf{H}$$



Ferromagnetism or Ferrimagnetism
Paramagnetism of localized electrons
Antiferromagnetism
Paramagnetism of free electrons
Diamagnetism

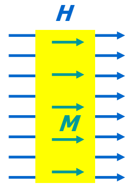
Names and definitions

H: magnetic field / magnetic field strength
B: magnetic induction / magnetic field

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

Material in magnetic field **H** $\mathbf{B} = \mu_0(\mathbf{H} + \mathbf{M})$

Magnetization $\mathbf{M} = \frac{\mu_{tot}}{V}$



Magnetic susceptibility $\mathbf{M} = \chi_m \mathbf{H}$

K_m=relative permeability $\mu = K_m \mu_0$ $\chi_m = K_m - 1$

Relative permeability @ 20ºC

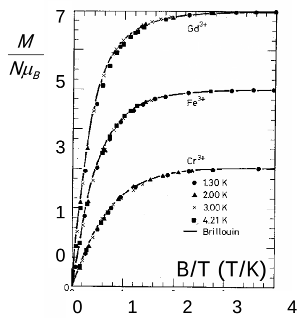
Material	$\chi_m = K_m - 1$ (x 10^{-5})
Paramagnetic	
Iron oxide (FeO)	720
Iron amonium alum	66
Uranium	40
Platinum	26
Tungsten	6.8
Cesium	5.1
Aluminum	2.2
Lithium	1.4
Magnesium	1.2
Sodium	0.72
Oxygen gas	0.19

Material	$\chi_m = K_m - 1$ (x 10^{-5})
Diamagnetic	
Ammonia	-.26
Bismuth	-16.6
Mercury	-2.9
Silver	-2.6
Carbon (diamond)	-2.1
Carbon (graphite)	-1.6
Lead	-1.8
Sodium chloride	-1.4
Copper	-1.0
Water	-0.91

Paramagnetic susceptibility of localized electrons

$$\mathbf{M} = \chi(T)\mathbf{H}$$

χ> 0
M parallel to H
→ Attractive force



localized electrons

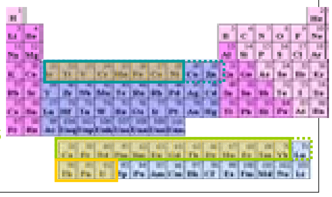
Some valence shells lie deep in the atom

→ have little overlap with neighbor atoms

→ atomic orbital moment "survives" band formation

Which electrons of the elements are these:

- 3d transition metals
- 4f Rare-earth metals
- 5f Early actinides

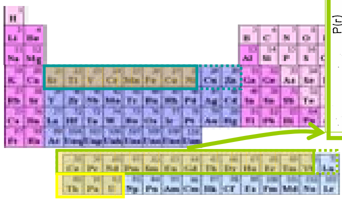


Champion in localization: RE 4f shell

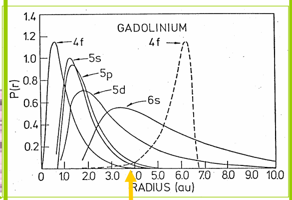
Rare earth:

Electron configuration $4f^N 5d^1 6s^2$

Thus three open valence shells!



Radial expectation value of hydrogen orbitals

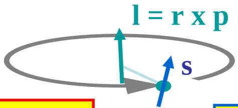


little overlap with neighbor atom

http://winter.group.shef.ac.uk/orbitron/AOs/4f/e-density-xzz-dots.html

Magnetic dipole moment of atom with 1 electron:

Electron has spin and orbital moment contributing each to the magnetic dipole moment



$$\boldsymbol{\mu}_{orbit} = -\frac{e}{2m}\mathbf{r}\times\mathbf{p} = -\mu_B \mathbf{l}$$

$$\boldsymbol{\mu}_{spin} = -\mu_B g_0 \mathbf{s}$$

$$\mu_B = \frac{e\hbar}{2m} = 9.2\text{x}10^{-24}\ \text{J/T}$$

$$g_0 = 2.0023$$

Orbital moment in field // z axis

$$\boldsymbol{\mu}_l = -\mu_B \mathbf{l}$$

$$\mu_{l,z} = -\mu_B m_l$$

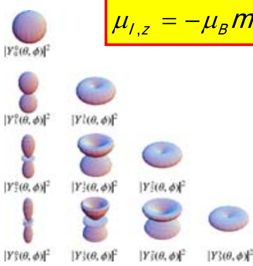
l=

0 (s)

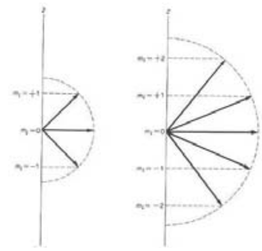
1 (p)

2 (d)

3 (f)



m_l= 0 1 2 3

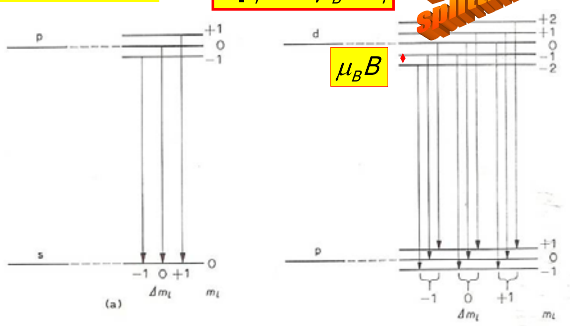


Orbital moment in magnetic field

Zeeman energy $-\boldsymbol{\mu}_l.\mathbf{B} = \mu_B B m_l$

Zeeman splitting

$\mu_B B$



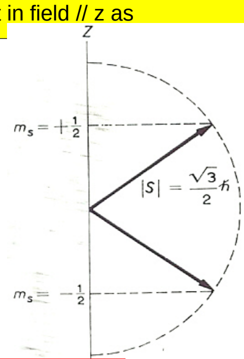
Spin moment in field // z as

$$\boldsymbol{\mu}_s = -g_0 \mu_B \mathbf{s}$$

$$\mu_{s,z} = -\mu_B g_0 m_s$$

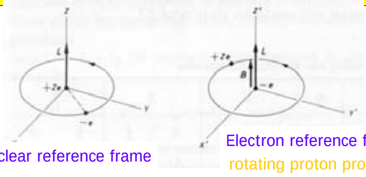
$$g_0 = 2.0023$$

$$\hbar s_z \cong \pm\tfrac{1}{2}\hbar$$



Zeeman energy $-\boldsymbol{\mu}_s.\mathbf{B} = \mu_B g_0 B m_s$

Spin-orbit interaction



Nuclear reference frame

Electron reference frame: rotating proton produces magnetic field (Relativistic effect)

Spin-orbit energy

$$E_{spin-orbit} = \lambda \mathbf{l} \cdot \mathbf{s}$$

$$\lambda \sim \frac{Z^2}{nl(l+1)(l+\frac{1}{2})}$$

for state with quantum number n,l:

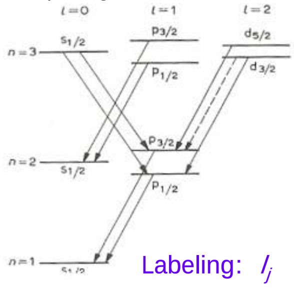
- No splitting if $l=0$ (s orbitals)
- Increases with Z, decreases with n, l
  - 10-100 meV for valence shell
  - 10-1000 eV for inner shell

Spin-orbit splitting

- Spin orbit interaction leads to splitting of levels
- New eigenstates with quantum number

  j=l+s or j=l-s

  m_j=j,j-1,…-j



Labeling: l_j

Total moment of valence shell nl^N

The total magnetic moment is the sum of all magnetic dipole moments

$$\boldsymbol{\mu} = -\mu_B(\mathbf{L} + 2\mathbf{S})$$

$$\hbar\mathbf{L} = \hbar\sum_{i=1}^{N} \mathbf{l}_i$$ Total atomic orbital-moment

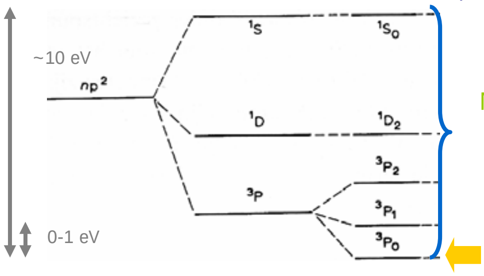
$$\hbar\mathbf{S} = \hbar\sum_{i=1}^{N} \mathbf{s}_i$$ Total atomic spin-moment

Full shells have no dipole moment: ns^2, np^6, nd^{10}, nf^{14}

Partly filled shells have permanent dipole moment

Multiplet splitting of np^2 configuration

Configuration | +Coulomb interaction | +Spin-orbit interaction | +magnetic field (Zeeman splitting)



Mulitplet state

Hund's rule ground state (here J=0)

Spectroscopic notation: $^{2S+1}L_J$

Coupling schemes for adding orbital and spin angular momenta

1. Russel Saunders or L-S coupling if spin-orbit interaction is weak ➔ eigenstates of the atom are also eigenstates of $\mathbf{L}^2$ and $\mathbf{S}^2$ with eigenvalues L(L+1) and S(S+1).
   - Add up all orbital moments $\mathbf{L} = \sum_{i=1}^{N} \mathbf{l}_i$
   - Add up all spin moments $\mathbf{S} = \sum_{i=1}^{N} \mathbf{s}_i$
   - Add these together to total atomic angular moment **J**=**L**+**S**

3 schemes for coupling of moments

Coupling schemes for adding orbital and spin angular moments

2. j-j coupling if spin-orbit interaction is dominant

   Add up orbital and spin moments of each electron *i*

   $$\mathbf{J}_i = \mathbf{l}_i + \mathbf{s}_i$$

   Add these **J***i* together to **J** $\mathbf{J} = \sum_{i=1}^{N} \mathbf{J}_i$

3. Intermediate coupling complicated no fixed rule

3 schemes for coupling of moments

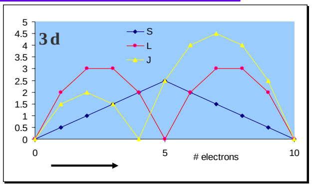
Hund's rules for J of ground state

Procedure for *J* of the ground state (L-S coupling):

1. Maximize $S=\Sigma s_{z,i}$
2. Maximize $L=\Sigma l_{z,i}$
3. J=|L-S| for less than half filled shell
   L+S for more than half filled shell

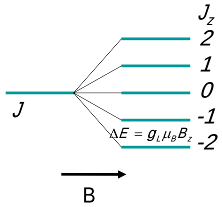
if subshell is exactly half-filled, *L=0*, so *J = S*

example:
3d transition metals:
Fill the 3d orbital (l=2)



Zeeman effect for state with total moment J

- Ground state J is 2J+1 times degenerated: J_z=-J, -J+1, ... J
- Splits in magnetic field into sublevels



$$H_p = -\boldsymbol{\mu}\cdot\mathbf{B} = -\mu_z \cdot B$$

$$E = \langle H_p \rangle = g_{Lande}\mu_B J_z B_z$$

$$g_{Lande} = \frac{3}{2} - \frac{L(L+1) - S(S+1)}{2J(J+1)}$$

- Spectroscopic splitting factor g_{Landee} depends on L, S, and J
- Splitting at B=1 Tesla in the order of meV
- Atom behaves as if it has effective moment: $\mu_{eff}=-g_L\mu_B\mathbf{J}$

Effective moment often called m_J

- once we have, ***J***, we can get the maximum component of the magnetic moment of the atom parallel to the magnetic field:

$$m_J = -g\mu_B J$$

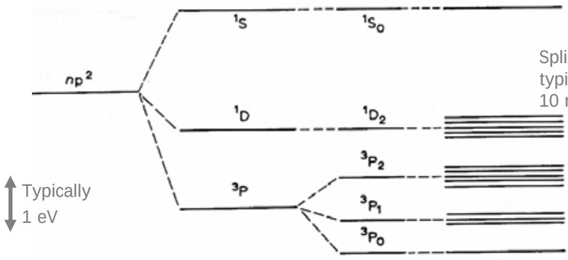
pure orbital motion = 1, pure spin = 2

g, Landé splitting factor:

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

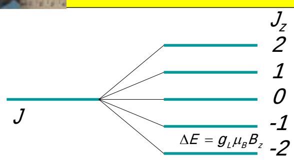
Multiplet + magnetic field: Zeeman effect

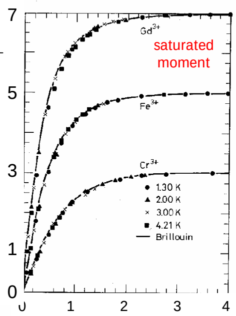
Configuration | +Coulomb interaction | +Spin-baan interaction | +magnetic field (Zeeman splitting)



Here: J=0 ground state is non-magnetic singlet

Temperature dependence





magnetic moment of system with N ions at T is determined by Boltzmann statistics:

$$M = \frac{\sum_{J_z=-J}^{J} -g\mu_B J_z \exp(-g\mu_B B J_z / k_B T)}{\sum_{J_z=-J}^{J} \exp(-g\mu_B B J_z / k_B T)}$$

$$M(B,T) = N\mu_B g J\, B_J\left(\frac{g\mu_B B J}{k_B T}\right)$$

B_J *Brillouin function*

Curie's law

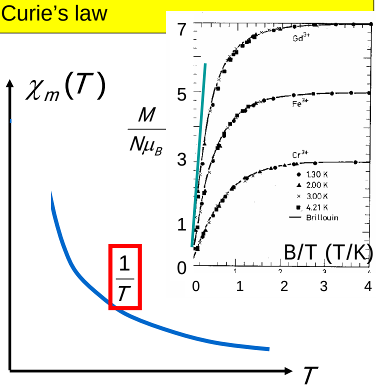
$$M(B,T) = N\mu_B g J\, B_J\left(\frac{g\mu_B B J}{k_B T}\right)$$

for not too small T:
Curie's law

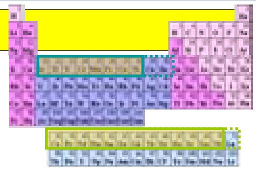
$$\chi_m(T) = \frac{N p^2 \mu_B^2 \mu_0}{3 k_B T}$$

$$p_J = g_{Landee}\left[J(J+1)\right]^{\frac{1}{2}}$$

Effective number of magnetons

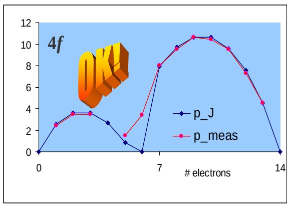


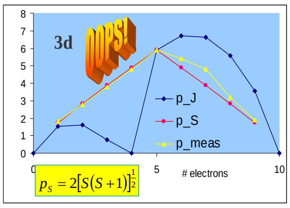
How well works Hund's rule?



Effective number magnetons

$$p_J = g_{Landee}\left[J(J+1)\right]^{\frac{1}{2}}$$





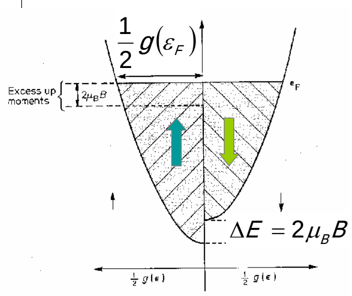
$$p_S = 2\left[S(S+1)\right]^{\frac{1}{2}}$$

In 3d transition metals delocalization destroys orbital moment (quenching)

Paramagnetism of band electrons

- Up to now: localized electrons
- When valence electrons form a band, orbital moment is quenched
- Yet we see a paramagnetic moment in metals
- Explained by Wolfgang Pauli

Paramagnetism of free electron gas



Field lifts spin degeneracy

Estimate:

$$M \approx \mu_B \Delta n = \mu_B^2 g(\varepsilon_F) B$$

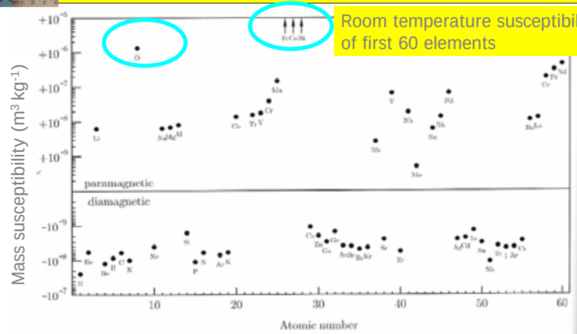
$$\chi(T) = \frac{M}{H} = \mu_0 \mu_B^2 g(\varepsilon_F)$$

Pauli paramagnetism

Temperature independent

Susceptibilities are small

Room temperature susceptibilities of first 60 elements



Typical density: 0.2 mol/cm³ ➔ Molar susc. $\chi_{mol} = 10^{-4} << 1$