Lecture contents

- Magnetic properties
- Diamagnetism
- Band paramagnetism
- Atomic paramagnetism

Magnetic units

Magnetic induction (tesla): $1\,T = 10^4\,\text{gauss}\ (= 1\,\text{Wb}\cdot\text{m}^{-2})$. **B**

B can be called magnetic induction, magnetic induction field or magnetic flux density.

Magnetic field (ampere / metre): $1\,A\cdot\text{m}^{-1} = 4\pi\times 10^{-3}\,\text{œrsted}$. **H**

The magnetic field **H** is often expressed in units of $\mu_0 H$, hence in tesla (T) or its submultiple, the gamma (γ) which is equal to 10^{-9} T. A field of $1\,A\cdot\text{m}^{-1}$ corresponds to $1.2566\,\mu T$.

Magnetisation (ampere / metre): $1\,A\cdot\text{m}^{-1} = 10^{-3}\,\text{emu}\cdot\text{cm}^{-3}$. **M**

Magnetic moment (ampere-square metre or joule per tesla): $1\,A\cdot\text{m}^2 = 1\,J\cdot T^{-1} = 10^3\,\text{emu}$. **μ**

Specific magnetic moment: $1\,A\cdot\text{m}^2\cdot\text{kg}^{-1} = 1\,\text{emu}\cdot\text{g}^{-1}$. **M/ρ**

Note that, sometimes, magnetisation (**M**), magnetic moment (m) and specific magnetic moment (σ) are expressed in tesla, Weber-meter and Weber-meter per kilogram, respectively : the reason is that we have adopted as definition of magnetisation (dm/dV): $\mathbf{M} = \mathbf{B}/\mu_0 - \mathbf{H}$, whereas some authors call "magnetisation" the quantity $\mathbf{B}_i = \mathbf{J} = \mathbf{B} - \mu_0\mathbf{H}$ which is usually called "(magnetic) polarisation".

$$1\,Wb = T\cdot m^2 \qquad 1\,T = \frac{V\cdot s}{m^2} \qquad 1H = \frac{Wb}{A} = \frac{T\cdot m^2}{A}$$

From Tremolet de Lacheisserie, 2005

Magnetic susceptibility

SI:
$$\begin{cases} \vec{B} = \mu_0\left(\vec{H} + \vec{M}\right) \\ \vec{B} = \mu_0\mu_R\vec{H} \\ \vec{M} = \chi\vec{H} \\ \mu_R = 1 + \chi \end{cases}$$

CGS:
$$\begin{cases} \vec{B} = \vec{H} + 4\pi\vec{M} \\ \vec{B} = \mu_R\vec{H} \\ \vec{M} = \chi\vec{H} \\ \mu_R = 1 + 4\pi\chi \end{cases}$$

susceptibility χ:

$$\chi = \frac{M}{H}\frac{\text{emu}}{\text{Oe}\cdot\text{cm}^3}.$$

Note that, since M has units $A\cdot cm^2/cm^3$, and H has units A/cm, χ is actually dimensionless. Since M is the magnetic moment per unit volume, χ also refers to unit volume and is sometimes called the *volume susceptibility* and given the symbol χ_v to emphasize this fact. Other susceptibilities can be defined, as follows:

$\chi_m = \chi_v/\rho =$ mass susceptibility (emu/Oe g),   where $\rho =$ density,

$\chi_A = \chi_m A =$ atomic susceptibility (emu/Oe g atom),   where $A =$ atomic weight,
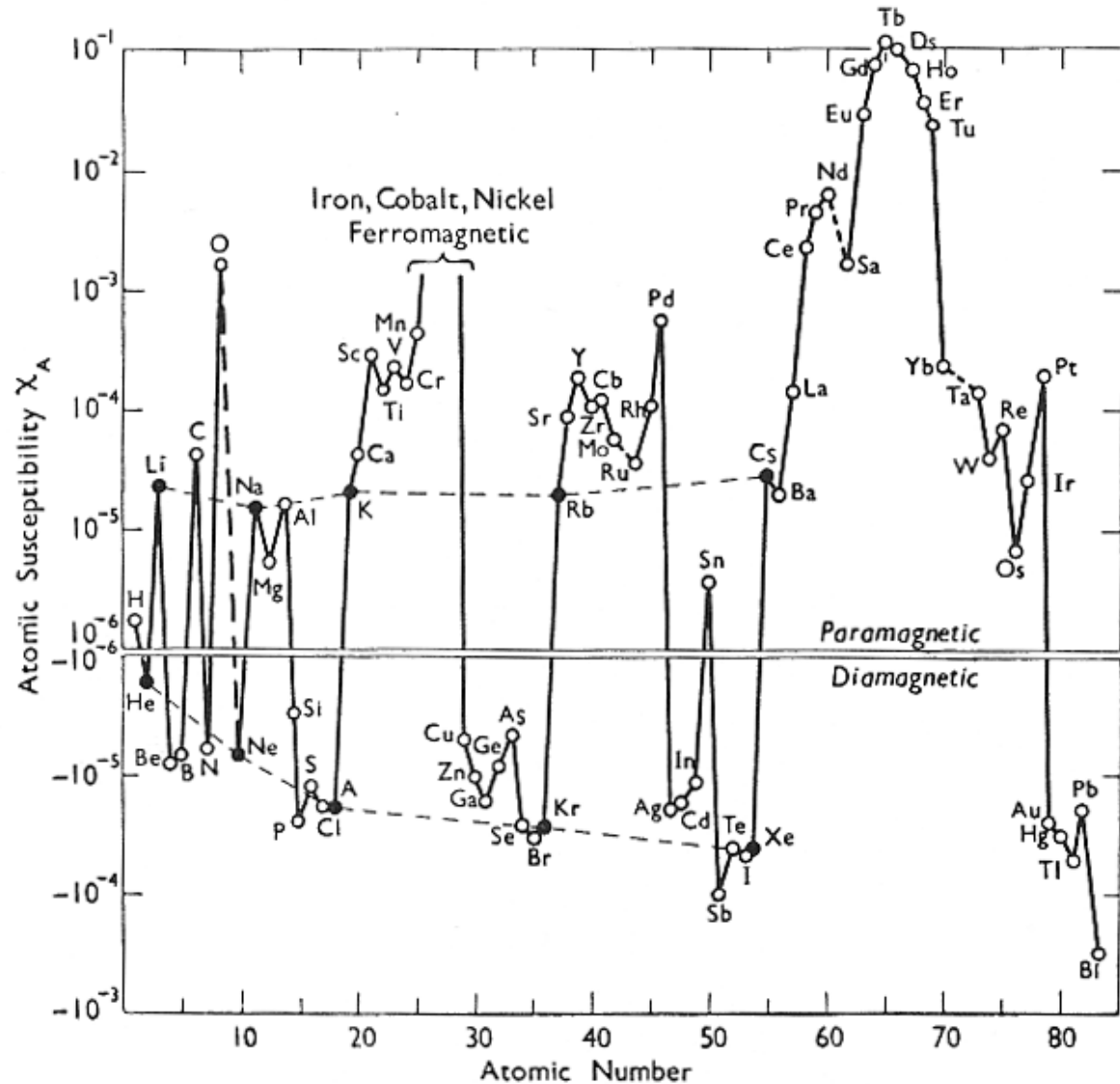
$\chi_M = \chi_m M' =$ molar susceptibility (emu/Oe mol),   where $M' =$ molecular weight.

From Cullity, 2009

Magnetic properties of materials

- M – magnetization or magnetic dipole density
- Diamagnetic $\chi \sim -10^{-5}$
- Paramagnetic $\chi \sim +10^{-5}$
- Ferromagnetic – spontaneous magnetization, large χ
- …

Material	χ_M (dim'less)
Bi	-1.6×10^{-4}
Ag	-2.4×10^{-5}
H_2O	-9.0×10^{-6}
Nb (4K)	-1
Na	8.5×10^{-6}
Al	2.1×10^{-5}
Pt	2.8×10^{-4}
Gd	0.48
Fe (annealed)	$20,000$
$NdFe_{14}B$	~ 0

From Cusack, 1963

Diamagnetism (classical)

- Arises from Lentz's law: when magnetic flux changes in a circuit, a current is induced which opposes the change of flux

$B=\mu_0 H$

B_{Lentz}

- Orbiting electron creates magnetic dipole (circulating current)
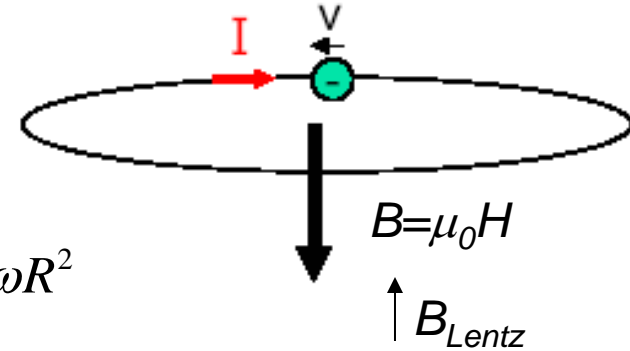
$$I = \frac{\text{charge}}{\text{period}} = q\frac{\omega}{2\pi} \qquad \mu = IA = \frac{1}{2}q\omega R^2$$

- In magnetic field, Lorentz's force is added to centrifugal force

v

$$m\omega^2 R = F - q\omega R \mu_0 H$$

- And corresponding change of rotational frequency

$$\omega^2 - \omega_0^2 = -\frac{q\omega\mu_0 H}{m}$$

- If change in orbital motion is small ($\omega \approx \omega_0$)

$$\Delta\omega = -\frac{q\mu_0 H}{2m}$$

- The energy associated with this frequency is

$$\Delta E = \hbar\Delta\omega = -\frac{q\hbar\mu_0 H}{2m} = -\mu_B\mu_0 H$$

Bohr magneton

$$\mu_B = \frac{q\hbar}{2m} = 9.274\cdot 10^{-24}\left\{\frac{\text{J}}{\text{T}}\right\} \equiv \left\{A\cdot m^2\right\}$$

- The change in frequency can be associated with induced magnetic dipole moment:

$$\mu_m = -\frac{q^2 R^2}{4m}\mu_0 H$$

Diamagnetism (classical) contd.

- Small magnetic field-induced magnetic dipole moment:

$$\mu_m = -\frac{q^2 R^2}{4m}\mu_0 H$$

- Now we can apply the result to spherical closed-shell atom
  - Averaging over 3D gives mean square radial distance
  - Sum over all Z electrons in the atom
  - Sum over all atoms in a unit volume, density N, to obtain magnetization

$$\langle R^2 \rangle = \frac{3}{2}R^2 \begin{cases} \langle x^2 \rangle + \langle y^2 \rangle = R^2 \\ \langle x^2 \rangle = \langle y^2 \rangle = \langle z^2 \rangle = \frac{1}{3}\langle R^2 \rangle \end{cases}$$

$$M = -\frac{q^2 ZN}{6m}\mu_0 H \langle R^2 \rangle$$

- Finally susceptibility

$$\boxed{\chi = \frac{M}{H} = -\frac{q^2 ZN\mu_0}{6m}\langle R^2 \rangle}$$

Larmor or Langevin diamagnetic susceptibility

- All atoms and ions display diamagnetic response

- Almost independent of temperature

- Molar susceptibility is often used to describe magnetism of atoms (should be multiplied by molar volume to obtain dimensionless susceptibility)

Molar susceptibilities of some atoms and ions ($\times 10^{-6}$ cm^3/mole)

Ion	χ_M	Atom	χ_M	Ion	χ_M
		He	−1.9	Li$^+$	−0.7
F$^-$	−9.4	Ne	−7.2	Na$^+$	−6.1
Cl$^-$	−24.2	A	−19.4	K$^+$	−14.6
Br$^-$	−34.5	Kr	−28	Rb$^+$	−22.0
I$^-$	−50.6	Xe	−43	Cs$^+$	−35.1

From Burns, 1990

Paramagnetism

- Contrary to diamagnetism, paramagnetism arises from non-zero magnetic moments:
  - Free electron (Pauli) spin paramagnetism
  - Langevin atomic paramagnetism
- An electron has an intrinsic magnetic dipole moment associated with its spin S, equal to Bohr magneton:

$= 2.0023$

$= \dfrac{\hbar}{2}$

$$\vec{\mu} = -g_s \frac{q}{2m} \vec{S}$$

$$\mu_B = \frac{q\hbar}{2m} = 9.274 \cdot 10^{-24} \left\{ \frac{\text{J}}{\text{T}} \right\} \equiv \left\{ A \cdot m^2 \right\}$$

- We can expect that the magnetic dipoles will rotate towards low-energy state $(U = from \quad -\vec{\mu}\cdot\vec{B} \quad to \quad +\vec{\mu}\cdot\vec{B})$

For B = 1 T (H = 8x10^5 A/m)

$$U = \mu_B B = 58 \ \mu\text{eV} \rightarrow 0.67 \text{ K}$$

Field alignment is weak !

- The fraction of electrons with magnetic moments parallel to magnetic field exceeds the anti-parallel fraction by

$$\approx \frac{\mu_B \mu_0 H}{k_B T}$$

- For *n* free electrons, the magnetization
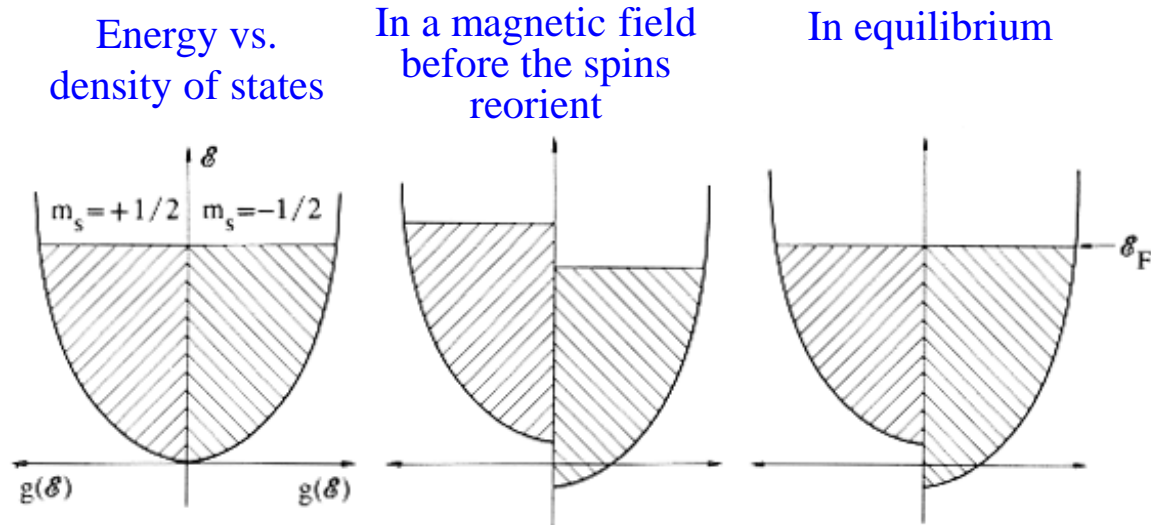- But we need to take band structure into account !

$$M \approx n\mu_B \frac{\mu_B \mu_0 H}{k_B T}$$

Paramagnetism of free spins

- Magnetization $$M \approx n\mu_B \frac{\mu_B \mu_0 H}{k_B T}$$

 is ~100 times higher than observed in real materials

- In a band only a "thermal" fraction of electrons contributes to paramagnetism (compare to transport) $$\approx \frac{k_B T}{E_F}$$

Energy vs. density of states

In a magnetic field before the spins reorient

In equilibrium

- Magnetization is $$M \approx n\mu_B \frac{\mu_B \mu_0}{k_B T_F} H$$

- Similar to transport, more accurate averaging over the distribution function gives susceptibility

$$\boxed{\chi = \frac{3\mu_0}{2} \frac{n\mu_B^2}{k_B T_F}}$$
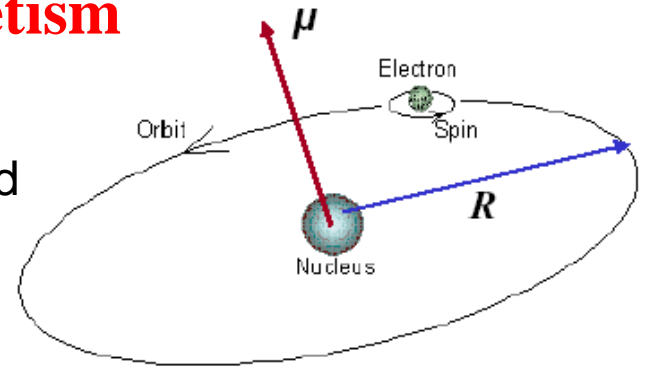
- For example, for Na $$\chi = -8.4 \cdot 10^{-6}$$

From Burns, 1990

Langevin atomic paramagnetism

- Similar to free spins, if an atom has a magnetic moment μ_{eff}, it can align along the magnetic field

- Magnetization of a material with atomic density N is (averaging included)

$$M = \frac{1}{3} N \mu_{eff} \frac{\mu_{eff} \mu_0 H}{k_B T}$$

- And susceptibility

$$\chi = \frac{\mu_0}{3} \frac{N \mu_{eff}^2}{k_B T}$$

$$\chi = \frac{C}{T}$$

Curie law for paramagnetics
With Curie constant

$$C = \frac{N \mu_0 \mu_{eff}^2}{3 k_B}$$

- Atom with orbital, spin and total angular momenta, L, S, and $J = L+S$, will have magnetic moment

$$\mu_{eff} = g_J \mu_B J \qquad \left[= \mu_B \langle L + 2S \rangle \right]$$

With Lindé g-factor

$$g_J = 1 + \frac{J^2 + S^2 - L^2}{2J^2}$$

= 2.0023

- Complications

  - Quantum mechanical averaging of m_J

  - Ions

  - Quenching of orbital momentum in the crystal field (Stark splitting of 2L+1 degeneracy)

Often "spin-only" moment is used
with convention:
$g_J=2$, L=0, J=S
and maximum moment $\mu_H=2J\mu_B$

Need to be careful with scientific texts!

Atomic paramagnetism - Quantum theory

Magnetic moment vs. H/T

- Quantum mechanical averaging over (2J+1) projections

M_{sat}

$$M = N \frac{\sum\limits_{-J}^{+J} g_J \mu_B m_J e^{\frac{g_J \mu_B m_J B}{k_B T}}}{\sum\limits_{-J}^{+J} e^{\frac{g_J \mu_B m_J B}{k_B T}}} \equiv N g_J \mu_B J B_J(y) \equiv N \mu_{eff} B_J(y)$$

- With Brillouin function:

$$B_J(y) = \frac{2J+1}{2J} \coth\left(\frac{2J+1}{2J} y\right) - \frac{1}{2J} \coth\left(\frac{y}{2J}\right)$$

with $y = \dfrac{\mu_{eff} B}{k_B T} = \dfrac{g_J \mu_B J B}{k_B T}$

- If magnetic energy is small compared to thermal energy, y << 1 , Brillouin function gives

$$B_J(y << 1) \approx y \frac{J+1}{3J}$$

- This results in classic susceptibility

$$\chi = \frac{\mu_0}{3} \frac{N \mu_{eff}^2}{k_B T}$$

with quantum averaged $\mu_{eff}^2 = \left(g_J \mu_B\right)^2 J(J+1)$

Magnetic moment vs. H/T plot: M/μ_B per ion (0.00 to 7.00) vs. H/T in Oe °K^{-1} (0 to 40).
Curves: S = 7/2 (Gd^{3+}), S = 5/2 (Fe^{3+}), S = 3/2 (Cr^{3+}).
Data: ○ 1.30 °K, △ 2.00 °K, × 3.00 °K, □ 4.21 °K, — Brillouin funct.
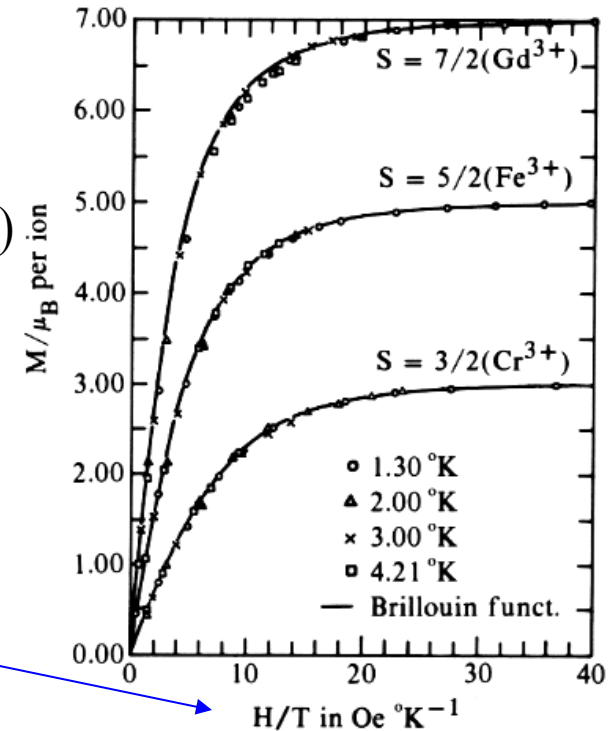
Magnetic moments of ions

Ground states of ions predicted by Hund's rules

Values of magnetic moments of 4f and 3d ions in insulating compounds

f-shell ($\ell = 3$) $\quad {}^{2S+1}L_J$

n	$m_\ell=3, 2, 1, 0, -1, -2, -3$	S	L=$|\Sigma m_\ell|$	J	term	g_J	ion
0		0	0	0	${}^1S_0$	0	La^{3+}
1		1/2	3	5/2	${}^2F_{5/2}$	6/7	Ce^{3+}
2		1	5	4	${}^3H_4$	4/5	Pr^{3+}
3		3/2	6	9/2	${}^4I_{9/2}$	8/11	Nd^{3+}
4		2	6	4	${}^5I_4$	3/5	Pm^{3+}
5		5/2	5	5/2	${}^6H_{5/2}$	2/7	Sm^{3+}
6		3	3	0	${}^7F_0$	–	Eu^{3+}
7		7/2	0	7/2	${}^8S_{7/2}$	2	Gd^{3+}
8		3	3	6	${}^7F_6$	3/2	Tb^{3+}
9		5/2	5	15/2	${}^6H_{15/2}$	4/3	Dg^{3+}
10		2	6	8	${}^5I_8$	5/4	Ho^{3+}
11		3/2	6	16/2	${}^4I_{15/2}$	6/5	Er^{3+}
12		1	5	6	${}^3H_6$	7/6	Tm^{3+}
13		1/2	3	7/2	${}^2F_{7/2}$	8/7	Yb^{3+}
14		0	0	0	${}^1S_0$	0	Lu^{3+}

d-shell ($\ell = 2$)

n	$m_\ell=2, 1, 0, -1, -2$	S	L=$|\Sigma m_\ell|$	J	term	ion
1		1/2	2	3/2	${}^2D_{3/2}$	Ti^{3+}
2		1	3	2	${}^3F_2$	V^{3+}
3		3/2	3	3/2	${}^4F_{3/2}$	Cr^{3+}
4		2	2	0	${}^5D_0$	Cr^{2+}
5		5/2	0	5/2	${}^6S_{5/2}$	Fe^{3+},Mn^{2+}
6		2	2	4	${}^5D_4$	Fe^{2+}
7		3/2	3	9/2	${}^4F_{9/2}$	Co^{2+}
8		1	3	4	${}^3F_4$	Ni^{2+}
9		1/2	2	5/2	${}^2D_{5/2}$	Cu^{2+}
10		0	0	0	${}^1S_0$	

Ion	$4f^n$	State	μ_{eff}/μ_B (Calc.)	μ_{eff}/μ_B (Exp.)
La^{3+}	$4f^0$	${}^1S_0$	0	0
Ce^{3+}	$4f^1$	${}^2F_{5/2}$	2.54	2.4
Pr^{3+}	$4f^2$	${}^3H_4$	3.58	3.5
Nd^{3+}	$4f^3$	${}^4I_{9/2}$	3.62	3.5
Pm^{3+}	$4f^4$	${}^5I_4$	2.68	–
Sm^{3+}	$4f^5$	${}^6H_{5/2}$	0.84	1.5
Eu^{3+}	$4f^6$	${}^7F_0$	0	3.4
Gd^{3+}	$4f^7$	${}^8S_{7/2}$	7.94	8.0
Tb^{3+}	$4f^8$	${}^7F_6$	9.72	9.5
Dy^{3+}	$4f^9$	${}^6H_{15/2}$	10.63	10.6
Ho^{3+}	$4f^{10}$	${}^5I_8$	10.60	10.4
Er^{3+}	$4f^{11}$	${}^4I_{15/2}$	9.59	9.5
Tm^{3+}	$4f^{12}$	${}^3H_6$	7.57	7.3
Yb^{3+}	$4f^{13}$	${}^2F_{7/2}$	4.54	4.5

Ion	$3d^n$	State	μ_{eff}/μ_B (Calc.-J)	μ_{eff}/μ_B (Calc.-J=S)	μ_{eff}/μ_B (Exp.)
Ti^{3+}, V^{4+}	$3d^1$	${}^2D_{3/2}$	1.55	1.73	1.8
V^{3+}	$3d^2$	${}^3F_2$	1.63	2.83	2.8
Cr^{3+}, V^{2+}	$3d^3$	${}^4F_{3/2}$	0.77	3.87	3.8
Mn^{3+}, Cr^{2+}	$3d^4$	${}^5D_0$	0	4.90	4.9
Fe^{3+}, Mn^{2+}	$3d^5$	${}^6S_{5/2}$	5.92	5.92	5.9
Fe^{2+}	$3d^6$	${}^5D_4$	6.70	4.90	5.4
Co^{2+}	$3d^7$	${}^4F_{9/2}$	6.63	3.87	4.8
Ni^{2+}	$3d^8$	${}^3F_4$	5.59	2.83	3.2
Cu^{2+}	$3d^9$	${}^2D_{5/2}$	3.55	1.73	1.9

From Burns, 1990

Atomic paramagnetism - Example

- In $KCr(SO_4)_2 \cdot 12\,H_2O$ compound, the only magnetic atom is Cr^{3+} :

- 3 d-electrons:
  - $S=3/2,\ L=3,\ J=3/2$ →

$$g_J = 1 + \frac{J^2 + S^2 - L^2}{2J^2} = \frac{2}{5}$$

- From experiment: $g_J=2,\ L=0,\ J = S = 3/2$, moment is determined by spin, orbital component is quenched
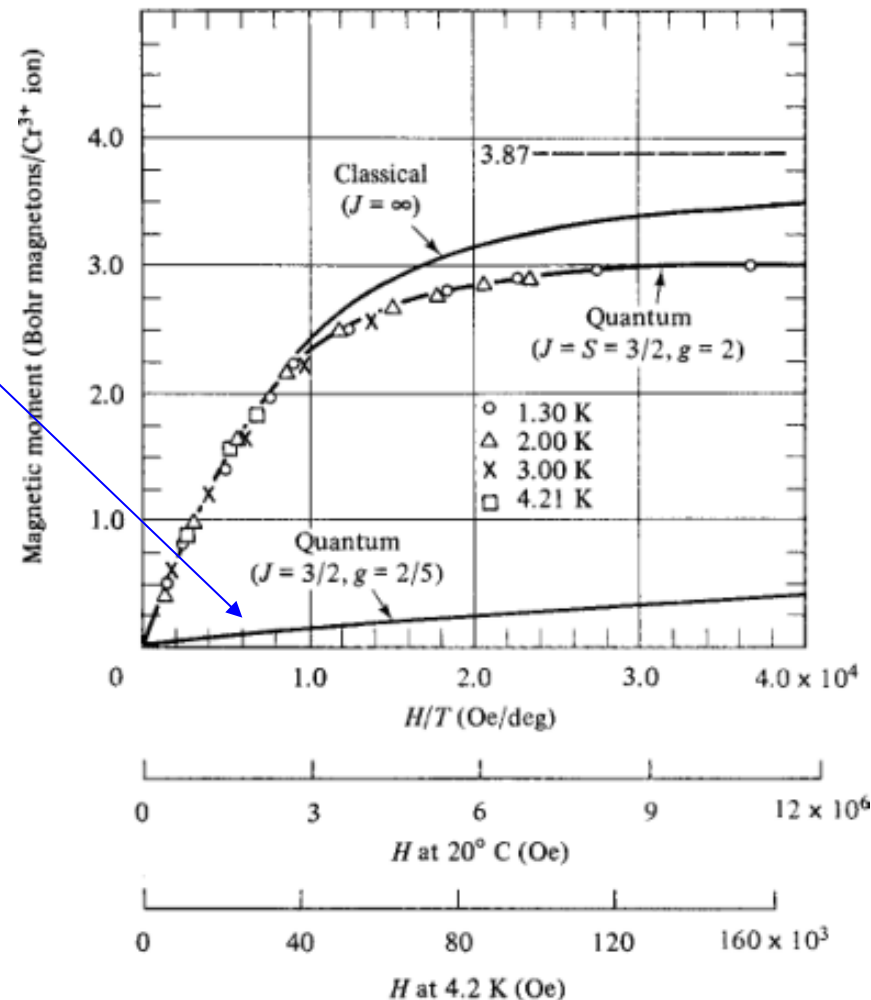
$$\mu_{eff}^2 = g_J \sqrt{J(J+1)}\,\mu_B = \sqrt{15}\,\mu_B = 3.87\,\mu_B$$

- Maximum (asymptotic) value:

$$\mu_H = 2J\mu_B = 3\mu_B$$

(compare to the classic value)

Magnetic moment of $KCr(SO_4)_2 \cdot 12\,H_2O$, at fields up to 50,000 Oe and at 4.2 K

From Cullity, 2009

Lecture recap

- Diamagnetism (susceptibility is negative)
    - All atoms
    - Classical, due to addition of magnetic moment to the electron orbital current

- Band (Pauli) paramagnetism
    - Due to alignment of spins of free electrons
    - Spins of the electrons at the Fermi surface can be affected

- Atomic paramagnetism
    - Due to alignment of existing magnetic moments of atomic electrons
    - Needs quantum assessment of magnetic moments of electrons (S, L, J) and statistics