# Solid State Physics

# MAGNETISM II
## Lecture 28

**A.H. Harker**
**Physics and Astronomy**
*UCL*

## 10.5.2 General $J$ ionic paramagnetism

An atomic angular momentum $J$, made of spin $S$ and orbital angular momentum quantum number $L$, will have a magnetic moment $g_J \mu_B J$, where $g_J$ is the Landé g-factor

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

If we write $x = g_J \mu_B \mathcal{B}/k_B T$, the average atomic magnetic moment will be

$$\langle \mu \rangle = \frac{\sum_{m=-J}^{J} m g_J \mu_B e^{mx}}{\sum_{m=-J}^{J} e^{mx}}.$$

If we assume that $T$ is large and/or $\mathcal{B}$ is small, we can expand the exponential, giving

$$\langle \mu \rangle \approx g_J \mu_B \frac{\sum_{m=-J}^{J} m(1+mx)}{\sum_{m=-J}^{J}(1+mx)}.$$

**We can evaluate this if we note that**

$$\sum_{m=-J}^{J} 1 = 2J+1$$

$$\sum_{m=-J}^{J} m = 0$$

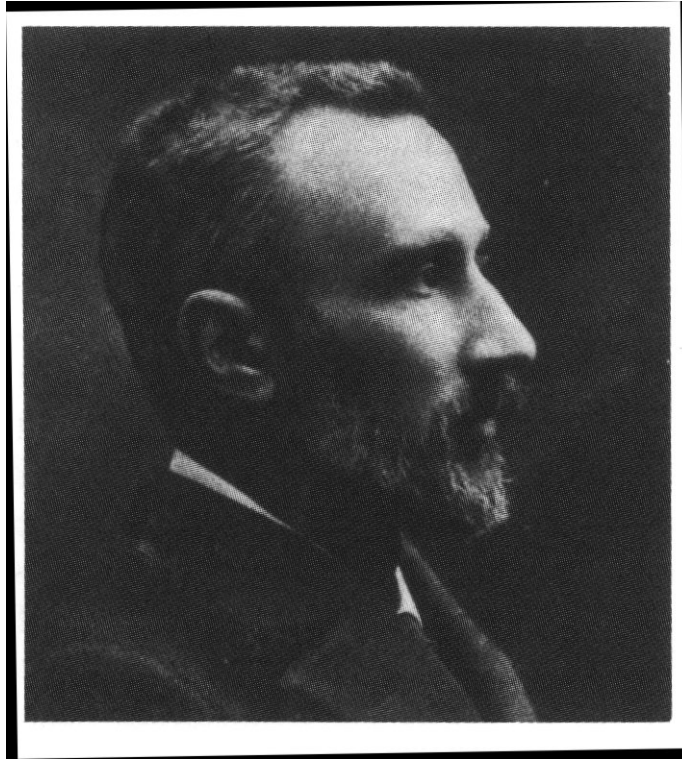$$\sum_{m=-J}^{J} m^2 = \frac{1}{3}J(J+1)(2J+1)$$

**then**

$$\langle \mu \rangle \approx g_J \mu_{\mathrm{B}} \frac{xJ(J+1)(2J+1)}{3(2J+1)}$$

$$= \frac{g_J^2 \mu_{\mathrm{B}}^2 \mathcal{B} J(J+1)}{3k_{\mathrm{B}}T},$$

**leading to a susceptibility**

$$\chi = \frac{\mu_0 n g_J^2 \mu_{\mathrm{B}}^2 J(J+1)}{3k_{\mathrm{B}}T}.$$
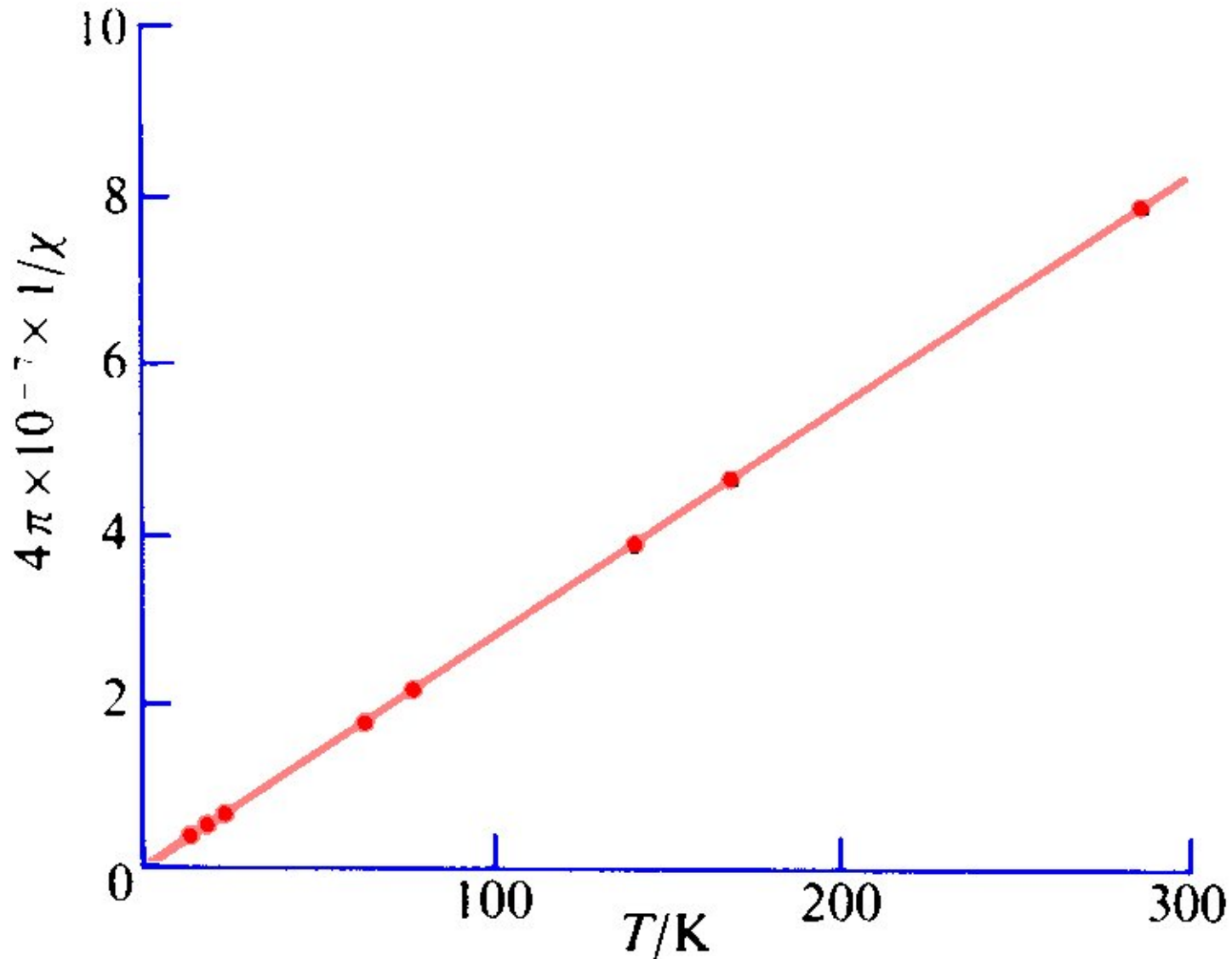
**This is *Curie's Law*, often written**

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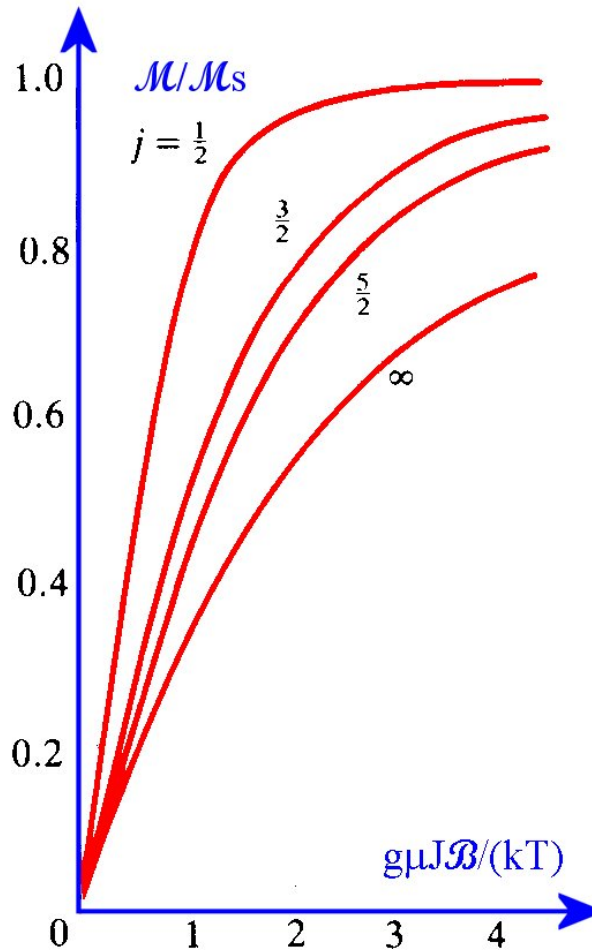


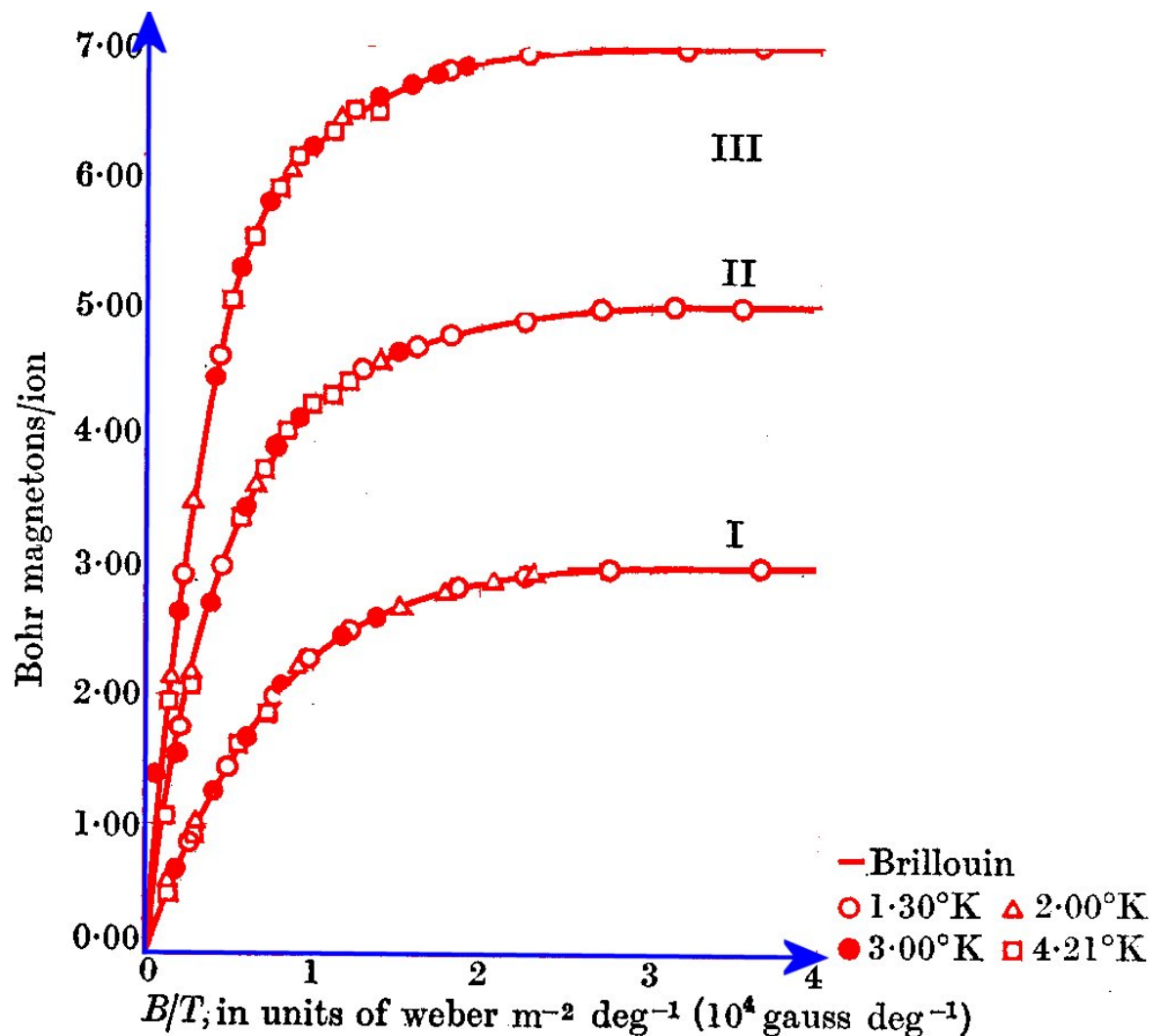**Pierre Curie**

**Chromium potassium alum.**



$1/\chi$ **is proportional to** $T$**, confirming Curie's law.**

**Of course, eventually $\mathcal{M}$ must saturate, as for the spin-1/2 system. The larger $J$ the slower the saturation. A full treatment results in the *Brillouin function*, $B_J(g_J\mu_B J\mathcal{B}/k_B T)$ giving the variation of $\mathcal{M}/\mathcal{M}_s$.**

# Experimental results confirm this.



Plot of average magnetic moment per ion $\mathfrak{m}$ against $B/T$ for (I) potassium chromium alum ($J = S = \frac{3}{2}$), (II) iron ammonium alum ($J = S = \frac{5}{2}$), and (III) gadolinium sulphate octahydrate ($J = S = \frac{7}{2}$).

*Ionic paramagnetic susceptibility:*

- **Positive**

- **Typically $10^{-5}$ to $10^{-3}$**

- **Temperature-dependent**

- **Arises from permanent dipole moments on the atoms**

- **Saturates for large $\mathcal{B}$ or low $T$**

## 10.5.3    States of ions in solids

The ions which concern us here are those with part-filled shells, giving a nett angular momentum.

IA ... VIII

Part-filled d shell

Part-filled f shell

| IA | IIA | IIIA | IVA | VA | VIA | VIIA | VIIIA | | | IB | IIB | IIIB | IVB | VB | VIB | VIIB | VIII |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| H | | | | | | | | | | | | | | | | | He |
| Li | Be | | | | | | | | | | | B | C | N | O | F | Ne |
| Na | Mg | | | | | | | | | | | Al | Si | P | S | Cl | Ar |
| K | Ca | Sc | Ti | V | Cr | Mn | Fe | Co | Ni | Cu | Zn | Ga | Ge | As | Se | Br | Kr |
| Rb | Sr | Y | Zr | Nb | Mo | Tc | Ru | Rh | Pd | Ag | Cd | In | Sn | Sb | Te | I | Xe |
| Cs | Ba | La | Hf | Ta | W | Re | Os | Ir | Pt | Au | Hg | Tl | Pb | Bi | Po | At | Rn |
| Fr | Ra | Ac | | | | | | | | | | | | | | | |

| Ce | Pr | Nd | Pm | Sm | Eu | Gd | Tb | Dy | Ho | Er | Tm | Yb | Lu |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Th | Pa | U | Np | Pu | Am | Cm | Bk | Cf | Es | | | | |

Best studied are the first and second transition series, (Ti to Cu and Zr to Hg) and the rare earths (La to Lu).

From atomic physics we know that a free atom or ion is characterised by quantum numbers $L$, $S$ and $J$, and for a given $L$ and $S$ may take up $J$ values between $|L - S|$ and $L + S$. Hund's rules tell us that the ground state is that for which

- $S$ is as large as possible

- $L$ is as large as possible for that $S$

- $J = \begin{cases} |L - S| & \text{if the shell is less than half full} \\ L + S & \text{if the shell is more than half full} \end{cases}$

representing the effects of exchange, correlation, and spin-orbit coupling respectively.

**We can deduce the magnetic moment per atom $p\mu_B$ from the susceptibility, and compare with what Hund's rules tell us.**

| Ion | State | Term | $g\sqrt{J(J+1)}$ | Experimental $p$ |
|---|---|---|---|---|
| $Ce^{3+}$ | $4f^1 5s^2 p^6$ | $^2F_{5/2}$ | 2.54 | 2.4 |
| $Pr^{3+}$ | $4f^2 5s^2 p^6$ | $^3H_4$ | 3.58 | 3.5 |
| $Nd^{3+}$ | $4f^3 5s^2 p^6$ | $^4I_{9/2}$ | 3.62 | 3.5 |
| $Pm^{3+}$ | $4f^4 5s^2 p^6$ | $^5I_4$ | 2.68 | - |
| $Sm^{3+}$ | $4f^5 5s^2 p^6$ | $^6H_{5/2}$ | 0.84 | 1.5 |
| $Eu^{3+}$ | $4f^6 5s^2 p^6$ | $^7F_0$ | 0.00 | 3.4 |
| $Gd^{3+}$ | $4f^7 5s^2 p^6$ | $^8S_{7/2}$ | 7.94 | 8.0 |
| $Tb^{3+}$ | $4f^8 5s^2 p^6$ | $^7F_6$ | 9.72 | 9.5 |
| $Dy^{3+}$ | $4f^9 5s^2 p^6$ | $^6H_{15/2}$ | 10.63 | 10.6 |
| $Ho^{3+}$ | $4f^{10} 5s^2 p^6$ | $^5I_8$ | 10.60 | 10.4 |
| $Er^{3+}$ | $4f^{11} 5s^2 p^6$ | $^4I_{15/2}$ | 9.59 | 9.5 |
| $Tm^{3+}$ | $4f^{12} 5s^2 p^6$ | $^3H_6$ | 7.57 | 7.3 |
| $Yb^{3+}$ | $4f^{13} 5s^2 p^6$ | $^2F_{7/2}$ | 4.54 | 4.5 |

**All looks fine – except for Sm and Eu, where higher $J$ levels are very close to the ground state which means they are partly occupied above $0 \text{ K}$.**

## Now look at the first transition series.

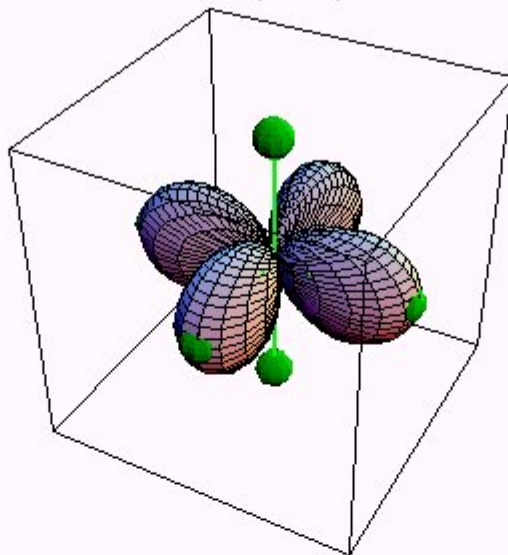| Ion | State | Term | $g\sqrt{J(J+1)}$ | Experimental $p$ |
|---|---|---|---|---|
| $Ti^{3+}, V^{4+}$ | $3d^1$ | $^2D_{3/2}$ | 1.55 | 1.8 |
| $V^{3+}$ | $3d^2$ | $^3F_2$ | 1.63 | 2.8 |
| $Cr^{3+}, V^{2+}$ | $3d^3$ | $^4F_{3/2}$ | 0.77 | 3.8 |
| $Mn^{3+}, Cr^{2+}$ | $3d^5$ | $^5D_0$ | 0.00 | 4.9 |
| $Fe^{3+}, Mn^{2+}$ | $3d^5$ | $^6S_{5/2}$ | 5.92 | 5.9 |
| $Fe^{2+}$ | $3d^6$ | $^5D_4$ | 6.70 | 5.4 |
| $Co^{2+}$ | $3d^7$ | $^4F_{9/2}$ | 6.63 | 4.8 |
| $Ni^{2+}$ | $3d^8$ | $^3F_4$ | 5.59 | 3.2 |
| $Cu^{2+}$ | $3d^9$ | $^2D_{5/2}$ | 3.55 | 1.9 |

**The agreement is very poor.**

# The problem is *crystal field splitting*. Look at the electronic $d$ states in a cubic crystal.
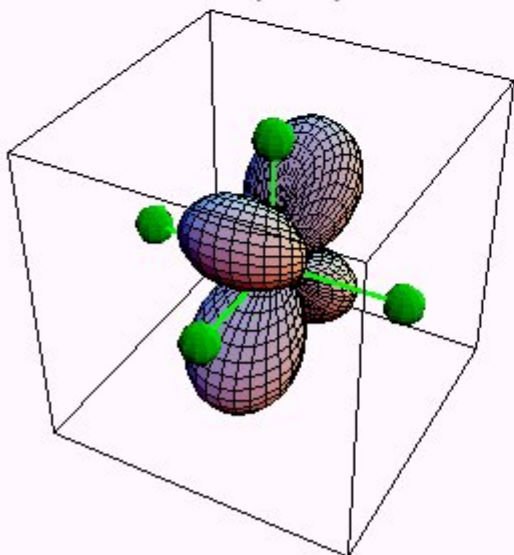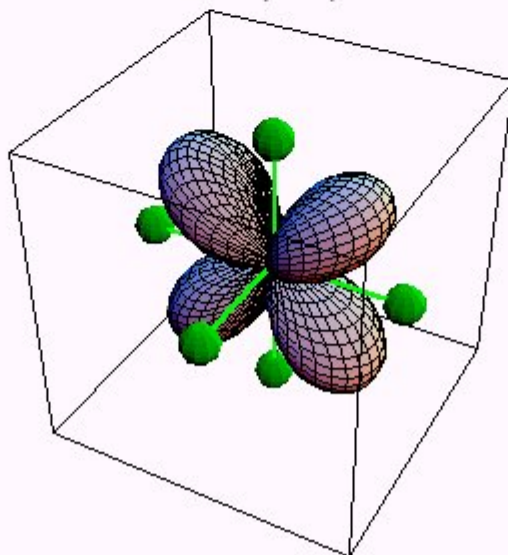


d function, Cos, m=0
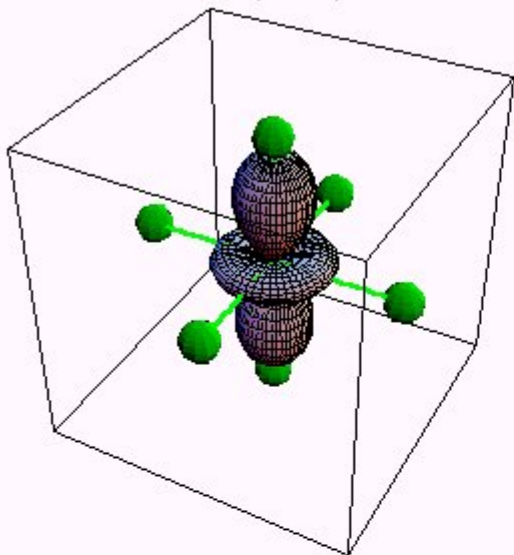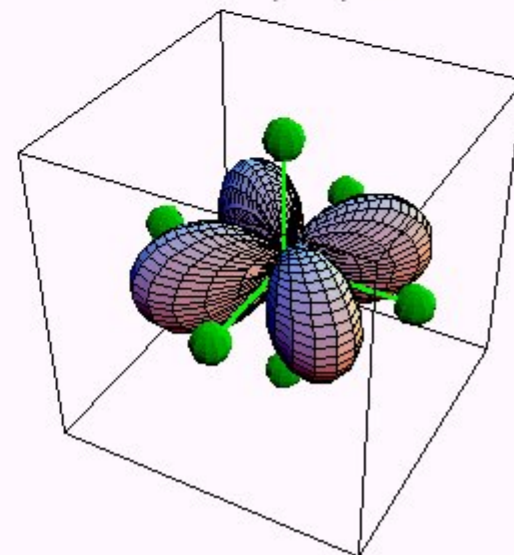
d function, Cos, m=2

d function, Cos, m=1

d function, Sin, m=1

d function, Sin, m=2

**Two states point directly towards neighbouring ions, three states point between neighbours. These states have different electrostatic energies. So the $d$ states are 'locked' to the crystal, and no longer behave like an $l = 2$ state with $2l + 1$ *degenerate* $m$ values. This is called *quenching* of the orbital angular momentum. In the first transition series, the magnetic moments arise almost entirely from spin.**

| Ion | State | Term | $g\sqrt{S(S+1)}$ | Experimental $p$ |
|---|---|---|---|---|
| $Ti^{3+}, V^{4+}$ | $3d^1$ | $^2D_{3/2}$ | 1.73 | 1.8 |
| $V^{3+}$ | $3d^2$ | $^3F_2$ | 2.83 | 2.8 |
| $Cr^{3+}, V^{2+}$ | $3d^3$ | $^4F_{3/2}$ | 3.87 | 3.8 |
| $Mn^{3+}, Cr^{2+}$ | $3d^5$ | $^5D_0$ | 4.90 | 4.9 |
| $Fe^{3+}, Mn^{2+}$ | $3d^5$ | $^6S_{5/2}$ | 5.92 | 5.9 |
| $Fe^{2+}$ | $3d^6$ | $^5D_4$ | 4.90 | 5.4 |
| $Co^{2+}$ | $3d^7$ | $^4F_{9/2}$ | 3.87 | 4.8 |
| $Ni^{2+}$ | $3d^8$ | $^3F_4$ | 2.83 | 3.2 |
| $Cu^{2+}$ | $3d^9$ | $^2D_{5/2}$ | 1.73 | 1.9 |

The rare earths behave differently because the 4f electrons are in smaller orbits than the 3d ones, and because spin-orbit coupling is larger in the 4f ions.

# 10.6   Interacting magnetic moments

So far we have no explanation for the existence of ferromagnetism.
By measuring the magnetic moment of a specimen of a ferromagnet,
we can see that the magnetisation must be near saturation. A quick
look at the Brillouin function
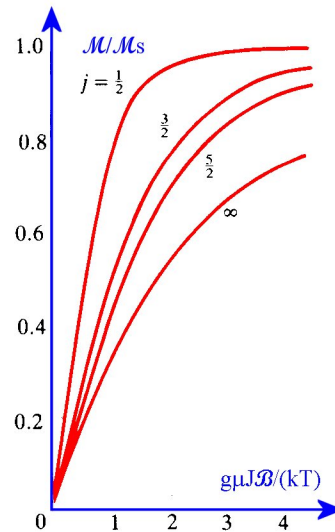


shows that at room temperature this needs

$$\frac{g_J \mu_B \mathcal{B}}{k_B T} \approx 1,$$

or, at room temperature, taking $g_J \approx 2$, $\mathcal{B} \approx 200 \text{ T}$.

## 10.6.1    Direct magnetic interaction

Where can such a large field come from? Can it be direct interactions between spins a lattice spacing (say $0.25$ nm) apart? The field from one Bohr magneton at a distance $r$ is of order

$$\mathcal{B} = \frac{\mu_0 \mu_{\mathrm{B}}}{4\pi r^3} \approx 0.06 \text{ T},$$

so direct magnetic interations are irrelevant (though they are significant in, for example, limiting the temperatures that can be reached by adiabatic demagnetisation).

## 10.6.2 Exchange interaction

The interaction is *quantum mechanical*, a form of *exchange interaction*. Recall Hund's rules – there exchange favoured parallel spins. We write the Hamiltonian for the interaction between two spins on different sites $i$ and $j$ as

$$\mathcal{H}_{ij}^{\text{spin}} = -2J_{ij}\mathbf{S}_i.\mathbf{S}_j,$$

where $J_{ij}$, the exchange integral, depends on the overlap between wavefunctions on different sites. Positive $J$ favours parallel spins, negative $J$ favours antiparallel spins. For the whole crystal,

$$\mathcal{H}^{\text{spin}} = -\sum_{i,j} J_{ij}\mathbf{S}_i.\mathbf{S}_j,$$

or

$$\mathcal{H}^{\text{spin}} = -2\sum_{i<j} J_{ij}\mathbf{S}_i.\mathbf{S}_j.$$

### 10.6.3 Effective field model

**For a particular spin, $i$, we can write the interaction term as**

$$\mathcal{H}_i^{\mathrm{spin}} = -2 \sum_{j \neq i} J_{ij} \mathbf{S}_i . \mathbf{S}_j$$

$$= - \left( 2 \sum_{j \neq i} J_{ij} \mathbf{S}_j \right) . \mathbf{S}_i.$$

**Now note two points:**

- **The form of the interaction, $-(...).\mathbf{S}$, looks like the interaction of a spin with a magnetic field.**

- **Write**

$$\mathcal{H}_i^{\mathrm{spin}} = - \left( 2 \sum_{j \neq i} (J_{ij}/(g_S \mu_{\mathrm{B}})) \mathbf{S}_j \right) . (g_S \mu_{\mathrm{B}} \mathbf{S}_i)$$

$$= - \mathcal{B}_{\mathrm{eff}} . \mathbf{m}_i,$$

**where $m_i$ is the magnetic moment on atom $i$.**

- **The summation suggests that we should be able to do some averaging over the spins.**

## 10.6.4    The mean field approximation

**Assume that each spin interacts only with its $z$ nearest neighbours. Then**

$$\mathcal{B}_{\text{eff}} = \left( 2 \sum_{j=1}^{z} \frac{J}{g_S \mu_B} \mathbf{S}_j \right)$$

$$= 2 \sum_{j=1}^{z} \frac{J}{g_S \mu_B} \frac{\mathbf{m}_j}{g_S \mu_B}$$

$$= 2 \frac{J}{g_S \mu_B} \frac{z \langle \mathbf{m}_j \rangle}{g_S \mu_B}.$$

**Now identify the average magnetic moment per volume with the magnetisation:**

$$n \langle \mathbf{m}_j \rangle = \mathcal{M},$$

**for** $n$ **spins per unit volume, giving**

$$\mathcal{B}_{\text{eff}} = 2\frac{J}{g_S\mu_B}\frac{z\mathcal{M}}{ng_S\mu_B}$$

$$= \frac{2zJ}{ng_S^2\mu_B^2}\mathcal{M}.$$

**This gives the** *Weiss internal field model* **(not originally derived in this way) – the energy of a dipole in the ferromagnet is equivalent to an effective field**

$$\mathcal{B}_{\text{eff}} = \lambda\mathcal{M}.$$

**Note that this is** *NOT* **a** *real* **magnetic field – the origin is quantum-mechanical exchange, not magnetism, and as the interaction that underlies exchange is the Coulomb interaction it can be much stronger.**