

MAGNETISM II

Lecture 28

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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

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

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

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

We can evaluate this if we note that

$$\begin{aligned} \sum_{m=-J}^J 1 &= 2J + 1 \\ \sum_{m=-J}^J m &= 0 \\ \sum_{m=-J}^J m^2 &= \frac{1}{3} J(J+1)(2J+1) \end{aligned}$$

then

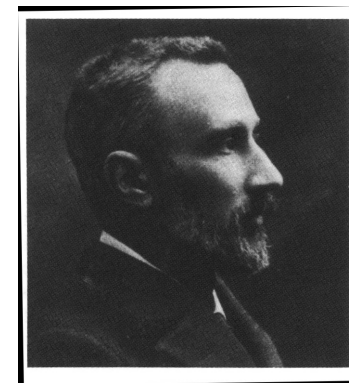
$$\begin{aligned} \langle \mu \rangle &\approx g_J \mu_B \frac{x J(J+1)(2J+1)}{3(2J+1)} \\ &= \frac{g_J^2 \mu_B^2 \mathcal{B} J(J+1)}{3k_B T}, \end{aligned}$$

leading to a susceptibility

$$\chi = \frac{\mu_0 n g_J^2 \mu_B^2 J(J+1)}{3k_B T}.$$

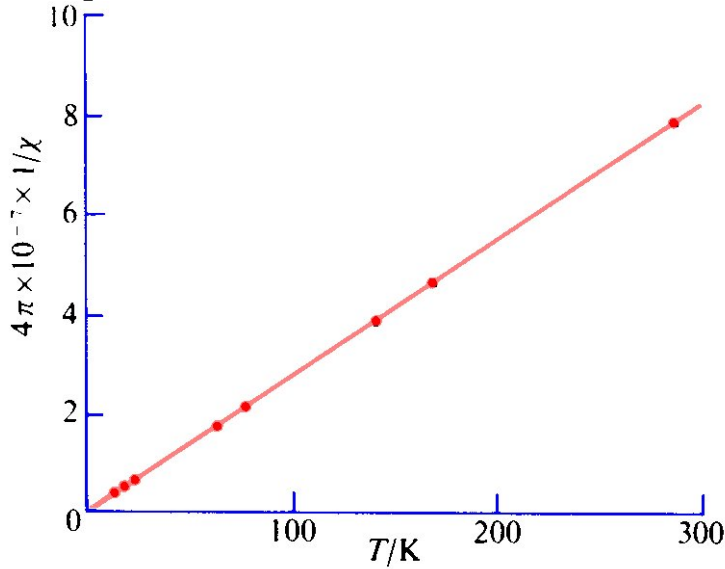
This is *Curie's Law*, often written

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



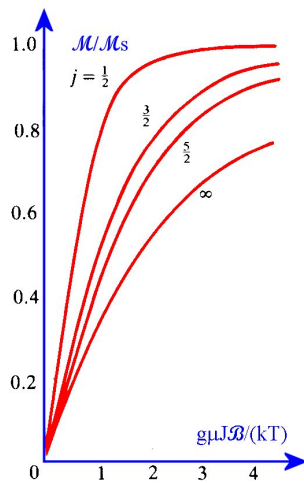
Pierre Curie

Chromium potassium alum.

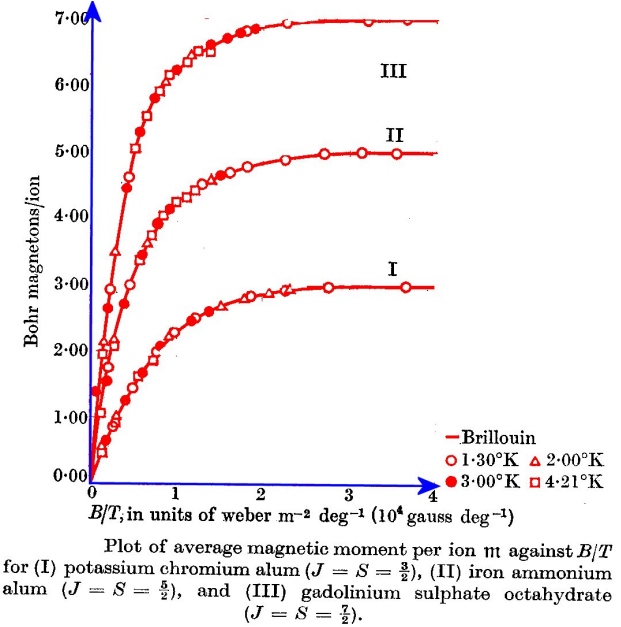


$1/\chi$ is proportional to T , confirming Curie's law.

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.



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.

Part-filled d shell (Red)

Part-filled f shell (Cyan)

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	² F _{5/2}	2.54	2.4
Pr ³⁺	4f ² 5s ² p ⁶	³ H ₄	3.58	3.5
Nd ³⁺	4f ³ 5s ² p ⁶	⁴ I _{9/2}	3.62	3.5
Pm ³⁺	4f ⁴ 5s ² p ⁶	⁵ I ₄	2.68	-
Sm ³⁺	4f ⁵ 5s ² p ⁶	⁶ H _{5/2}	0.84	1.5
Eu ³⁺	4f ⁶ 5s ² p ⁶	⁷ F ₀	0.00	3.4
Gd ³⁺	4f ⁷ 5s ² p ⁶	⁸ S _{7/2}	7.94	8.0
Tb ³⁺	4f ⁸ 5s ² p ⁶	⁷ F ₆	9.72	9.5
Dy ³⁺	4f ⁹ 5s ² p ⁶	⁶ H _{15/2}	10.63	10.6
Ho ³⁺	4f ¹⁰ 5s ² p ⁶	⁵ I ₈	10.60	10.4
Er ³⁺	4f ¹¹ 5s ² p ⁶	⁴ I _{15/2}	9.59	9.5
Tm ³⁺	4f ¹² 5s ² p ⁶	³ H ₆	7.57	7.3
Yb ³⁺	4f ¹³ 5s ² p ⁶	² F _{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 K.

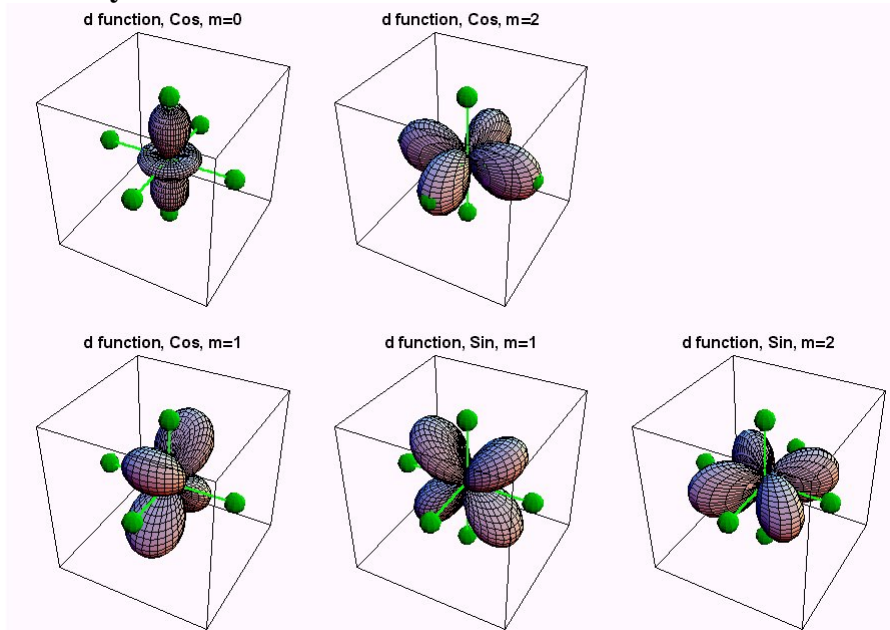
Now look at the first transition series.

Ion	State	Term	$g\sqrt{J(J+1)}$	Experimental p
Ti ³⁺ , V ⁴⁺	3d ¹	² D _{3/2}	1.55	1.8
V ³⁺	3d ²	³ F ₂	1.63	2.8
Cr ³⁺ , V ²⁺	3d ³	⁴ F _{3/2}	0.77	3.8
Mn ³⁺ , Cr ²⁺	3d ⁵	⁵ D ₀	0.00	4.9
Fe ³⁺ , Mn ²⁺	3d ⁵	⁶ S _{5/2}	5.92	5.9
Fe ²⁺	3d ⁶	⁵ D ₄	6.70	5.4
Co ²⁺	3d ⁷	⁴ F _{9/2}	6.63	4.8
Ni ²⁺	3d ⁸	³ F ₄	5.59	3.2
Cu ²⁺	3d ⁹	² D _{5/2}	3.55	1.9

The agreement is very poor.

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.

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

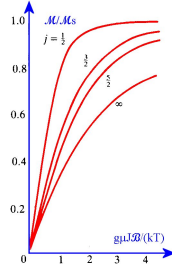


Ion	State	Term	$g\sqrt{S(S+1)}$	Experimental p
Ti ³⁺ , V ⁴⁺	3d ¹	² D _{3/2}	1.73	1.8
V ³⁺	3d ²	³ F ₂	2.83	2.8
Cr ³⁺ , V ²⁺	3d ³	⁴ F _{3/2}	3.87	3.8
Mn ³⁺ , Cr ²⁺	3d ⁵	⁵ D ₀	4.90	4.9
Fe ³⁺ , Mn ²⁺	3d ⁵	⁶ S _{5/2}	5.92	5.9
Fe ²⁺	3d ⁶	⁵ D ₄	4.90	5.4
Co ²⁺	3d ⁷	⁴ F _{9/2}	3.87	4.8
Ni ²⁺	3d ⁸	³ F ₄	2.83	3.2
Cu ²⁺	3d ⁹	² D _{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

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

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

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

so direct magnetic interactions 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

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

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,

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

or

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

10.6.3 Effective field model

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

$$\begin{aligned} \mathcal{H}_i^{\text{spin}} &= -2 \sum_{j \neq i} J_{ij} \mathbf{S}_i \cdot \mathbf{S}_j \\ &= - \left(2 \sum_{j \neq i} J_{ij} \mathbf{S}_j \right) \cdot \mathbf{S}_i. \end{aligned}$$

Now note two points:

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

$$\begin{aligned} \mathcal{H}_i^{\text{spin}} &= - \left(2 \sum_{j \neq i} (J_{ij}/(g_S\mu_B)) \mathbf{S}_j \right) \cdot (g_S\mu_B \mathbf{S}_i) \\ &= -\mathcal{B}_{\text{eff}} \cdot \mathbf{m}_i, \end{aligned}$$

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.

for n spins per unit volume, giving

$$\begin{aligned}\mathcal{B}_{\text{eff}} &= 2 \frac{J}{g_S \mu_B} \frac{z \mathcal{M}}{n g_S \mu_B} \\ &= \frac{2zJ}{n g_S^2 \mu_B^2} \mathcal{M}.\end{aligned}$$

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.

10.6.4 The mean field approximation

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

Then

$$\begin{aligned}\mathcal{B}_{\text{eff}} &= \left(2 \sum_{j=1}^z \frac{J}{g_S \mu_B} \mathbf{S}_j \right) \\ &= 2 \sum_{j=1}^z \frac{J}{g_S \mu_B} \frac{\mathbf{m}_j}{g_S \mu_B} \\ &= 2 \frac{J}{g_S \mu_B} \frac{z \langle \mathbf{m}_j \rangle}{g_S \mu_B}.\end{aligned}$$

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

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