PARAMAGNETS

From last week:-

$M$ directly proportional to $H$

$\chi$ small and positive ($\sim 10^{-3} - 10^{-5}$)

![Graph showing relationship between $M$ and $H$]

Also (for most PMs), $\chi \propto \frac{1}{T}$

WHY?
Langevin Localized Moment Model

- each atom has its own magnetic dipole moment
- the dipole moments DON'T interact with each other

A Classical theory

**zero field**

⇒ random alignment

a) (because of thermal energy)

```
H = 0
```

**apply field**

- reorients moments

b)

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H overcomes thermal randomization
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The effect is small because \( E = -M \cdot H \)

is small compared with \( kT \)!
Use Langevin theory to derive expression for $\Theta$:

- If there were no external field, the fraction of moments lying between angles $\Theta$ to $\Theta + d\Theta$ would be
  \[
  \frac{dA}{A} = \frac{2\pi r^2 \sin \Theta}{4\pi r^2} = \frac{1}{2} \sin \Theta d\Theta
  \]

- But energy depends on $\Theta$:
  \[
  E = -mH \cdot H = -mH \cos \Theta
  \]
  probability of having energy $E$ is $e^{-E/kT} = e^{mH \cos \Theta}/kT$

So, overall probability of magnetic moment making an angle between $\Theta$ and $\Theta + d\Theta$ is

\[
p(\Theta) = \frac{e^{mH \cos \Theta}/kT}{\pi \int e^{mH \cos \Theta}/kT \sin \Theta d\Theta}
\]
A moment, $m$, at an angle $\theta$ contributes $m \cos \theta$ to $M$.

\[ M = Nm \langle \cos \theta \rangle = Nm \int_0^\pi \cos \theta \rho(\theta) d\theta \]

\[ = Nm \left[ \coth \left( \frac{mH}{kT} \right) - \frac{kT}{mH} \right] \]

\[ M = Nm L \left( \frac{mH}{kT} \right) \]

$L$ is the Langevin function, which looks like this:

Large $\alpha$ $\implies$ Large $M$, i.e., magnetization greatest at high field, low temp.
What happened to $M \propto H / T$?

In general, $\alpha = \frac{m H}{kT}$ is small

(i.e. magnetic energy $\ll$ thermal energy)

so $Z(\alpha) = \frac{\alpha}{3} - \frac{\alpha^3}{45} + \ldots$

and (keeping just the first term)

$$M = \frac{N M \alpha}{3} = \frac{N m^2}{3k} \left\{ \frac{H}{T} \right\}$$

$$\Rightarrow \chi = \frac{M}{H} = C / T$$

Curie Law

$$C = \frac{N m^2}{3k}$$
Extension to include quantum mechanics

So far we have assumed that the magnetic dipole moment can take all possible orientations with respect to the applied magnetic field, whereas in reality it can have only discrete orientations because of spatial quantization. If we incorporate the quantization into the derivation of the total magnetization, we obtain:

\[ M = NgJ \mu_B \left( \frac{2J+1}{2J} \coth\left( \frac{2J+1}{2J} \alpha \right) - \frac{1}{2J} \coth\left( \frac{\alpha}{2J} \right) \right) \]  
\[ = NgJ \mu_B B_J(\alpha) \]  

(5.12)  
(5.13)

Where \( B_J(\alpha) \) is the Brillouin function, which is equal to the Langevin function in the limit that \( J \to \infty \). The Brillouin function can also be expanded in a Taylor series:

\[ B_J(\alpha) = \frac{J+1}{3J} \alpha - \frac{[(J+1)^2 + J^2](J+1)}{90J^3} \alpha + \ldots \]  

(5.14)

Keeping only the first term in the expansion, the expression for the susceptibility becomes

\[ \chi = \frac{Ng^2 J(J+1) \mu_B^2}{3kT} = \frac{C}{T} \]  

(5.15)

The overall form of the response is the same as in the classical case, but this time the proportionality constant, \( C \), is given by

\[ \frac{Ng^2 J(J+1) \mu_B^2}{3k} = \frac{NMeff^2}{3k} \]

where

\[ Meff = g \sqrt{3(J+1)} \mu_B \]

look familiar?

Remember from last lecture:

- CPT. of mag. mmt. along field dir.? = \( g M_{s} / \mu_B \)
- total mag. mmt. = \( g \sqrt{3(J+1)} \mu_B \)
Why are some diatomic gases paramagnetic?

*eg.* oxygen, $O_2 \ (1s)^2 \ (2s)^2 \ (2p)^4$

If these were reversed, $O_2$ would be DIAMAGNETIC.

$O_2$: Ti bonds - weakly bonding or antibonding.

$\sigma$ bond - strongly bonding or antibonding.
Does it work? (from S. Chikazumi, Physics of Ferromagnetism, OUP (1997)).

YES Except that saturation magnetizations correspond to SPIN ONLY angular momenta.
(OK for Gd$^{3+}$, Fe$^{3+}$ - these have $L=0$)

![Image of graph](image-url)

**Fig. 5.10.** Magnetization curves of paramagnetic salts: I potassium chromium alum, II ferric ammonium alum, and III gadolinium sulfate octahydrate. (After W. E. Henry')

In Cr$^{3+}$ there is QUENCHING of the orbital angular momentum - the E field from the surrounding ions causes the orbitals to couple strongly to the lattice : they can't reorient towards $H$. 

Phys. Rev. 88, 559 (1952)
5.3 Quenching of orbital angular momentum

The total magnetization in a paramagnet depends on the magnetic moment, $m$, of the constituent ions. Once we know the $g$-factor of an ion, and the $J$ value, we can calculate its magnetic moment - it's just $m = g \mu_B \sqrt{J(J+1)}$. (This after all was the whole purpose of Chapter 3!) In general this formula works very well for paramagnetic salts, even though the ions have formed into crystals and are no longer 'free'. As an example we show the calculated and experimental values for the rare earth ions in Table 5.1. In all cases the agreement is very good.

However for the first row transition metals, things do not work out quite so nicely, and in fact the measured magnetic moment is closer to that which we would calculate if we completely ignored the orbital angular momentum of the electrons. Table 5.2 lists the measured magnetic moments, and the calculated values using the total and spin-only angular momenta. It's clear that the spin-only values are in much better agreement with experiment than the values calculated using the total angular momentum. This phenomenon is known as quenching of the orbital angular momentum, and is a result of the electric field generated by the surrounding ions in the solid. Qualitatively, these electric fields cause the orbitals to be coupled strongly to the crystal lattice, so that they are not able to re-orient towards an applied field, and so do not contribute to the observed magnetic moment. The spins, on the other hand are only weakly coupled to the lattice - the result is that only the spins contribute to the magnetization process, and, consequently, to the resultant magnetic moment of the specimen.

<table>
<thead>
<tr>
<th>ion</th>
<th>configuration</th>
<th>$g\sqrt{J(J+1)}$</th>
<th>$g\sqrt{S(S+1)}$</th>
<th>$m_{\mu_B}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ti$^{3+}$, V$^{4+}$</td>
<td>3d$^1$</td>
<td>1.55</td>
<td>1.73</td>
<td>1.8</td>
</tr>
<tr>
<td>V$^{3+}$</td>
<td>3d$^2$</td>
<td>1.63</td>
<td>2.83</td>
<td>2.8</td>
</tr>
<tr>
<td>Cr$^{3+}$, V$^{2+}$</td>
<td>3d$^3$</td>
<td>0.77</td>
<td>3.87</td>
<td>3.8</td>
</tr>
<tr>
<td>Mn$^{3+}$, Cr$^{2+}$</td>
<td>3d$^4$</td>
<td>0.00</td>
<td>4.90</td>
<td>4.9</td>
</tr>
<tr>
<td>Fe$^{3+}$, Mn$^{2+}$</td>
<td>3d$^5$</td>
<td>5.92</td>
<td>5.92</td>
<td>5.9</td>
</tr>
<tr>
<td>Fe$^{2+}$</td>
<td>3d$^6$</td>
<td>6.70</td>
<td>4.90</td>
<td>5.4</td>
</tr>
<tr>
<td>Co$^{2+}$</td>
<td>3d$^7$</td>
<td>6.63 $\mu_B$</td>
<td>3.87 $\mu_B$</td>
<td>4.8</td>
</tr>
<tr>
<td>Ni$^{2+}$</td>
<td>3d$^8$</td>
<td>5.59</td>
<td>2.83</td>
<td>3.2</td>
</tr>
<tr>
<td>Cu$^{2+}$</td>
<td>3d$^9$</td>
<td>3.55</td>
<td>1.73</td>
<td>1.9</td>
</tr>
</tbody>
</table>

Table 5.2: Calculated and measured effective magnetic moments for the first row transition metal ions.

<table>
<thead>
<tr>
<th>ion</th>
<th>configuration</th>
<th>$g\sqrt{J(J+1)}$</th>
<th>$m_{\mu_B}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ce$^{3+}$</td>
<td>4f$^1$5s$^2$5p$^6$</td>
<td>2.54</td>
<td>2.4</td>
</tr>
<tr>
<td>Pr$^{3+}$</td>
<td>4f$^2$5s$^2$5p$^6$</td>
<td>3.58</td>
<td>3.5</td>
</tr>
<tr>
<td>Nd$^{3+}$</td>
<td>4f$^3$5s$^2$5p$^6$</td>
<td>3.62</td>
<td>3.5</td>
</tr>
<tr>
<td>Pm$^{3+}$</td>
<td>4f$^4$5s$^2$5p$^6$</td>
<td>2.68</td>
<td>-</td>
</tr>
<tr>
<td>Sm$^{3+}$</td>
<td>4f$^5$5s$^2$5p$^6$</td>
<td>0.84</td>
<td>1.5</td>
</tr>
<tr>
<td>Eu$^{3+}$</td>
<td>4f$^6$5s$^2$5p$^6$</td>
<td>0.00</td>
<td>3.5</td>
</tr>
<tr>
<td>Gd$^{3+}$</td>
<td>4f$^7$5s$^2$5p$^6$</td>
<td>7.94</td>
<td>8.1</td>
</tr>
<tr>
<td>Tb$^{3+}$</td>
<td>4f$^8$5s$^2$5p$^6$</td>
<td>9.72</td>
<td>9.1</td>
</tr>
<tr>
<td>Dy$^{3+}$</td>
<td>4f$^9$5s$^2$5p$^6$</td>
<td>10.63</td>
<td>10.1</td>
</tr>
<tr>
<td>Ho$^{3+}$</td>
<td>4f$^{10}$5s$^2$5p$^6$</td>
<td>10.60</td>
<td>10.1</td>
</tr>
<tr>
<td>Er$^{3+}$</td>
<td>4f$^{11}$5s$^2$5p$^6$</td>
<td>9.59</td>
<td>9.1</td>
</tr>
<tr>
<td>Tm$^{3+}$</td>
<td>4f$^{12}$5s$^2$5p$^6$</td>
<td>7.57</td>
<td>7.1</td>
</tr>
<tr>
<td>Yb$^{3+}$</td>
<td>4f$^{13}$5s$^2$5p$^6$</td>
<td>4.54</td>
<td>4.1</td>
</tr>
</tbody>
</table>

Table 5.1: Calculated and measured effective magnetic moments for the rare earth ions.
5.2 The Curie-Weiss Law

In fact many paramagnetic materials do not obey the Curie Law which we just derived, but instead follow a more general temperature dependence given by the Curie-Weiss law:

\[ \chi = \frac{C}{T - \theta} \]  (5.16)

Paramagnets which follow the Curie-Weiss law undergo spontaneous ordering and become ferromagnetic below some critical temperature, \( T_c \), (which we'll see later is for all practical purposes equal to \( \theta \)).

In our derivation of the Curie law we assumed that the localized atomic magnetic moments do not interact with each other at all - they are just reoriented by the applied magnetic field. Weiss explained the observed Curie-Weiss behavior by postulating the existence of an internal interaction between the localized moments which he called a "molecular field". He did not speculate as to the origin of his molecular field, beyond suggesting that it is a mutual interaction between the electrons which tends to align the dipole moments parallel to each other. (We can't really criticize Weiss for this - remember that the electron had been discovered only 10 years earlier, and quantum mechanics hadn't been 'invented' yet!)

Weiss assumed that the intensity of the molecular field is directly proportional to the magnetization:

\[ H_w = \gamma M \]  (5.17)

where \( \gamma \) is called the molecular field constant. So the total field acting on the materials is

\[ H_{tot} = H + H_w. \]  (5.18)

We just derived

\[ \chi = \frac{M}{H} = \frac{C}{T} \]  (5.19)

so, replacing \( H \) by \( H_{tot} \)

\[ \frac{M}{H + \gamma M} = \frac{C}{T} \]  (5.20)

or

\[ M = \frac{CH}{T - C\gamma}. \]  (5.21)

Therefore

\[ \chi = \frac{M}{H} = \frac{C}{T - \theta} \]  (5.22)

the Curie-Weiss law!

When \( T = \theta \) there is a divergence in the susceptibility, which corresponds to the phase transition to the spontaneously ordered phase. A positive value of \( \theta \) indicates that the molecular field is acting in the same direction as the applied field, and tending to make the elementary magnetic moments align parallel to one another and to the applied field. This is the case in a ferromagnetic material.

We can estimate the size of the Weiss molecular field. Below the critical temperature, \( T_c \), (also called the Curie temperature), paramagnetic materials exhibit
ferromagnetic behavior. Above $T_c$, the thermal energy outweighs $H_m$, and the ferromagnetic ordering is destroyed. Therefore at $T_c$, the interaction energy, $\mu_B H_m$, must be approximately equal to the thermal energy, $kT_c$. So $H_m \approx \frac{kT_c}{\mu_B} \approx \frac{10^{-16} \cdot 10^6}{10^8} \approx 10^4 Oe$.

This is extremely large! In the next Chapter we will apply Weiss’s molecular field theory below the Curie temperature to understand the ferromagnetic phase, and we will discuss the origin of the molecular field.

$$E = -M \cdot H \approx M_B H_m = kT_c \text{ at Curie temp.}$$

What does this $X$ look like?

$X$ diverges @ $T_c$

$X = M/H$ so this means that an infinitesimally small applied field produces a large magnetization.

This is the temperature at which the material spontaneously orders!
Uses of PMs

- alloyed with DMs $\Rightarrow$ zero X

- in production of low Ts
  1. cool w. liquid He, then $x = \frac{MH}{kT}$
     no magnetization is saturated in an applied field

  2. turn off H slowly - spins start to randomize but must do work against the remaining field - they use their thermal energy to do this.

    $\therefore T \downarrow \to \sim \frac{1}{1000} \text{s of a degree}$

- Fundamental Physics - more straightforward than FMs.
PAULI PARAMAGNETISM

In metals, $\chi$ is INDEPENDENT of $T$
- a result of energy band formation

Band Formation in Sodium:

- atoms move closer together
- filled orbitals $\Rightarrow$ filled bands
- partially occupied $3s$ orbital $\Rightarrow$ partially occupied overlapping $3s/3p$ band

$E_F$ - Fermi level

Filled levels:
- $3p$
- $3s$
- $2p$
- $2s$

Empty levels:
- $1s$

Broad bands

Narrow bands

![Diagram showing band formation in sodium with overlapping energy levels and Fermi level.](image-url)
Look at the upper, partially occupied band:

No external field - band energies for ↑ + ↓ spin e⁻s are the same

\[ E \]

\[ E_F \]

Up Spin  Down Spin

\[ H=0 \]

\[ \downarrow \]

NO NET MAGNETIC MOMENT

Apply \( H - e⁻\)'s with magnetic moment \( \parallel \) applied field have lower energy than anti-\( \parallel \) e⁻'s

\[ E \]

\[ E_F \]

Up Spin  Down Spin

\[ \downarrow \]

NET MAGNETIC MOMENT

N.B. Pauli principle \( \Rightarrow \) only 1↑ + 1↓ e⁻/per level

\( \therefore \) only e⁻'s close to \( E_F \) can flip their spins!
Free Electron Theory — valence e⁻s feel no potential (ion cores balance out other e⁻s)

Schrödinger Equation is \(-\frac{\hbar^2}{2m} \nabla^2 \Psi_k(r) = E_k \Psi_k(r)\)

Solve by cheating — confine e⁻s to cube of length \(L\)

Apply periodic BCs

\[ \Psi_k(r) = e^{i \mathbf{k} \cdot \mathbf{r}} \]

\[ E_k = \frac{\hbar^2 \mathbf{k}^2}{2m} \quad \left( \mathbf{k}_x, \mathbf{k}_y, \mathbf{k}_z \right) = \pm \frac{2\pi n}{L} \]

Actually we need the number of e⁻s near \(E_f\) which are able to reverse spin. The density of states
We just showed that the energy of a particular k-state is given by $E = \frac{\hbar^2}{2m} k^2$. In particular the Fermi energy is given by $E = \frac{\hbar^2}{2m} k_f^2$, where $k_f$ is the wavevector of the highest filled state. $k_f$ lies on a sphere of volume $\frac{4}{3} \pi k_f^3$, within which all states are filled. Now we just showed that the components of the k-vector, $k_x, k_y$ and $k_z$ are quantized in multiples of $\frac{2\pi}{L}$. So the volume occupied by a single quantum state in k-space must be $\left(\frac{2\pi}{L}\right)^3$. Therefore the total number of electrons, which is equal to twice the number of occupied orbitals (one electron each of up and down-spin), is given by

$$N = \frac{\text{volume of Fermi sphere}}{\text{volume per k-state}} \times 2 \quad \text{for } \uparrow + \downarrow$$

(5.27)

$$= \left(\frac{4}{3} \pi k_f^3\right) \times 2$$

(5.28)

$$= \frac{V}{3\pi^2} k_f^3$$

(5.29)

$$= \frac{V}{3\pi^2} \left(\frac{2mE_f}{\hbar^2}\right)^{\frac{3}{2}}$$

(5.30)

where $V$ is the volume of the crystal. The density of states, $D(E)$ is defined as the derivative of the number of electron states with respect to energy. So differentiating the above expression gives us

$$D(E_f) = \frac{V}{2\pi^2} \left(\frac{2m}{\hbar^2}\right)^{\frac{3}{2}} E_f^{\frac{1}{2}}$$

(5.31)

The number of electronic states per unit energy range is therefore proportional to the square root of the energy, as shown in Figure 5.7 (a). We can simplify the expression by substituting for $N$ to obtain

$$D(E_f) = \frac{3}{2} \frac{N}{E_f}$$

(5.32)

This is the result we will use in the next Section when we calculate the susceptibility of the free electron gas. So next let's use this expression for the density of states to derive the susceptibility of our Pauli paramagnet.
zero field

applied field
5.4.3 Susceptibility of Pauli paramagnets

We saw in Chapter 3 that a single free electron, with only spin angular momentum, has a magnetic moment along the field direction of one Bohr magneton. (Remember, \( m = g_e \mu_B m_s = \mu_B \). Also, the application of a magnetic field will change the energy of the electron by an amount \( \mu_B \cos \theta \) where \( \theta \) is the angle between the axis of the magnetic moment and the applied field. So a spin parallel to the field will be lowered in energy by an amount \( \mu_B H \), and one antiparallel to the field will be increased in energy by \( \mu_B H \). Thus a magnetic field changes the density of states in a free electron gas as shown in Figure 5.7 (b).

There is a spill-over of electrons from down-spin to up-spin until the Fermi levels for up- and down-spin are equal (and in fact very close to the original Fermi level, \( E_f \)). The zero of energy for the up spin density of states is at \(-\mu_B H\) and for the down-spin density of states at \(+\mu_B H\). Therefore the total number of up-spin electrons is then given by

\[
\frac{1}{2} \int_{-\mu_B H}^{E_f} D(E + \mu_B H) dE
\]  

and of down-spin electrons:

\[
\frac{1}{2} \int_{+\mu_B H}^{E_f} D(E - \mu_B H) dE
\]  

(The \( \frac{1}{2} \) is because only 1 electron occupies an up- or down-spin state, and the density of states was defined for two electrons per orbital).

The net magnetic moment, \( M \), is the number of up-spin electrons minus the number of down-spin electrons, multiplied by the moment per spin, \( \mu_B \):

\[
M = \frac{\mu_B}{2} \left[ \int_{-\mu_B H}^{E_f} D(E + \mu_B H) dE - \int_{+\mu_B H}^{E_f} D(E - \mu_B H) dE \right].
\]  

(5.35)

Changing variables gives

\[
M = \frac{\mu_B}{2} \int_{E_f - \mu_B H}^{E_f + \mu_B H} D(E) dE
\]  

(5.36)

The integration is a strip of width \( 2\mu_B H \) centered around \( E_f \). This area is \( 2\mu_B H D(E_f) \), so the net magnetic moment in the direction of the field is given by

\[
M = \mu_B^2 H D(E_f)
\]  

(5.37)

where \( D(E_f) \) is the density of states at the Fermi level, which we derived earlier:

\[
D(E_f) = \frac{3N}{2E_f}
\]  

(5.38)

So the susceptibility,

\[
\chi = \frac{M}{H} = \frac{3N\mu_B^2}{2E_f}
\]  

(5.39)

which is independent of temperature! Remember that there is also a diamagnetic contribution to the susceptibility, which it turns out is one-third of the Pauli paramagnetism. Thus the total susceptibility of a metal which fits the free-electron gas model is

\[
\chi = \frac{\mu_B^2 N}{E_f}.
\]  

(5.40)