Physics 551 Lecture #30

Title: Paramagnetism and Diamagnetism

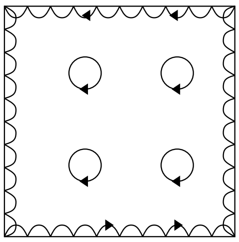
A discussion of the types a magnetism follows naturally from our previous discussion on the interaction between "free" electrons and a magnetic field. So far we have enumerated two types of response of solids due to the application of a magnetic field (i.e. Landau Levels and Pauli susceptibility). We have also mentioned what is meant by a magnetic susceptibility

$$\vec{H}\chi \equiv \vec{M} \ \ \text{(cgs)} \qquad \vec{H} \equiv \text{magnetic intensity}$$
$$\vec{B} = \vec{H} + 4\pi\vec{M} \qquad \vec{M} \equiv \text{magnetization} \ \rightarrow \ \text{net magnetic dipole moment/unit volume}$$
$$\vec{B} = \mu\vec{H} = (1+4\pi\chi)\vec{H} \qquad \mu \equiv \text{magnetic permeability} \ = (1+4\pi\chi)$$

Unless a material is isotropic and $\vec{M}||\vec{H}$, then χ is a tensor (Matrix)
By definition, a material is said to be *diamagnetic* if $\chi < 0$ and
paramagnetic if $\chi > 0$ (This also assumes that if $\vec{H} = 0$, then $\vec{M} = 0$)
Since $\chi_{\text{pauli}} > 0$, it is paramagnetic.

Metals also exhibit it diamagnetism. There are two identifiable sources for this diamagnetism, the conduction electrons and the core electrons.

For the conduction electrons we must invoke quantum mechanics. Classically there can be no net dipole moment for the circulating conduction electrons. The argument is this: A circulating electron is equivalent to a circulating current. This current possesses a dipole moment $\mu = IA$ where A is the area of the loop.



In a classical system, the net dipole moment is zero because the $(IA)_{\text{clockwise}} = (IA)_{\text{counterclockwise}}$.
Quantum Mechanically: Since the electron state energies increase with increasing magnetic field,

$$E_{p,z} \ = \ \frac{\hbar^2}{2m}k_z^2 \ + \ \hbar\omega_c(p+1/2) \ \ \text{with} \ \ \omega_c = \frac{eB}{mc} \ \ \text{cgs},$$

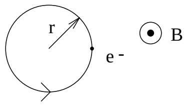
the system energy increases. Thus there should be a diamagnetic response.

$$\chi_{\text{Metal}} = -\frac{\mu_0 n \mu_B^2 m e^2}{2\epsilon_F m^{*2}}$$

The math is complicated but this information is included for completeness.

Core electron diamagnetism: (This can be done either classically or quantum mechanically).

The dipole moment $\mu = \text{current} \times \text{area}$



$\mu = \frac{dQ}{dt}\,\pi r^2$

$\mu = -\frac{e}{\frac{2\pi}{\omega}}\,\pi r^2 = -\frac{e\omega r^2}{2}$

$\mu = -\frac{e}{2m}(m\omega r^2) = -\frac{e}{2m}\,L \quad (L = \text{ angular momentum})$

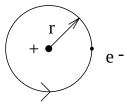
$\vec{\mu} = -\frac{e}{2m}\,\vec{L}$

The magnetic field exerts a torque so

$$\frac{d\vec{L}}{dt} = \vec{\mu} \times \vec{B} \Longrightarrow \frac{d}{dt}\left(\frac{2m\vec{\mu}}{-e}\right) = \vec{\mu} \times \vec{B}$$

$$\begin{aligned} \text{If } \vec{B} \parallel \vec{z},\ \mu_x &= A\ \cos(\omega_L t),\ \mu_z = \text{const.} \\ \mu_y &= A\ \sin(\omega_L t) \quad \omega_L = \text{Larmor angular precession} \end{aligned}$$

Let us go back to our Bohr atom: $\omega_L = \frac{eB}{2mc}$



$\vec{F} = -\frac{e^2}{r^2}\,\hat{r} \pm -\frac{e}{c}(\vec{v} \times \vec{B}) \Longrightarrow (\frac{e^2}{r^2} \pm er\omega B) = m\omega^2 r$

$\pm$ depends on whether the orbit is CW or CCW

So $\omega^2 \pm -\frac{eB}{cm}\,\omega - \frac{e^2}{mr^3} = 0$

(SI) $\omega = \pm\frac{eB}{c2m} \pm \sqrt{\frac{e^2B^2}{4m^2c^2} + \omega_0^2} \qquad \omega_0^2 = \frac{4e^2}{mr^3}$

if B is small, $e^2B^2/4m^2c^2 << \omega_0^2$

choose $\pm\sqrt{\omega_0^2} \Longrightarrow \omega_0$

$$\omega \approx \omega_0 \pm \frac{eB}{2mc} \qquad \begin{array}{lll} \text{if counter} & \text{clockwise} & \omega = \omega_0 + \frac{eB}{2mc} \\ \text{if} & \text{clockwise} & \omega = \omega_0 - \frac{eB}{2mc} \end{array}$$

This gives an induced dipole moment over and above the intrinsic one. The net intrinsic dipoles cancel out but the induced one does not.

$$|\vec{\mu}|_{\text{induced}} = IA = -e\frac{\Delta\omega}{2\pi}\,\pi r^2 = -\frac{2}{2\pi}\left(\frac{eB}{2mc}\right)\pi r^2$$

For Z electrons in a spherically symmetric atom

$$< x^2 >=< y^2 >=< z^2 > \qquad < r^2 >=< x^2 > + < y^2 > + < z^2 >$$

$$< p^2 >=< x^2 > + < y^2 >$$

$$< p^2 >= \tfrac{2}{3} < r^2 >'$$

$$|\vec{\mu}|_{in} = -\frac{Ze^2B}{4mc} \; < p^2 >$$

$$\begin{aligned} \vec{B}\chi &= \vec{M} = N\vec{\mu} = -\frac{NZe^2}{6m}\,\vec{B} < r^2 > \\ \chi &= -\frac{NZe^2}{6mc} < r^2 > \quad \text{which is diamagnetic} \end{aligned}$$

The measured χ is a combination of all the susceptibilities. It is also possible for non-conduction electrons to exhibit paramagnetic susceptibilities. If there are unpaired spins, a solid will exhibit a net magnetic moment $\vec{\mu} = -g\mu_B\vec{J}$ where $\vec{J}$ = total angular momentum and g = g-factor

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

In this case we assume L=0, $m_J = \pm\frac{1}{2}$

$$g = 1 + \frac{3/4 + 3/4}{3/2} = 2 \qquad \vec{\mu} = \pm m_J\, g\, \mu_B$$

$U = \pm\vec{\mu}_B \cdot \vec{B}$, Note: we can safely ignore interactions between spins since the magnetic dipole moment falls with a 1/r^3 dependence. Since $m_J = \pm 1/2$, there are two possibilities, parallel to the magnetic field and anti-parallel to the magnetic field.

Thus the Boltzman factor has two $\exp(-E_{\text{state}}/k_BT)$ possibilities. So

$$\text{Probability}_\downarrow = \frac{e^{-\mu B/k_BT}}{e^{\mu B/k_BT} + e^{-\mu B/k_BT}}$$

$$\text{Probability}_\uparrow = \frac{e^{\mu B/k_BT}}{e^{\mu B/k_BT} + e^{-\mu B/k_BT}}$$

$$\text{Number}_\downarrow = N_{\text{Total}}P_\downarrow \quad , \quad \text{Number}_\uparrow = N_{\text{Total}}P_\uparrow$$

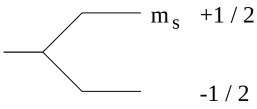
$$\vec{M} = (N_\downarrow - N_\uparrow)\vec{\mu} = N\vec{\mu}\ \tanh(\mu B/k_B T) = \chi\vec{H} \simeq \chi\vec{B}$$

If $\mu B << k_B T \qquad M \approx N\mu_B^2 B/k_B T \propto \frac{C}{T},\ C \equiv$ Curie constant.

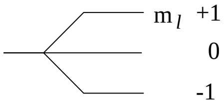
Hund's Rules

The magnetic behavior of transition-metal and rare-earth salts show an exceedingly complex paramagnetic response which is systematic. Thus using Hund's rules, the ground state can be determined.

$$|S| = \sqrt{s(s+1)}\,\hbar \qquad m_s = \pm 1/2$$



$$|L| = \sqrt{\ell(\ell+1)}\,\hbar \qquad m_\ell = 0, \pm 1, ..., \ell$$



$$E_s = \frac{e\hbar}{mc} m_s B = +2\mu_B \vec{S} \cdot \vec{B} \qquad E = -\vec{\mu} \cdot \vec{B}$$

$$E_\ell = \frac{e\hbar}{2mc}\, m_\ell B \quad \text{but orbital and spin angular momentum are coupled}$$

$$\vec{J} = \vec{L} + \vec{S} \quad \text{and} \quad E = -\mu B = g\frac{e\hbar}{2mc} m_j B$$

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

Rules:

(1) States of highest spin multiplicity are lowest in energy

(2) Maximum L consistent with (1) are lowest in energy

(3) $J =$ $|L - S|$ for shells less than half-filled
$|L + S|$ for shells more than half-filled

Transition Metals $\Longrightarrow$ d-shells   Rare-earths $\Longrightarrow$ f-shell

For example:

	$\uparrow$	3	
	$\uparrow$	2	$S = 1$
Praseodymium		1	$L = 5$
$2f$		0	$J = \|L - S\| = 4$
		-1	$g = 0.55$
		-2	
		-3	