Magnetism

Ch 11 (8th Edition) Diamagnetism ✓ & Paramagnetism 4

Ch 12 (") Ferromagnetism & Antiferromagnetism

chapters are different in 7th edition

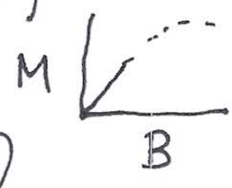
Electrons ⟨ spin, charge ⟩ $\Rightarrow$ magnetic moment (spin, orbital)

What we have already done!

Atomic Magnetism (Localized electrons!)

$\downarrow$

Magnetization $M = \chi B$ (for small B)



χ : magnetic susceptibility

Two types: Diamagnetism $\chi < 0 \Rightarrow$ B $\uparrow \downarrow$ M

Paramagnetism $\chi > 0 \Rightarrow$ B $\uparrow \uparrow$ M

Where do they come from!

- **Diamagnetism**: usually very small in magnitude

  Filled Shells

  $$\chi = -\frac{NZe^2}{6mc^2}\langle r^2\rangle \quad \sim 10^{-5} \sim 10^{-6} \ cm^3/mole$$

  (CGS unit)

  (Page 301 of the book)

- **Paramagnetism**

  $$\vec{\mu} = -\mu_B(\vec{L} + 2\vec{S}) \qquad \mu_B = \frac{e\hbar}{2mc} > 0$$

<u>Spin - orbit interaction</u> $\lambda \vec{L}\cdot\vec{S}$

Total angular momentum $\vec{J} = \vec{L} + \vec{S}$

Hund's Rules $\Rightarrow$ Lowest multiplet ${}^{2S+1}L_J$

$$\vec{\mu} = \text{magnetic moment} = -g_J \mu_B \vec{J}$$

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

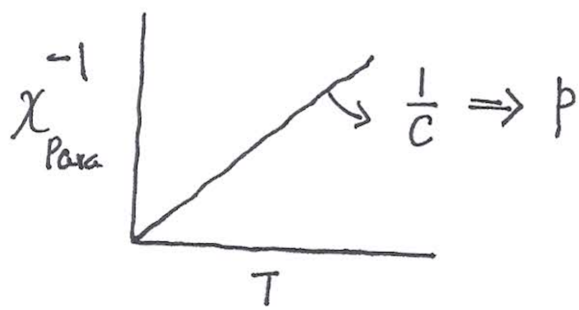
$$= 2 \quad (L=0) \text{ only spin}$$

$$= 1 \quad (S=0) \text{ Only orbital}$$

$$\chi_{para} = N \frac{g_J^2 \mu_B^2 J(J+1)}{3k_B T} = N \frac{p^2 \mu_B^2}{3k_B T} = \frac{C}{T}$$

(Curie Law) (Eqn. 22 page 304)

$$p = g_J \sqrt{J(J+1)}$$



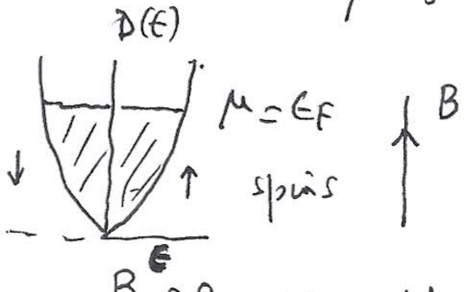
<u>Strong T- dependent</u>

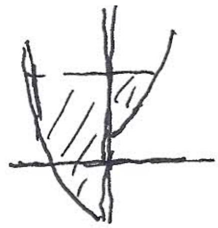
$\vec{B}$ } splitting of energy levels : each level has diff. magnetic moment.

How good this model is when the magnetic atoms are in a solid.

Pauli paramagnetism (Itinerant electrons + Pauli principle)

Comes only from electron spin.





Not to scale

$N_{\uparrow} = N_{\downarrow}$ $\qquad$ $N_{\downarrow} - N_{\uparrow} \neq 0$

$M \cancel{\propto} (N_{\uparrow} - N_{\downarrow}) = 0$ $\qquad$ $M \sim (N_{\uparrow} - N_{\downarrow}) \neq 0$

for $\mu_B B \ll \epsilon_F = \mu$

$$M = \chi_{Pauli} B$$

$$\chi_{Pauli} = \mu_B^2 D(\epsilon_F) = N \frac{3\mu_B^2}{2\epsilon_F}$$

T-independent : Small: $\sim 10^{-6} - 10^{-5}$ $cm^3/mole$

What's Next?

Q.1: What happens to atomic magnetism when we have a solid formed out of magnetic atoms or ions

Example: $FeCl_2 \rightarrow Fe^{2+} (Cl^{1-})_2$

Fe^{2+} ion: $3d^6$

(Gd) $EuCl_3 \rightarrow Eu^{3+} (Cl^{1-})_3$

$(Gd^{3+}) Eu^{3+}$ ion $(4f^7)\, 4f^6$

Ionic solids: d and f electrons are localized.

Q2: What happens to itinerant Pauli paramagnetism when we take interaction between electrons into account

Q3: ~~where~~ Where do Ferromagnetism & Antiferromagnetism come from!

Question 1

3d electrons Vs 4f electrons

Experiment

$p = g_J \sqrt{J(J+1)}$

$p_{sp} = 2\sqrt{S(S+1)}$ spin only

System	Config.	Ground mult.	p	p_{sp}	p_{exp}
Ti^{3+}	$3d^1$	$^2D_{3/2}$	1.55	1.73	1.8
Mn^{3+}	$3d^4$	$^5D_0$	0	4.90	4.9
Co^{2+}	$3d^7$	$^4F_{9/2}$	6.63	3.87	4.8

d-electrons

$J = L - S$ < half-filled

or

$L + S$ > half-filled

System	Config.	G. mult.	p	p_{exp}
~~Ce^{3+}~~	~~$^2F_{5/2}$~~	~~2~~		
Ce^{3+}	f^1	$^2F_{5/2}$	2.54	2.4
Gd^{3+}	f^7	$^8S_{7/2}$	7.94	8.0
Er^{3+}	f^{11}	$^4I_{15/2}$	9.59	9.5

f-electrons

Theory & Expt. agree quite well for f-electrons but NOT (in fact bad) for d-electrons.

Why! Quenching of orbital angular momentum (L) for d-electrons in solid (Crystal & electric field effect).

J is good +

$^{+}$ $4f^n, \underbrace{5s^2 sp^6}_{\text{shielding}}$

$-$

$+$ d $3d^n +$ $L \simeq 0$ S remains

$-$

Quenching of orbital angular momentum (also orbital mag. mom) in Crystalline electric field.

OR Atom or ion in a crystal.

Isolated atom

Central potential $V(r)$.

Look at p-states: $\psi_{n\ell m}(\vec{r}) = R_{n\ell}(r) Y_{\ell m}(\theta,\phi)$

$\ell = 1,\ m = 1, 0, -1 : \ Y_{1m}(\theta,\phi)$

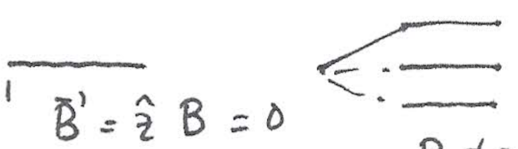
$\vec{L}^2$ and L_z are good quantum numbers

$\swarrow \hbar^2 \ell(\ell+1) \quad \longrightarrow \hbar m$

EXAMPLE

$\ell = 1$

$m = 1, 0, -1 \quad \vec{B} = \hat{z} B = 0$

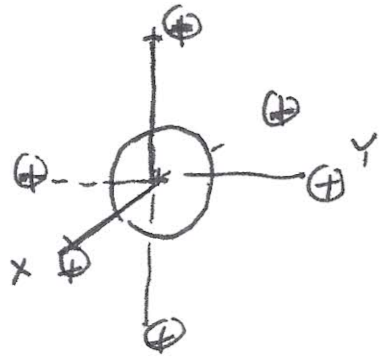


split: Each state is magnetic ($m=0$ not)

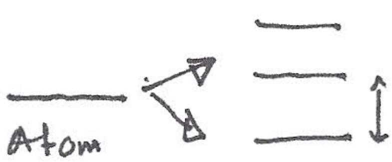
$\chi \sim \mu_{eff}^2 / k_B T$ Curie Law

(Ignore spin)

What happens if we put the atom in a crystal field



$$V_{tot} = \underset{\uparrow \text{atom}}{V(r)} + V_{cryst}(\vec{r})$$



large splitting ($\gg \mu_B B$)

$\boxed{B=0}$ Atom in crystal

$|x\rangle \equiv U_x(\vec{r}) = \frac{x}{r} f(r) \sim c_x (Y_{11} + Y_{1-1}) f(r)$

$|y\rangle = U_y(\vec{r}) = \frac{y}{r} f(r) \sim c_y (Y_{11} - Y_{1-1}) f(r)$

$|z\rangle = U_z(\vec{r}) = \frac{z}{r} f(r) \sim c_z Y_{10} f(r)$

$\langle x | \vec{L}^2 | x \rangle = \hbar^2 1(1+1) = 2\hbar^2$

$\langle x | L_z | x \rangle = 0$

Similarly

$\langle y | \quad | y \rangle$

$\langle z | \quad | z \rangle$

Now if we apply an external field $\vec{B} = \hat{z} B$

Nothing happens when $B \neq 0$

$-\mu_z B \approx - L_z B$

$\langle \chi | L_z | \chi \rangle = 0$

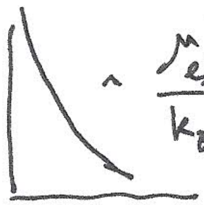
...

$B = 0$

<u>No orbital magnetism.</u>

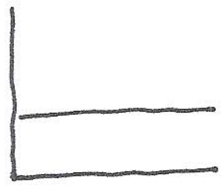
<u>BUT</u> <u>There are some special cases:</u> Van Vleck orbital <u>Paramagnetism</u>.

Recall: χ



$\sim \frac{\mu_{eff}^2}{k_B T}$ → ordinary Paramagnetism (spin + orbit)

χ



T

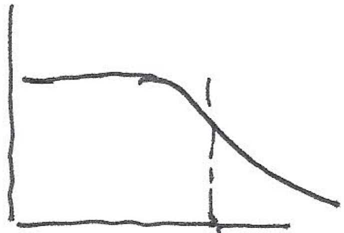
Pauli Paramagnetism

All non interacting moments.

Once in a while

Mixture of above 2

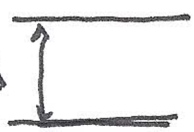
χ



T → $T_{cross-over} \sim 10-100\,K$.

<u>Physics</u>

$|s\rangle = \psi_s$



Δ

$|0\rangle\ \psi_0$

$\uparrow B \neq 0$

$\langle 0 | \mu_z | 0 \rangle = \langle s | \mu_z | s \rangle = 0$ (As in the quenched case)

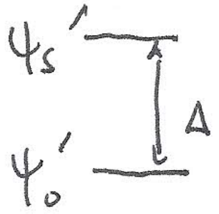
But $\langle s | \mu_z | 0 \rangle = \langle 0 | \mu_z | s \rangle^* = 0$

μ_z = magnetic moment operator

$-\mu_z B$ magnetic coupling.

$$\psi_0' = \psi_0 - \frac{\langle s|\mu_z B|0\rangle}{E_0 - E_s}\psi_s = \psi_0 + \frac{B}{\Delta}\langle s|\mu_z|0\rangle\,\psi_s$$

$$\psi_s' = \psi_s - \frac{\langle 0|\mu_z B|s\rangle}{E_s - E_0}\psi_0 = \psi_s - \frac{B}{\Delta}\langle 0|\mu_z|s\rangle\,\psi_0$$



magnetic coupling mixes ψ_0 and ψ_s.

Now: $$\langle\psi_0'|\mu_z|\psi_0'\rangle = \underbrace{\langle 0|\mu_z|0\rangle}_{=0} + \frac{2B}{\Delta}|\langle s|\mu_z|0\rangle|^2 + O(B^2)$$

$$\langle\psi_s'|\mu_z|\psi_s'\rangle = \underbrace{\langle\psi_s|\mu_z|\psi_s\rangle}_{=0} - \frac{2B}{\Delta}|\langle 0|\mu_z|s\rangle|^2 + O(B^2)$$

Each state becomes magnetic. What is χ?

(i) ~~$k_BT \gg \Delta$~~

$$M = N\left[\frac{1}{1+e^{-\Delta/k_BT}} - \frac{e^{-\Delta/k_BT}}{1+e^{-\Delta/k_BT}}\right]\frac{2B}{\Delta}|\langle s|\mu_z|0\rangle|^2$$

$$\chi = \frac{M}{B} = N\left[\frac{1-e^{-\Delta/k_BT}}{1+e^{-\Delta/k_BT}}\right]\frac{2}{\Delta}|\langle s|\mu_z|0\rangle|^2 \quad \cancel{B}$$

Two limiting Cases:

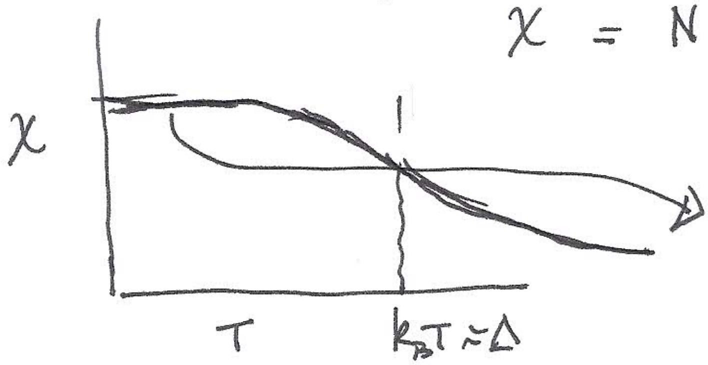
$k_BT \gg \Delta$

$$\chi \cong N\cdot\frac{\Delta}{2k_BT}\cdot\frac{2}{\Delta}\cdot|\langle s|\mu_z|0\rangle|^2$$

$$= N\cdot\frac{|\langle s|\mu_z|0\rangle|^2}{k_BT} = N\frac{\mu_{eff}^2}{k_BT} \quad \text{Curie Law}$$

$k_BT \ll \Delta$

$$\chi = N\frac{2|\langle s|\mu_z|0\rangle|^2}{\Delta} = N\cdot\frac{2\mu_{eff}^2}{\Delta} \quad \text{indep. of } T$$



Van Vleck Paramagnetism.

Conduction electron (or itinerant electron) ferromagnetism.

<u>T = 0</u> Non interacting electrons $\chi_{Pauli} = \mu_B^2 D(\epsilon_F)$

What happens if we bring in electron-electron interaction

$\uparrow \; \uparrow$ vs $\uparrow \downarrow$

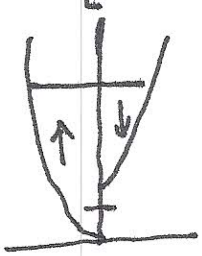
$\leftarrow \quad \rightarrow$

Kept apart by Pauli principle $\}$ Since electrons <u>repel</u>

$E_{\uparrow\uparrow} < E_{\uparrow\downarrow} \Rightarrow$ Exchange caused energy lowering.

So:

$B \neq 0$



E

$\Longrightarrow$ introduce Exchange effect

ϵ_F

$M \propto (N_\uparrow - N_\downarrow)$

M increases: So also χ_{Pauli}

$$\boxed{\chi_{Pauli} = \chi^0_{Pauli} / (1-\alpha)}$$

Exchange enhancement of Pauli susceptibility

α: Exchange enhancement parameter
Depends on strength of electron-electron interaction
Density of states at ϵ_F

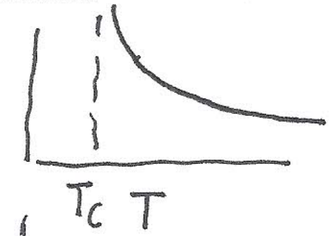
To derive this we need to use <u>Energy minimum</u> <u>Principle</u>.

Problem # 6 Chapter 11 : $\boxed{\alpha = \frac{3}{4} \cdot \frac{NV}{\epsilon_F}} \boxed{= \frac{1}{2} V D(\epsilon_F)}$

V = strength of el-el. interaction. $\sim \frac{1}{N}$
(EXPLAIN)

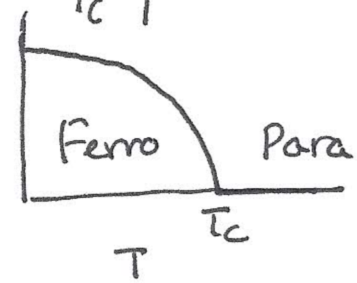
Ferromagnetism, Ferromagnetic Order.

Ferromag (Iron metal ...)



$\chi \to \infty$ as $T \to T_c{+}$

spontaneous magnetization



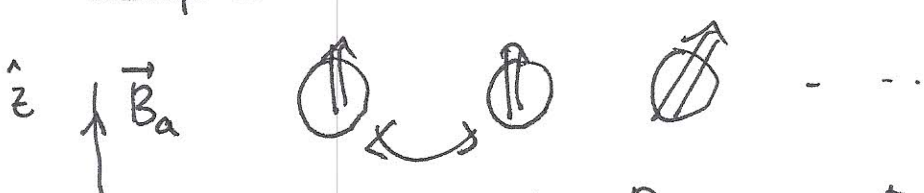
$$M_s = \lim_{B \to 0} M(B)$$

$$\chi \neq \frac{C}{T} \quad \text{Curie Law}$$

$$= \frac{C}{T - T_c} \quad T > T_c$$

T_c = Curie temperature

Simple theory



Interact through EXCHANGE FIELD $\vec{B}_E$

$T > T_c$ (Paramag. Phase)

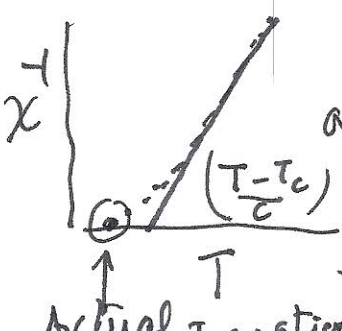
$$M = \chi_p (B_a + B_E)$$

χ_p is the usual paramag. susceptibility, $\frac{C}{T}$ (Curie law)

$$B_E = \lambda M \quad \text{(Mean field theory)}$$

$$M = \chi_p B_a + \chi_p \lambda M$$

$$M(1 - \chi_p \lambda) = \chi_p B_a$$



or $$\chi = \frac{M}{B_a} = \frac{\chi_p}{1 - \chi_p \lambda} = \frac{C/T}{1 - \frac{C}{T}\lambda} = \frac{C}{T - T_c}$$

Curie Weiss Law

Where $\boxed{T_c = C\lambda}$

$\vec{B}_E$ is called Weiss Molecular Field.