LECTURE 5

Note Title 9/17/2007

MAGNETIC PROPERTIES OF ATOMS AND IONS IN SOLIDS

Last time: n-electron atoms
classified using $\vec{L}$, $\vec{S}$, $\vec{J}$

$E(L, S, J)$ if spin-orbit effect is small

Russel-Saunders approximation

Hund's rules (empiric rules for electrons in multiple electronic configurations)

3 e^-

[↑ | ↑ | ↑] P ORB — I RULE MAXIMIZE SPIN

+1 0 −1

[↑ | ↑ |] 2 e^- — II RULE MAXIMIZE L

↓ $J = 1 - 1 = 0$

III RULE
$$\begin{cases} J = |L - S|, & N < 2\ell + 1 \\ J = L + S, & N > 2\ell + 1 \end{cases}$$

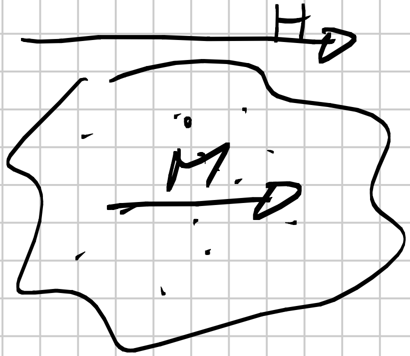
4 e^-

[↑↓ | ↑ | ↑] $S = 1 \quad L = 1 \Rightarrow J = 2$

Rules important for Magnetic properties of solids.

Magnetic properties of a Solid

FROM ASHCROFT-MERMIN CHAPT 31



$$M = \chi_M H$$ Magnetic Susceptibility

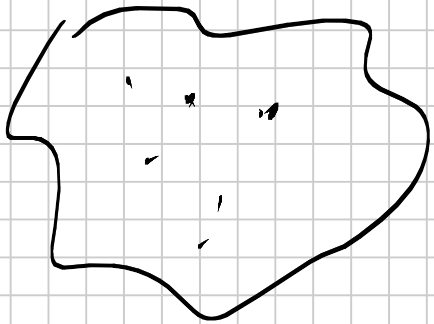
$$\text{Energy change} = E_0 = -\int M \cdot H \, dV$$

$$M = -\frac{1}{V}\frac{dE_0}{dH} \Rightarrow \chi_M = -\frac{1}{V}\frac{d^2 E_0}{dH^2}$$ at $T = 0$

$$E_0 \to \frac{\sum_n E_n e^{-\frac{E_M}{k_B T}}}{\sum_M e^{-\frac{E_M}{k_B T}}} \Rightarrow F$$ Free energy

$$M = -\frac{1}{V}\frac{dF}{dH} \qquad \chi_M = -\frac{1}{V}\frac{d^2F}{dH^2}$$

PARAMAGNETIC SALTS : IONS WITH PARTIALLY FILLED d OR f SHELLS



$Mn^{2+} \rightarrow (3d)^5$

$Mn \; [Ar] \; \cancel{(4s)^2} \; (3d)^5$

-2	-1	0	$+1$	$+2$
$\uparrow$	$\uparrow$	$\uparrow$	$\uparrow$	$\uparrow$

$\rightarrow \quad \vec{S}_{TOT} = \frac{5}{2}$

Atom or Ion in a H $\quad \uparrow H$

$H = \vec{\nabla} \times \vec{A}$

Kinetic energy

$$T_0 = \sum_i \frac{\vec{P}_i^{\,2}}{2m} \xrightarrow{\text{add } H} \sum_i \frac{\left(\vec{P}_i - \frac{e}{c}\vec{A}\right)^2}{2m} \Big\} \text{ orbital contribution}$$

$$\vec{A} = -\frac{1}{2}\,\vec{r} \times \vec{H}$$

$\mu_B = \frac{e\hbar}{2mc}$ Bohr Magneton

Spin - contribution $\mathcal{H}_{spin} = g\,\mu_B\,\vec{S}_{TOT} \cdot \vec{H}$

g = gironomagnetic factor of e^-, $g \sim 2$

without H

$$\mathcal{H} = \mathcal{H}^0 + \overbrace{\mu_B(\underline{\vec{L}} + g\,\underline{\vec{S}}) \cdot \vec{H}}^{\text{LINEAR IN } H} +$$

$$+ \overbrace{\frac{m}{2}\left(\frac{eH}{mc}\right)^2 \left[\sum_i \left(\frac{x_i}{2}\right)^2 + \left(\frac{y_i}{2}\right)^2\right]}^{\text{PROP TO } H^2}$$

ION WITH FULL SHELL

$L = 0$, $S = 0$ $\Rightarrow$ ONLY TERM $O(H^2)$

NOT ZERO. This term is small.

H adds positive contribution to energy

E_0

$$\chi = -\frac{N_{ions}}{V}\frac{\partial^2 E_0}{\partial H^2} < 0$$

Negative χ $\Rightarrow$ System is diamagnetic

Larmor diamagnetism. $NaCl$

$$\left.\begin{array}{ll} \underbrace{Na^+}_{[Ne]\,\cancel{(3s)^1}} & Cl^- \rightarrow [Ar] \end{array}\right\} \quad \underline{\text{Diamagnetic}}$$

MnO

$Mn \quad (4s)^2 (3d)^5$

$O \quad (2p)^4$

$Mn^{2+} \quad (3d)^5$

d

$l = 2$

-2	-1	0	$+1$	$+2$
$\uparrow$	$\uparrow$	$\uparrow$	$\uparrow$	$\uparrow$

$S = \frac{5}{2}$ $\qquad L = 0$

$$\mathcal{H} = \mu_B (\cancel{\vec{L}} + g\vec{S}) \cdot \vec{H} = g\mu_B \vec{S} \cdot \vec{H}$$

$$M = -\frac{N_{Mn}}{V} \frac{d}{dH} g\mu_B \frac{5}{2} H \Rightarrow M = -M_{Mn} 5 \mu_B$$

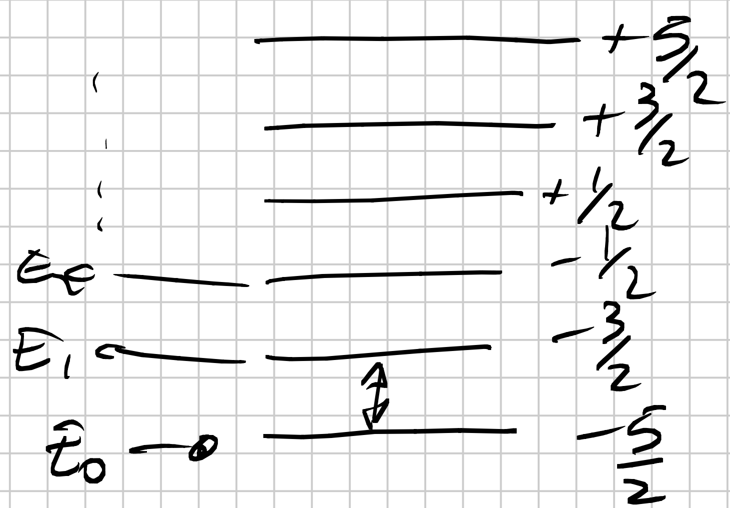
Calculate χ_M

E_m

$$F = \sum_m E_m e^{-\frac{E_m}{k_B T}} \Big/ \sum_m e^{-\frac{E_m}{k_B T}}$$

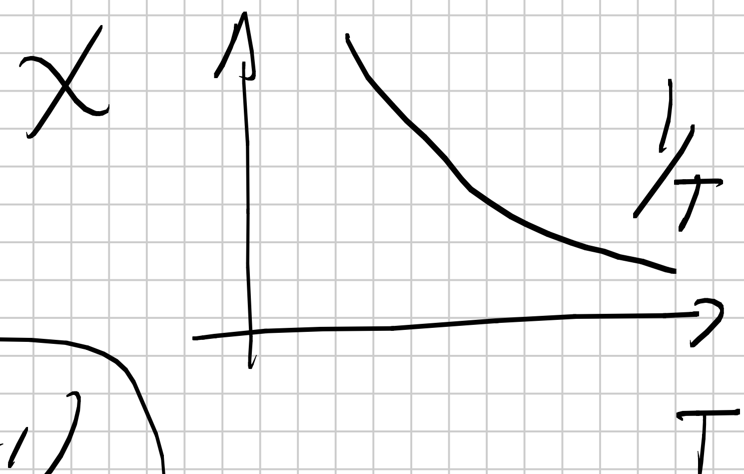
$$E_0 = - g \mu_B \frac{5}{2} H$$

$$E_1 = - g \mu_B \frac{3}{2} H$$



$$F(H, T)$$

$$k_B T \gg g \mu_B H$$



$$\boxed{\chi = \frac{N_{Mn}}{V} \frac{(g \mu_B)^2}{3} \frac{S(S+1)}{k_B T}}$$

$\chi > 0 \Rightarrow$ PARAMAGNETIC

$\chi \sim 1/T$ CURIE'S LAW

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