

Now as per Quantum Theory of paramagnetism the origin of magnetism can be explained by considering orbital and spin motions

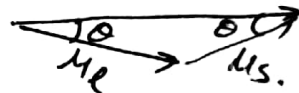
Now as per L-S Coupling

$$L = \sum_i \hbar i \quad \& \quad S = \sum_i s$$

$$\therefore \vec{J} = \vec{L} \oplus \vec{S}$$

here \vec{L} and \vec{S} are no longer constant by \vec{J} remains constant and the vectors \vec{L} and \vec{S} precess around \vec{J} .

Since μ_L and μ_S are tilted wrt μ ~~less~~ only at angle θ hence both precess about \vec{J} and only μ_J is observed.



$$\text{also } \vec{\mu}_J = g_J \mu_B \vec{J} \quad \text{--- (12)}$$

where $J = \sqrt{J(J+1)} \hbar = \text{total angular momentum}$

$g_J = \text{splitting factor}$

$$= 1 + \frac{J(J+1) + S(S+1) - L(L+1)}{2J(J+1)} \quad \text{--- (13)}$$

$$\mu_B = \text{Bohr magneton} = \frac{e\hbar}{2m}$$

Now energy gained in presence of magnetic field is

$$E = -\mu_J \cdot B = m_J g_J \mu_B B = \mu_B$$

$$\text{here } \mu = m_J g_J \mu_B$$

$m_J = \text{total magnetic quantum number}$
given as $m_J = m_L + m_S$ and has $(2J+1)$ values from $-J$ to $+J$

Let us consider a simple case (one e⁻ system)
 $S = L = l = 0$ and $S = \frac{1}{2}$.

$\therefore m_l = 0$ and $m_s = \pm \frac{1}{2} \Rightarrow m_j = m_l + m_s = \pm \frac{1}{2}$

also $g_j = 2$

Thus $\mu = m_j g_j \mu_B = \pm \mu_B$

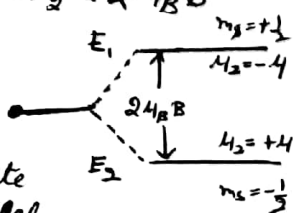
and $E = \pm \mu_B B$ — (14)

Thus the system has two energy states

$E_1 = +\mu_B B$ and $E_2 = -\mu_B B$

and difference $= E_1 - E_2 = 2\mu_B B$

In lower energy state μ is parallel while in upper energy state it is anti-parallel.



If now the system contains N atoms per unit volume out of which N_1 are parallel and N_2 are antiparallel to the field then

$N = N_1 + N_2$

as the values of N_1 & N_2 are given by Maxwell's Boltzmann statistics in thermal eq^m at temp T and in magnetic field B

$\frac{N_1}{N} = \frac{e^{+\mu_B B/KT}}{e^{+\mu_B B/KT} + e^{-\mu_B B/KT}}$

& $\frac{N_2}{N} = \frac{e^{-\mu_B B/KT}}{e^{+\mu_B B/KT} + e^{-\mu_B B/KT}}$

Resultant magnetic moment / volume.

$M = \mu (N_1 - N_2) = N\mu \frac{e^{+\mu_B B/KT} - e^{-\mu_B B/KT}}{e^{+\mu_B B/KT} + e^{-\mu_B B/KT}}$

$M = N\mu \tanh x$ where $x = \mu_B B/KT$ — (15)

Case I for $x \ll 1$, $\tanh x \approx x$ and we have (ie T is high & B is small)

$M = N\mu x = N\mu^2 B/KT = N m_j^2 g_j^2 \mu_B^2 B/KT$ — (16)

for $m_j = \frac{1}{2}$, $g_j = 2$ Thus

$M = N \mu_B^2 B/KT$ — (17)

also as $M = \frac{N \mu_B^2 B}{3KT}$ $\left[\mu_B = \frac{N \mu_B^2 B}{3KT} \right]$

These two results differ by a factor of $\frac{1}{3}$ but still our case is only a special case wherein $L = l = 0$ and $S = \frac{1}{2} \Rightarrow J = \frac{1}{2}$

Curie Law

In general in a magnetic field an atom with total angular momentum quantum number J has $(2J+1)$ equally spaced energy levels, in which case we have.

$M = N g_j J \mu_B B_j(x)$ — (18)

where $x = \mu_B B/KT = g_j J \mu_B B/KT$

also $B_j(x) = \frac{2J+1}{2J} \coth\left(\frac{2J+1}{2J} x\right) - \frac{1}{2J} \coth\left(\frac{x}{2J}\right)$

Called as Brillouin Function

Case II for $x \gg 1$ $\coth x = \frac{1}{x} + \frac{x}{3} + \frac{x^3}{45} + \dots$
 (Temp is low & B is high)

$\therefore B_j(x) = \frac{(J+1)x}{J} \cdot \frac{x}{3} = \frac{(J+1)g_j \mu_B B}{3KT}$

substituting it in eq (18)

$M = N J (J+1) g_j^2 \mu_B^2 B / 3KT$ — (20)

Thus Paramagnetic Susceptibility

$\chi_m = \frac{\mu_0 M}{B} = \frac{N \mu_0 \mu_B^2 g_j^2 J(J+1)}{3KT}$

$= \frac{\mu_0 N p^2 \mu_B^2}{3KT} = \frac{\mu_0 N \mu_{eff}^2}{3KT} = \frac{C}{T}$ — (21)

where $p^2 = g_j^2 J(J+1)$, $\mu_{eff}^2 = p^2 \mu_B^2 = g_j^2 J(J+1) \mu_B^2$
 as $\mu_{eff} = p \mu_B$ and thus p gives us the effective no. of Bohr magnetons.

and C is the const given as

$C = \frac{\mu_0 N \mu_B^2 g_j^2 J(J+1)}{3k}$

$C = N \mu_0 \left(\frac{e h g_j}{2m} \right)^2 \frac{J(J+1)}{3k}$

called as Curie's Constant

and the result of $\chi_m = \frac{C}{T}$ is called as Curie Law

Thus from eq (2) we get

$$\mu_{eff}^2 = \mu_j^2 = g_j^2 J(J+1) \mu_B^2$$

$$\text{or } \mu_j = g_j \mu_B \sqrt{J(J+1)} \quad \text{--- (23)}$$

FOR IONIC CRYSTALS

Now the property of paramagnetism is due to the existence of partly filled electronic shells. The paramagnetic compounds are those which contain Transition Group Elements i.e. rare earth group (incomplete 4f shell) and the iron group (incomplete 3d shell)

The prediction of above eq (21) i.e. χ_{para} wrt J is given by Hund's Rule. i.e.

$J = L - S$ for shells less than half full.

$J = 0$ for shells just half full.

$J = L + S$ for shells more than half full.

and these in general in good agreement with experimental results. But for iron group the agreement is not good for the reason that the partially filled 3d shell for these ions is the outermost shell and is exposed to the strong field due to the neighbouring ions in the crystal. This field is known as "CRYSTAL FIELD"

This breaks down the rotational symmetry and the total angular momentum $Q \cdot N_0(J)$ is less significant. Also the average values of L_z may be reduced to zero, the effect being known as Quenching of angular momentum

Thus $E = m_j g_j \mu_B B$ is to be replaced by

$$E = 2 m_s \mu_B B \quad [g_j = g_s = 2 \text{ for spin}]$$

$$E = 2 \frac{e \hbar}{2m} \cdot m B = \frac{e \hbar}{m} m_s B$$

#4.

Using the value of E and $m_s = \pm \frac{1}{2}$ we get

$$\chi_{para} = N \mu_0 \left(\frac{e \hbar}{m} \right) \frac{s(s+1)}{3kT} \quad \text{--- (24)}$$

This predicted result is in good agreement with experimental result.