6/2/25. Maybe

SPDF GHI ——— (Term) → (2S+1) symbol = (L)J. (2S+1 L J)

$(2L+1)(2S+1) = \sum_{J=|L-S|}^{L+S} (2J+1)$

$J = 3/2, 5/2, 7/2, 9/2$.

$(2\cdot 3/2+1)+(2\cdot 5/2+1)+(2\cdot 7/2+1)+(2\cdot 9/2+1)$.

$= 4+6+8+10 = (28)$

Which one is true for gs of particular ion?

⇒ Hund's rule.

1. Maximize S ✓
2. Minimize L. ✓
3. J = L − S, less than half filled
   J = L + S, more than half filled.

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

$P_i = \mu_{eff}/\mu_B$.

3D transition metal ions. (Magnetic gs for 3D ions using Hund's rule).

M	d shell (2) 1 0 -1 -2	ion(ex)	shell	S	L	J (L−S before ½ fill; L+S after ½ fill)	Term	$P_i (g_i\sqrt{J(J+1)})$	P_{exp}	$P_2 (2\sqrt{S(S+1)})$
1	↓	Ti^{3+}, V^{4+}	$3d^1$	1/2	2	3/2	$^2D_{3/2}$	1.55	1.7	1.73
2	↓ ↓	V^{3+}	$3d^2$	1	3	2	$^3F_2$	1.63	2.61	2.83
									Oxidation	
3	↓ ↓ ↓	Cr^{3+}, V^{4+}	$3d^3$	1+0+1/2 = 3/2	3	3/2	$^4F_{3/2}$	.77	3.8	3.87
4	↓ ↓ ↓ ↓	Mn^{3+}, Cr^{2+}	$3d^4$	2	2	0	$^5D_0$	0	4.82	4.9
5	↓ ↓ ↓ ↓ ↓ (Half filled)	Fe^{3+}, Mn^{2+}	$3d^5$	2+1/2 = 5/2	0	5/2	$^6S_{5/2}$	5.92	5.82	5.92

6	↑↓ ↑ ↑ ↑	Fe^{2+}	$3d^6$	2	2	4	$^5D_4$	6.7	5.36	4.98
7	↑↓ ↑↓ ↑	Co^{2+}	$3d^7$	3/2	3	9/2	$^4F_{9/2}$	6.63	4.9	3.87
8	↑↓ ↑↓ ↑↓	Ni^{2+}	$3d^8$	1	3	4	$^3F_4$	5.59	3.12	2.83
9	↑↓ ↑↓ ↑↓ ↑	Cu^{2+}	$3d^9$	1/2	2	5/2	$^2D_{5/2}$	3.55	1.83	1.73
10	↑↓ ↑↓ ↑↓ ↑↓	Zn^{2+}	$3d^{10}$ (perfectly non magnetic)	0	0	0	$^1S_0$	0	0	0

Reason for μ_s & μ_{exp} mismatch.

Due to crystal field effect there is quenching of orbital angular momentum (L). Thus, it matches μ_2 but not μ_1.

No μ_2 since no crystal field effect

Magnetic ground state for 4f ion using Hund's rule

Sl	4f Orbitation 3 2 1 0 -1 -2 -3	ion	4f^n	S	L	J	Term	μ_1	μ_{exp}	μ_2 (not req'd)
1	↓	Ce^{3+}	$4f^1$	1/2	3	5/2	$^2F_{5/2}$	2.54	2.51	
2	↓ ↓	Pr^{3+}	$4f^2$	1	5	4	$^3H_4$	3.58	3.56	
3	↓ ↓ ↓	Nd^{3+}	$4f^3$	3/2	6	9/2	$^4I_{9/2}$	3.62	3.7	
4	↓ ↓ ↓↓	Pm^{4+}	$4f^4$	2	6	4	$^5I_4$	2.68	—	
5	↓ ↓ ↓ ↓ ↓	Sm^{5+}	$4f^5$	5/2	5	5/2	$^6H_{5/2}$	0.85	1.74	
6			$4f^6$	3	3	0	$^7F_0$			
7			$4f^7$	7/2	0	7/2	$^8S_{7/2}$			

crystal field eff is unimportant for lanthanide series (rare earth ions) because their partially filled 4f shell lies deep inside the ion (beneath filled 5s & 5p).

On contrast, the partially filled d shell of transition metal ions are outermost electronic shells more strongly influenced by their crystalline env. thus exhibiting strong crystal field effect quenching of orbital momentum takes place (i.e $L \approx 0$).

$\therefore J = L$, $p = p_2 \Rightarrow g\sqrt{J(J+1)} = 2\sqrt{S(S+1)}$.

In 3D ions crystal field interaction is much stronger than the spin orbit interaction. crystal field is electric field originating / derived from neighbouring ions in the crystal (ligand field theory)

Role of d orbitals on central ion & their overlapping with the orbitals on surrounding ions.

The size & nature of crystal field depends on symmetry & env.

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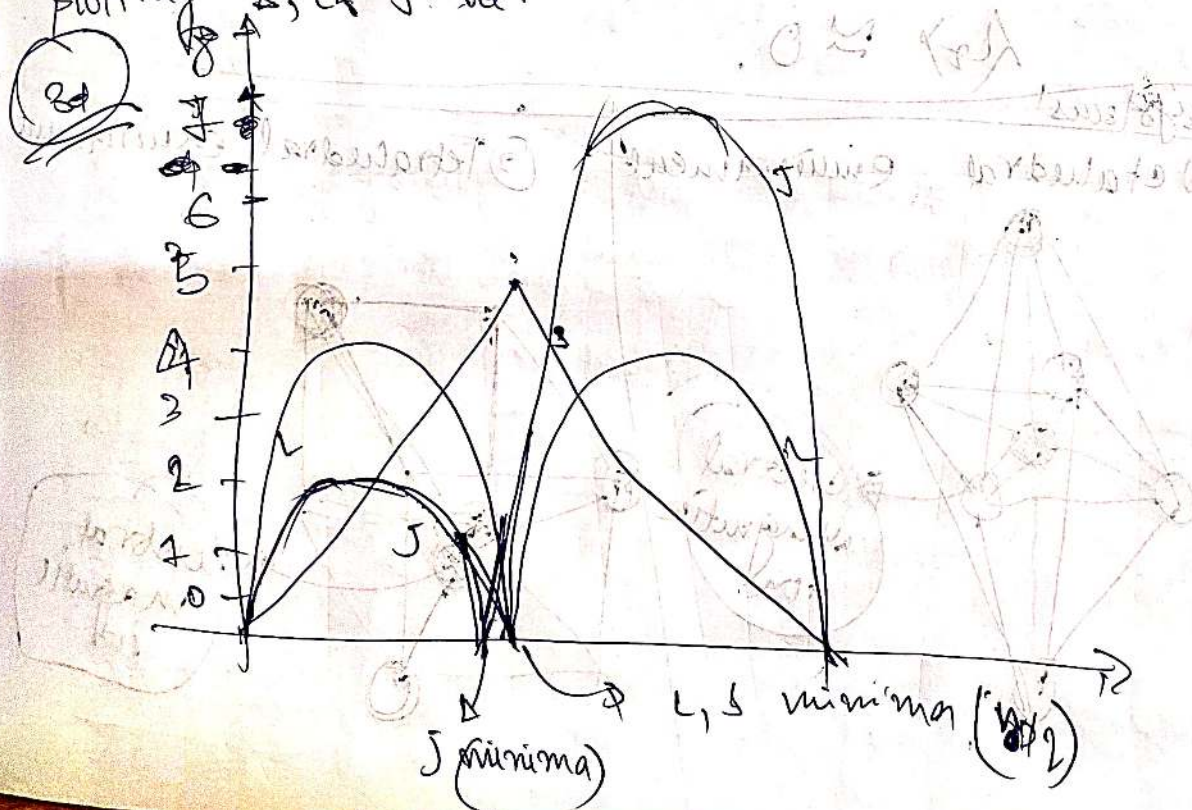
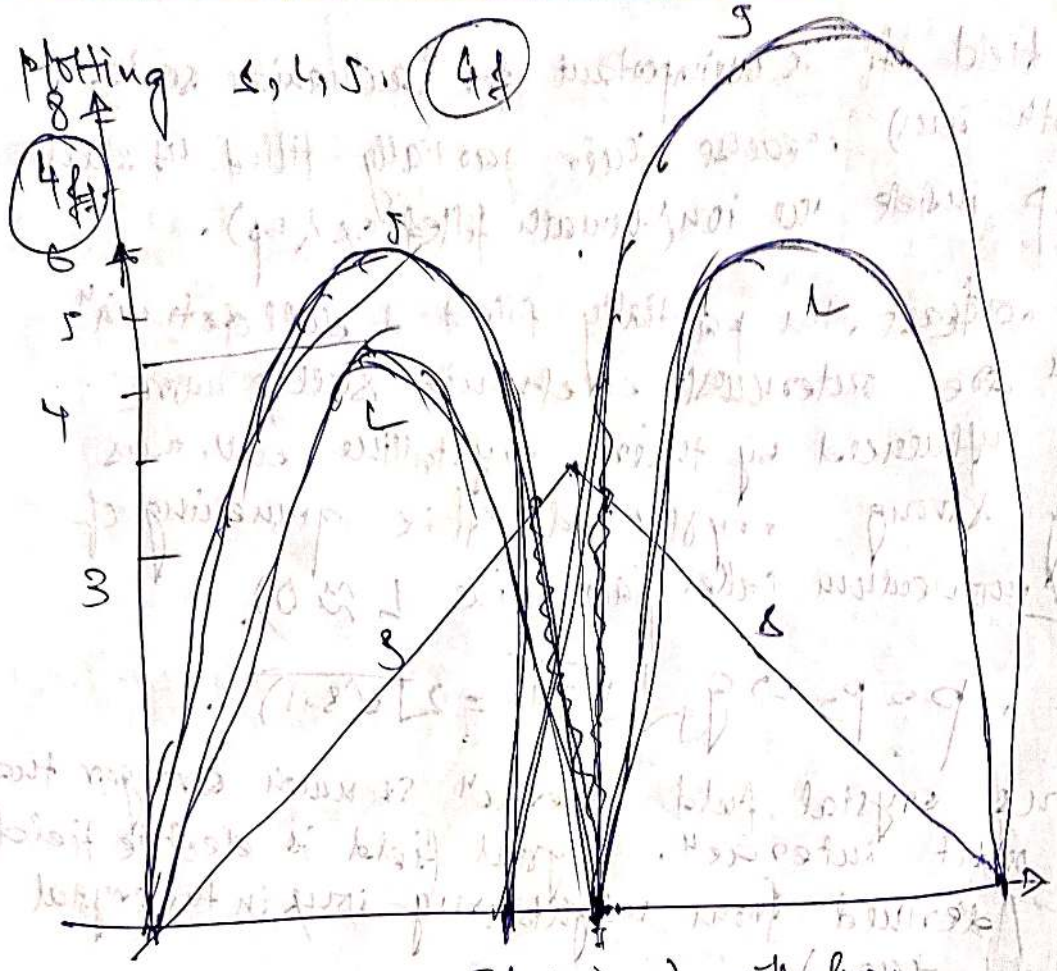
plotting E, L & J var.



plotting S, L, J. (4)



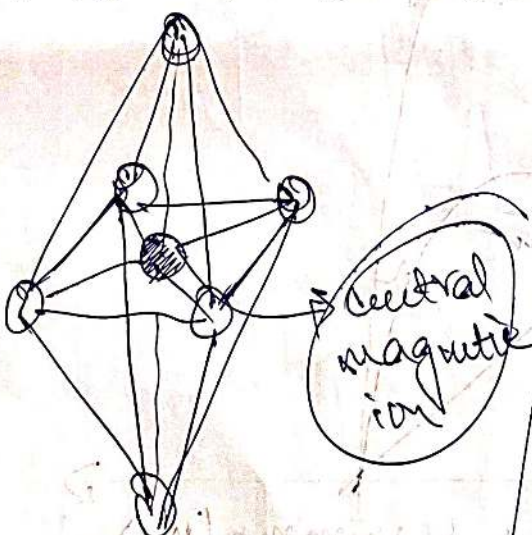
J (minima) diff from L & S minima.

A semiclassical interpretation of orbital L momentum quenching is that the orbital L momentum precesses in the crystal field so that its magnitude is unquenched but its components all average to zero.

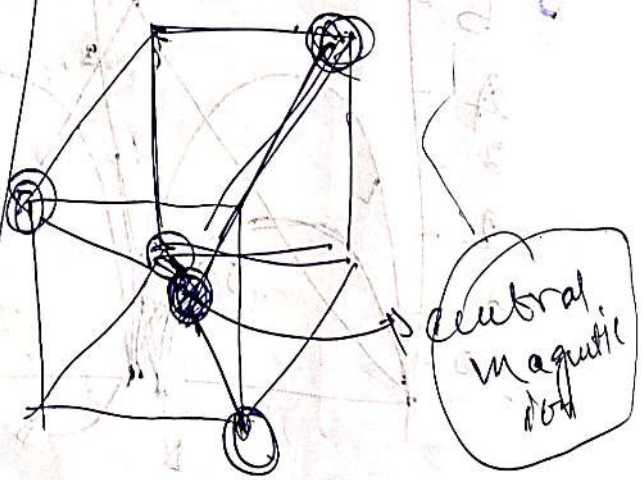
$\langle L_x \rangle \simeq 0$.

3d systems:

(1) Octahedral environment

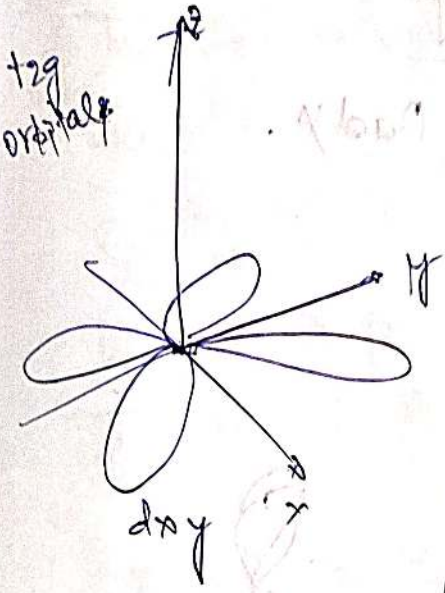


(2) Tetrahedral environment

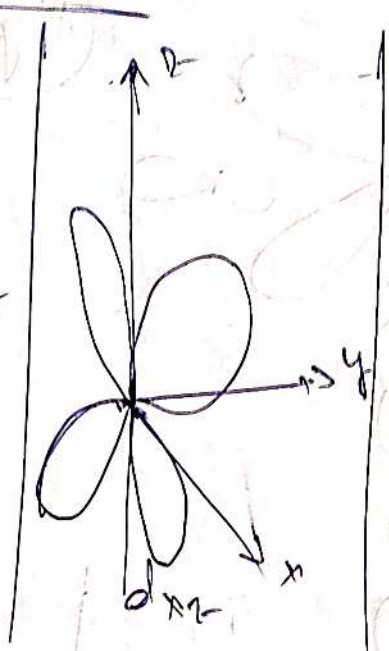


(3d) orbital shapes:

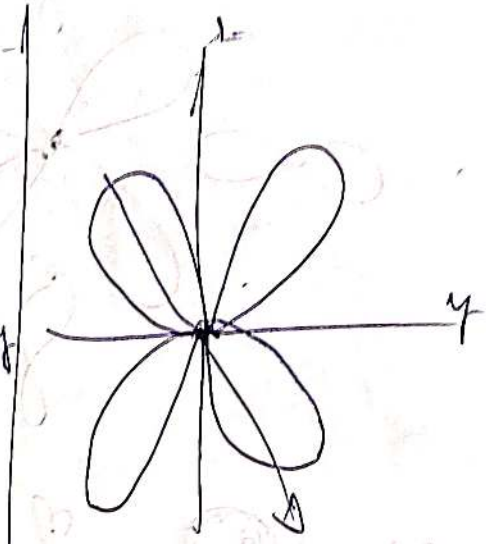
t2g orbitals



d_{xy}

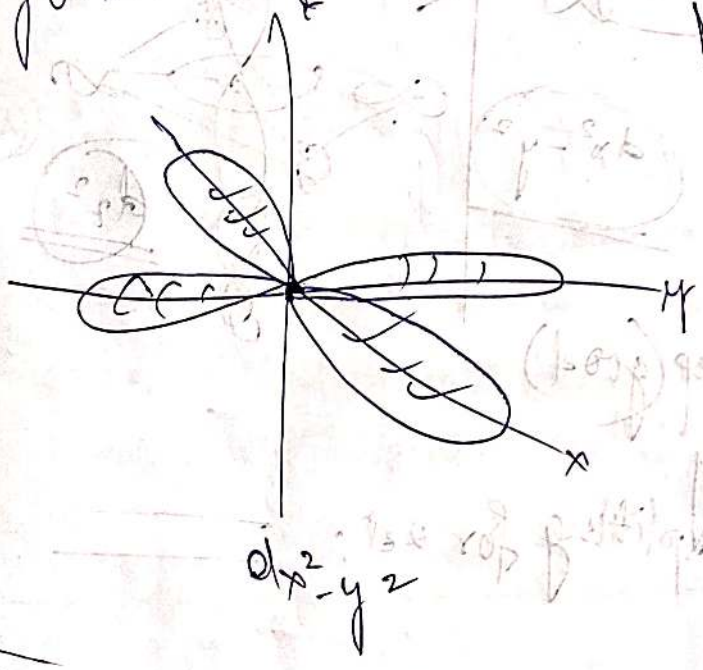


d_{xz}

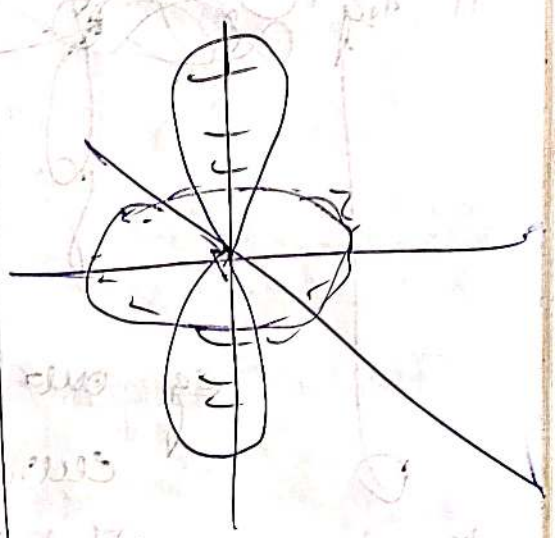


d_{yz}

eg orbitals:



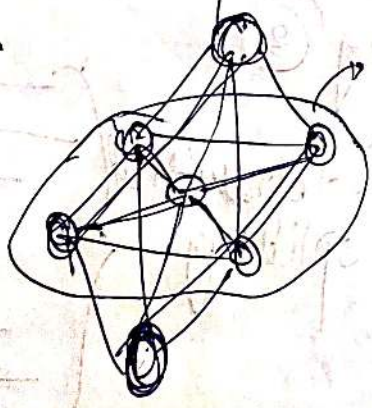
$d_{x^2-y^2}$

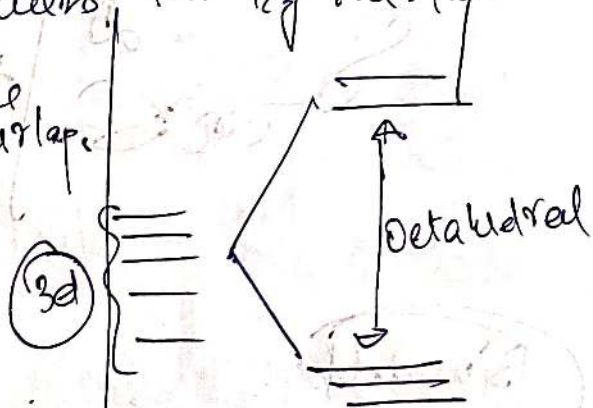


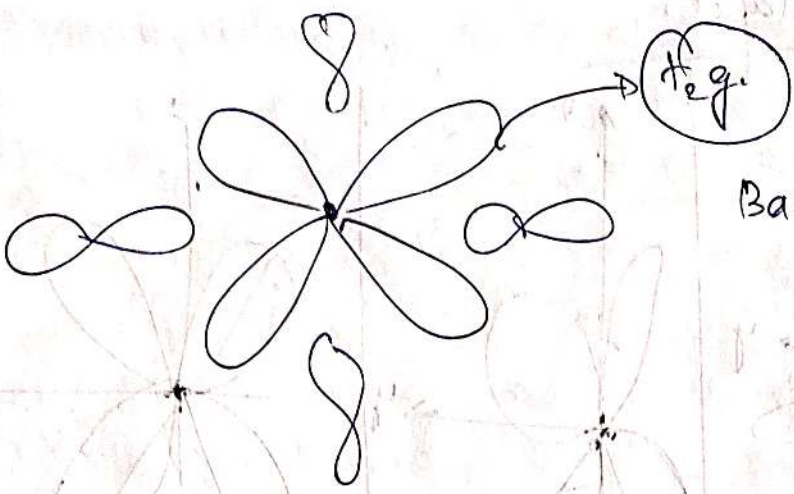
d_{z^2}.

In 3d systems (oct & tet), there is an increase in orbital overlap & ligand field strength.

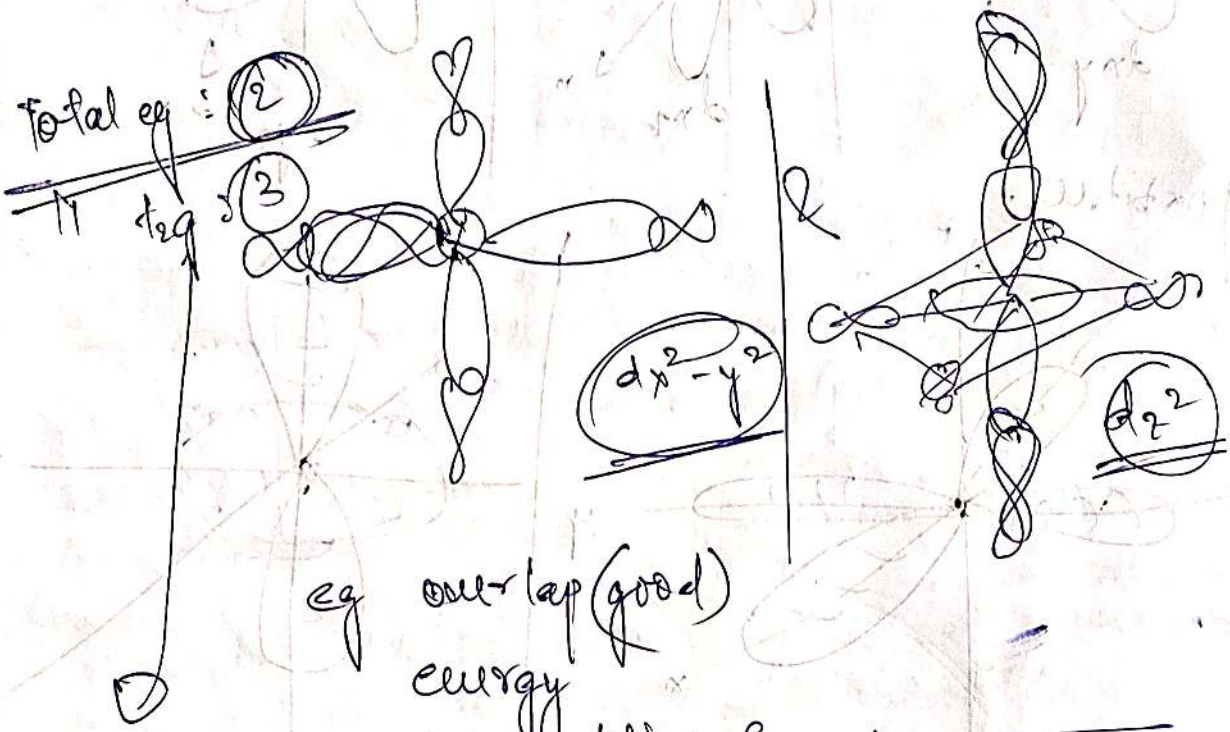
eg orbital overlap determines the t2g overlap strength.







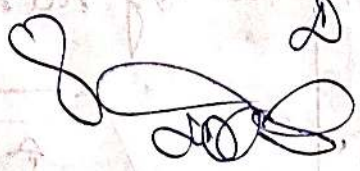
Badly.



eg overlap (good)
energy

Therefore orbital splitting for oct:

For tetrahedral env



t_{2g} is diagonal
interaction
t_{2g} (3)

∴ tetrahedral
splitting

Blundell

Problem.

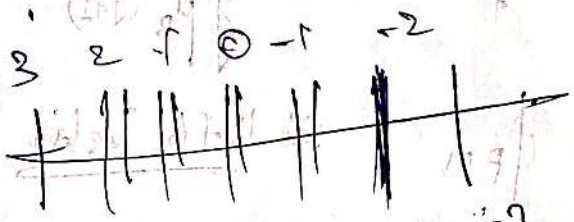
S P D F G H I.
0 1 2 3 4 5

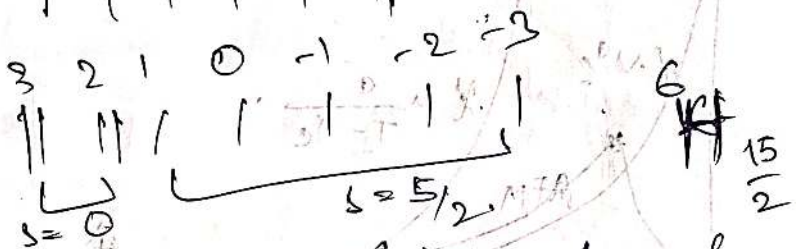
(1) Magnetic moment of Pr^{3+} ion has 9e in 4f shell what is L, S & J.

S → $5/2$

L → 5.

J → $15/2$

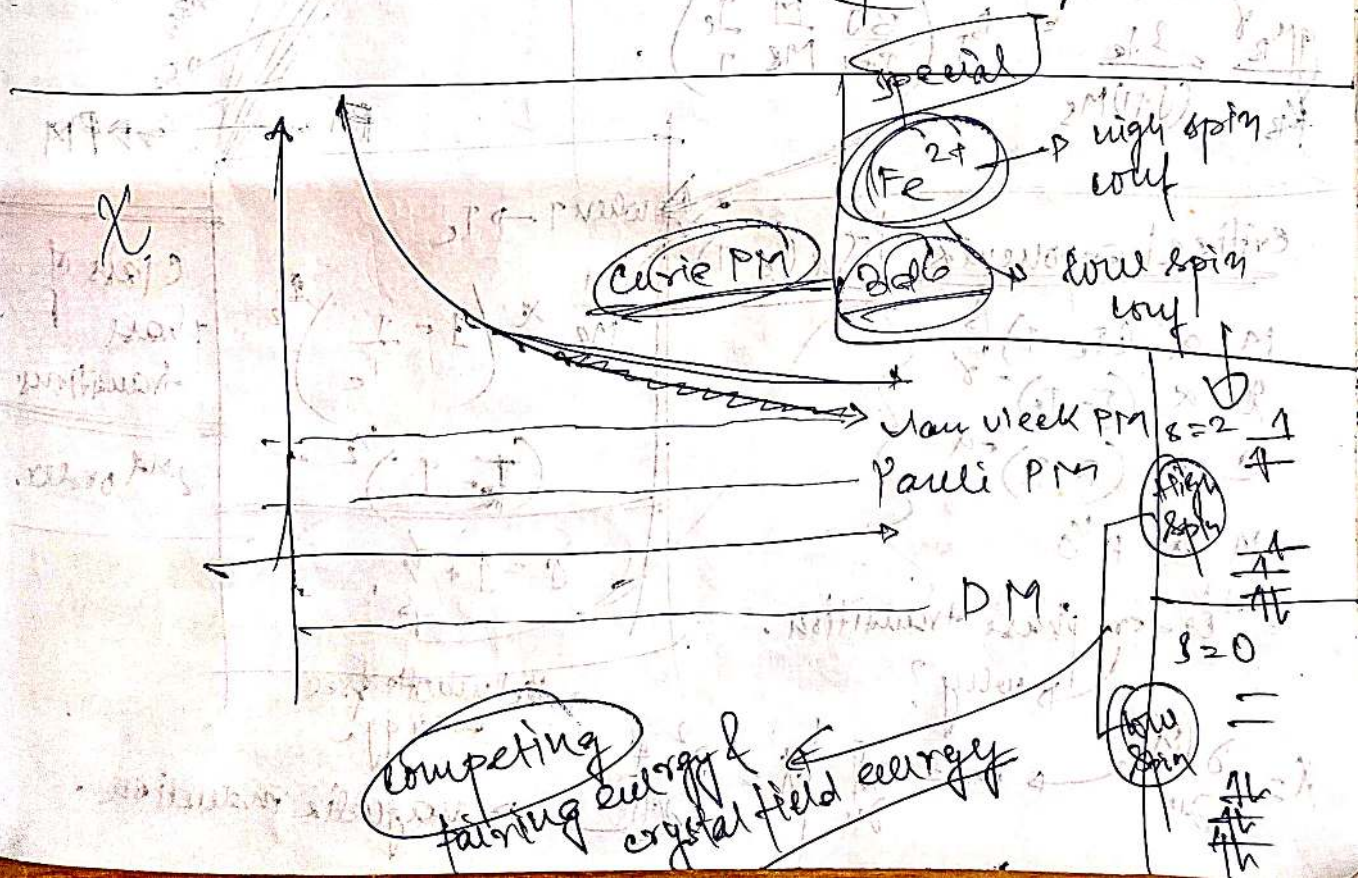




calculate susceptibility containing 1 gmol at 4K.

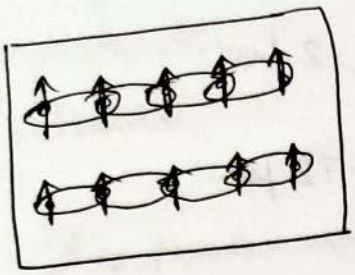
(2) Paramag of S = 1 system

Find the magnetization as a func^n of magnetic field & temp of a system with S = 1, moment m_0 & conc = N atoms/unit volume. Show that the limit $\mu_0 m H \gg k_B T$ reduces to $M \approx 2\mu_0 N m^2 H / 3 k_B T$.



7/2/25 / Friday

FERROMAGNETISM

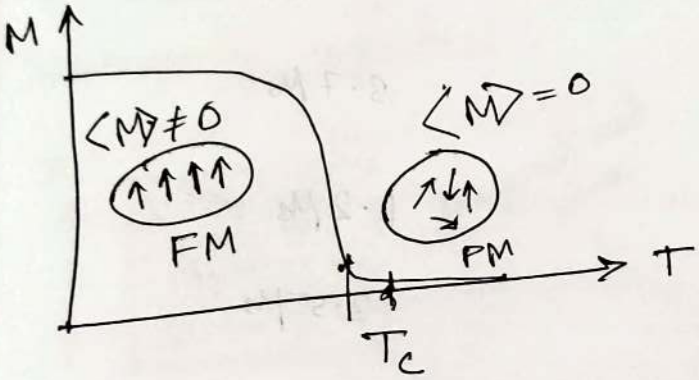


$H = 0$

$\langle M_{SP} \rangle \neq 0$

⇒ Collective Cooperative phenomenon

Example → Fe, Ni, Co, $La_{0.7}Sr_{0.3}MnO_3$, $SrRuO_3$



$\langle M_{SP} \rangle$ = order parameter

FM → PM → 2nd order phase transition

Order parameter changes drastically across the phase transition.

① Two distinct characteristics of FM →

① The FM has spontaneous magnetization. $\langle M_{SP} \rangle$

② The existance of magnetic ordering temp. (T_C)

Material	T_c(K)	Spontaneous Magnetization (μ_B/atom)
Fe	1043	2.2 μ_B
Co	1394	1.72 μ_B
Ni	631	0.61 μ_B
Gd	289	7.5 μ_B
$La_{0.7}Sr_{0.3}MnO_3$	360	3.7 μ_B
$SrRuO_3$	160	1.2 μ_B
MnSb	587	3.5 μ_B

* $\mu_B H_m \approx K_B T_c$

$H_m \approx$ internal molecular field that keeps the spin ~ each other in Ferromagnetism

$$H_m \approx \frac{K_B T_c}{\mu_B} = \frac{0.026 \times 2 \times 1.6 \times 10^{-19} \times 10^7 \text{ erg}}{9.21 \times 10^{-21} \text{ erg/Oe}}$$

$$= 10^7 \text{ Oe}$$

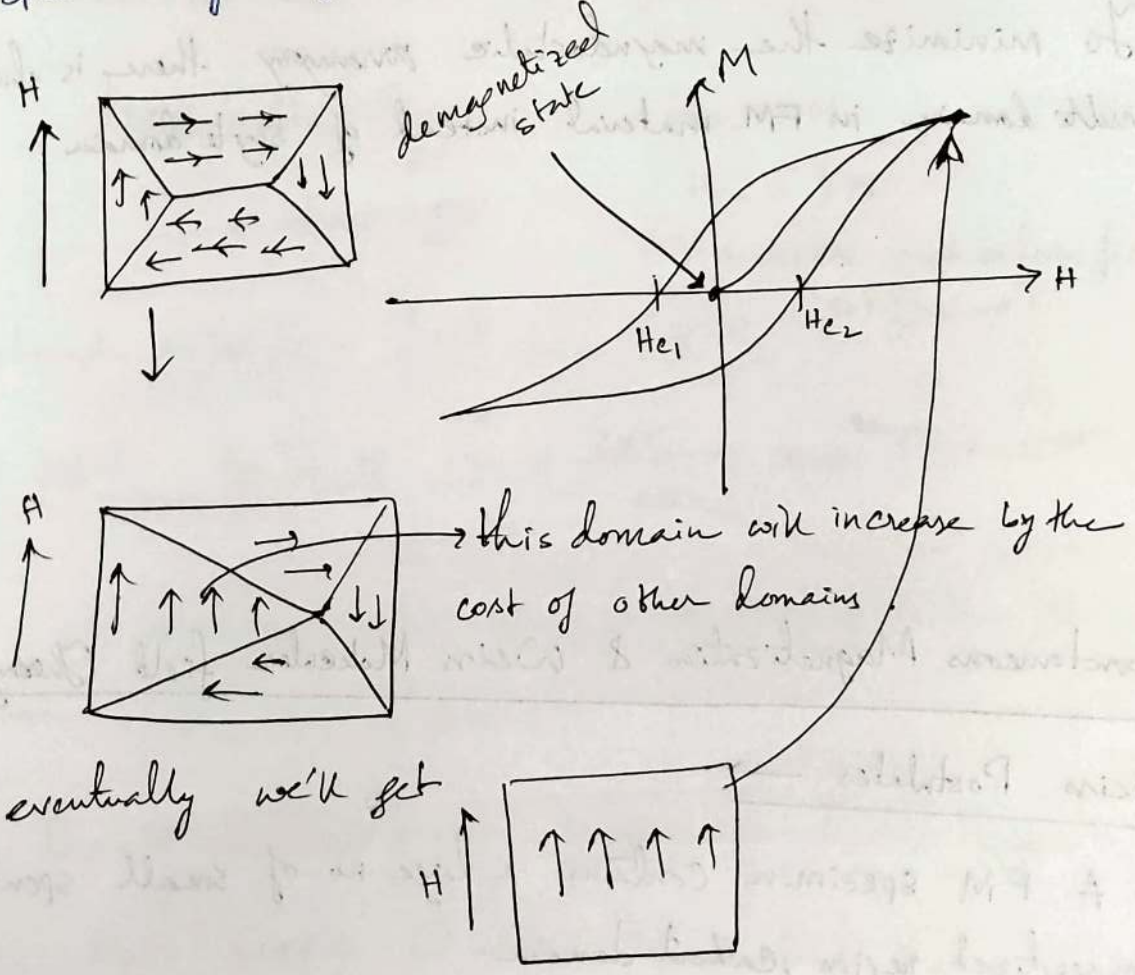
$$= 500 \text{ T}$$

② Properties :-

(a) They're very strongly magnetic for a given field. The magnetization is 10^6 times more than dia or paramagnetic substance.

(b) They possess spontaneous magnetization below a certain temp. (T_c). Above this temp. it behaves like PM.

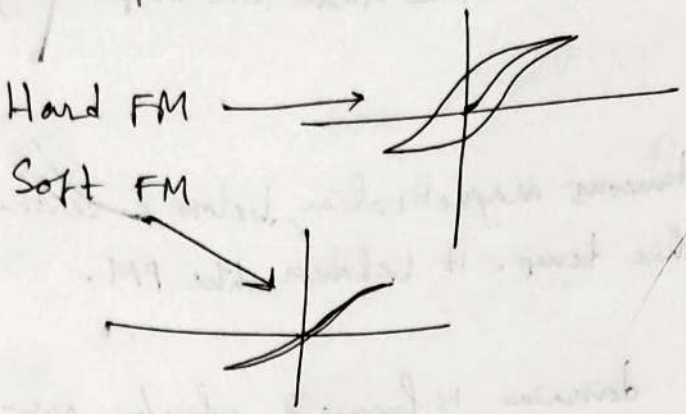
(c) In a bulk FM material domain is formed which are spontaneously magnetized.



Coercive field = H_c the amount of -ve field required to bring back the magnetization to zero.

$H_{c_1} \neq H_{c_2}$ always $\quad H_c = \dfrac{|H_{c_1}| + |H_{c_2}|}{2}$

we get the hysteresis loop and as well as we can take * snapshots of the domains by using Lorentz microscope.



To minimize the magnetostatic energy there is also multi domain in FM material instead of single domain.

⊙ Spontaneous Magnetization & Weiss Molecular field Theory

Weiss Postulates →

① A FM specimen contains a large no. of small spontaneously magnetized region, called domain.

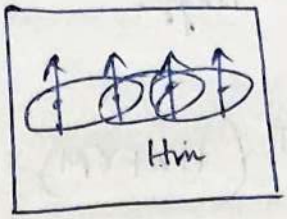
② Within each domain the spontaneous magnetization is due to existance of internal molecular field which tend to produce a parallel alignment of atomic dipole.

$H_{eff} = H_a + H_m$

↓ applied field

↓ internal molecular field.

H_a ↑



③ The strong interaction which tends to align atomic dipoles parallel in FM materials may be considered as equivalent to some internal molecular field. (H_m)

$H_{eff} = H_a + H_m$

$= H_a + \gamma M$

$H_m \propto M$

$H_m = \gamma M$

(γ = weiss molecular field coefficient)

Internal molecular field $H_m = \gamma M$

$\mu_B H_m = K_B T_c \Rightarrow H_m = \frac{K_B T_c}{\mu_B} \simeq 10^7 \text{ Oe} \simeq 1500 \text{ T}$.

Let us consider a FM material containing N atoms per unit volume $M = N J g \mu_B B_J(x)$

$B_J(x)$ = Brillouine fn where $x = \frac{g \mu_B J}{K_B T} H_{eff}$.

H_m = keeping all the dipoles along H_a.

$$\chi = \frac{g \mu_B J}{k_B T} H_{eff}$$

$$= \frac{g \mu_B J}{k_B T} (H_a + \gamma M)$$

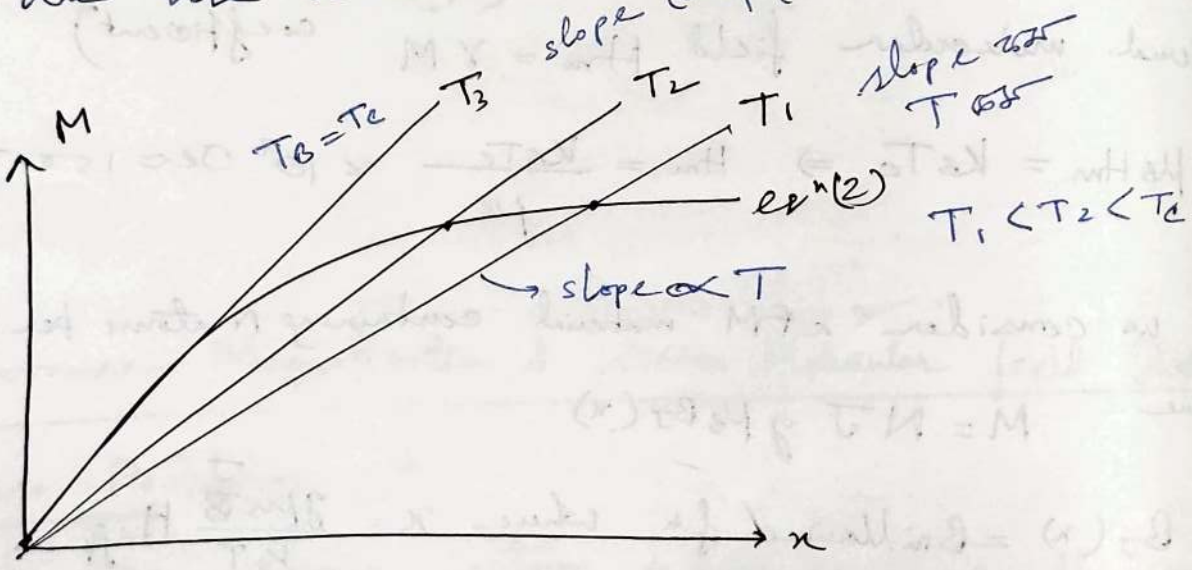
For spontaneous magnetization ($H_a = 0$)

$$\chi = \frac{g \mu_B J}{k_B T} \gamma M$$

$$M = \frac{\chi k_B T}{g \mu_B J \gamma} \quad \text{——— (1)}$$

$$M = N J g \mu_B B_J(x) \quad \text{——— (2)}$$

we use x as α.



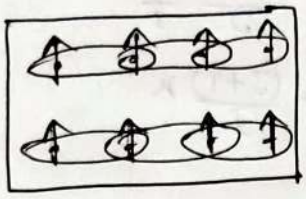
① if $T < T_c$ we get non zero value of M. so for $T < T_c$, There is a spontaneous magnetization.

② If at $T = T_c$ the curve ① just the tangent to curve ②. At the origin & spontaneous magnetization just vanishes.

③ $T > T_c$, no soln of spontaneous magnetization.

$T = T_c$ = Curie Temp. of Ferromagnetism.

④ Relation Between γ and T_c ⟶



$$H_m = \gamma M = K_B T_c$$

The expected relation is that T_c increases with increasing γ.

$x \ll 1$

$$B_J(x) = \frac{J+1}{J}\,\frac{x}{3}$$

eqn ② $M = N g \mu_B J B_J(x)$

$$= N g \mu_B J \frac{J+1}{J}\frac{x}{3} \quad (x \ll 1)$$

$$M = \frac{N g \mu_B (J+1)}{3} x$$

eqn ① $M = \dfrac{x K_B T}{g \mu_B J \gamma}$

when $x \ll 1$ both the slopes should be equal from the previous figure.

$$\frac{x K_B T}{g \mu_B J \gamma} = \frac{N g \mu_B (J+1)}{3}$$

$$T_c = \frac{N g^2 \mu_B^2 J(J+1)\gamma}{3 K_B} = C\gamma$$

$$\boxed{T_c = C\gamma}$$

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

$$\boxed{\frac{N \mu_{eff}^2}{3 K_B} = C}$$

for a strong ferromagnetic material γ = internal field coefficient as well as T_c becomes high.

Curie Weiss Law :-

$$M = N g \mu_B J B_J(x) = N g \mu_B J \frac{J+1}{J} \frac{x}{3}$$

$$= N g \mu_B \frac{(J+1)}{3} x$$

$$x = \frac{g \mu_B J}{kT} (H + \gamma M)$$

$$M = N g \frac{\mu_B (J+1)}{3} \frac{g \mu_B J}{kT} (H + \gamma M)$$

$$= \frac{N g^2 \mu_B^2 J (J+1)}{3kT} (H + \gamma M)$$

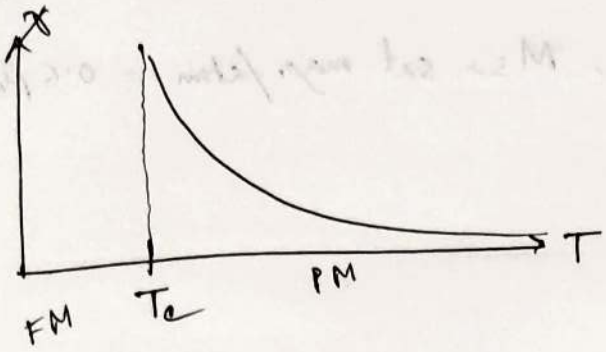
$$M = \frac{C}{T} (H + \gamma M)$$

$$M \left(1 - \frac{\gamma C}{T}\right) = \frac{C}{T} H$$

$$\Rightarrow \frac{M}{H} = \chi = \frac{\frac{C}{T}}{1 - \frac{\gamma C}{T}} = \frac{\frac{C}{T}}{1 - \frac{T_c}{T}} = \frac{\frac{C}{T}}{\frac{T - T_c}{T}}$$

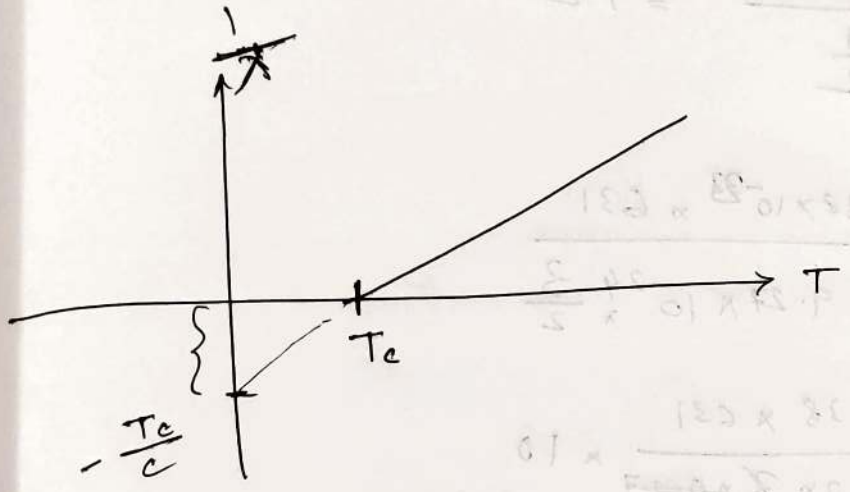
$$\Rightarrow \boxed{\chi = \frac{C}{T - T_c}}$$ Curie-Weiss Law.

$$\Rightarrow \frac{1}{\chi} = \frac{T}{C} - \frac{T_c}{C}$$



$$\chi = \frac{C}{T - T_c} \qquad \text{at } T = T_c \quad \chi = \infty$$

$$\frac{1}{\chi} = \frac{T}{C} - \frac{T_c}{C}$$



$$T_c = C\gamma = \frac{N g^2 J (J+1) \mu_B^2}{3 k_B} \gamma$$

$$= \frac{N g J \mu_B \gamma g (J+1) \mu_B}{3 k_B}$$

$$M = N g \mu_B J B_J(x)$$

$x \gg 1$

$B_J(x) = 1$

$$M = N g \mu_B J = M_S$$

$$T_c = \frac{M_S \gamma g (J+1) \mu_B}{3 k_B} = M_S \gamma \frac{g (J+1) \mu_B}{3 k_B}$$

$$\boxed{H_m = B_{mf} = \gamma M_S = \frac{3 k_B T_c}{g \mu_B (J+1)}}$$

** (problem)

Problem → Calculate the molecular field of Ni ...

$T_c = 631\ K$, $J = \frac{1}{2}$, M_s = sat magn./atom = $0.6\ \mu_B$

$$H_m = \frac{3 k_B T_c}{g \mu_B (J+1)}$$

$$M_s = N g \mu_B J = 0.6\ \mu_B/\text{atom} \times N = 0.6 N \mu_B$$

$$\Rightarrow N g \mu_B J = 0.6 N \mu_B$$

$$\Rightarrow g = \frac{0.6}{\frac{1}{2}} = 1.2$$

$$H_m = \frac{3 \times 1.38 \times 10^{-23} \times 631}{1.2 \times 9.27 \times 10^{-24} \times \frac{3}{2}}$$

$$= \frac{3 \times 2 \times 1.38 \times 631}{1.2 \times 9.27 \times 3} \times 10$$

$$= 156.57 \times 10 = 1565.7\ T$$