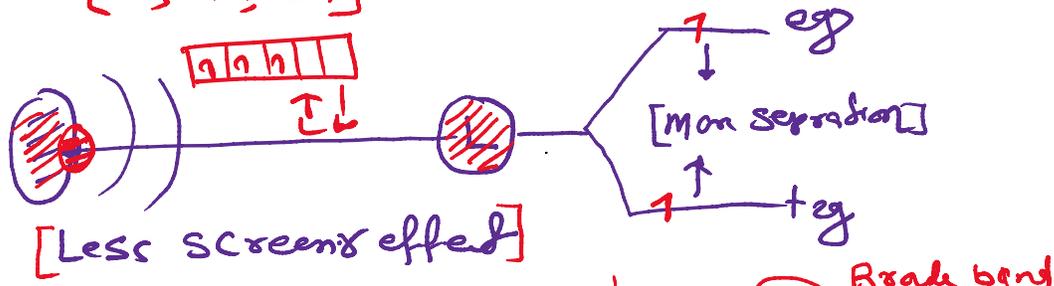


Imp

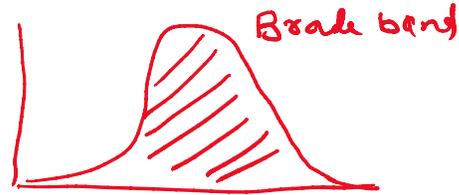
① Spectroscopic and ② magnetic properties

f-block spectra (L_n^{+3})

IN [3d, 4d, 5d] metal \Rightarrow Less screening effect



d-d transition
[g \rightarrow g] $\Delta S = 0$ ✓
 $\Delta L \neq \pm 1$ ✓



$\Delta S \neq 0$ } Shape (weak)
 $\Delta L \neq \pm 1$

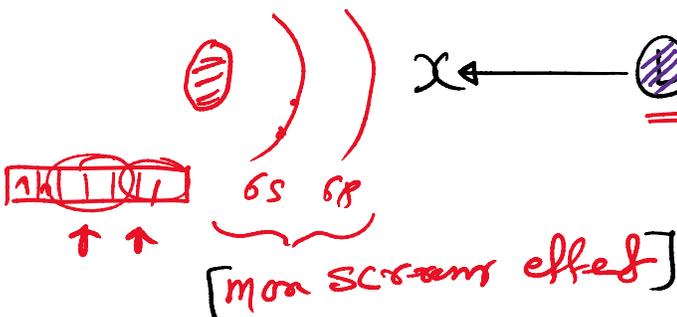
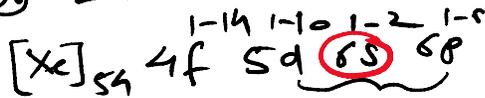
In transition spin orbital coupling is less imp

orbital quench

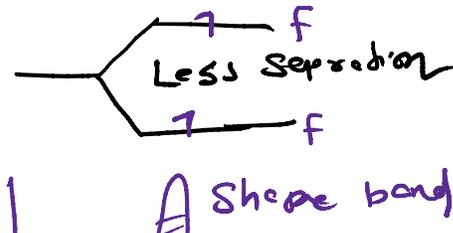
Spin only magnetic moment

transition metal depend on ligand field strength

4f @ Lanthanide \Rightarrow More screening effect

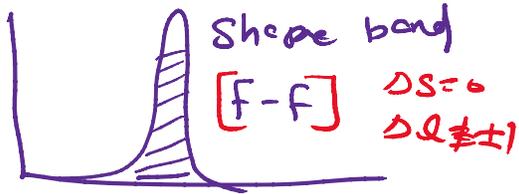


[Complex formation is
very difficult]



↑ ↑ [more screening effect]

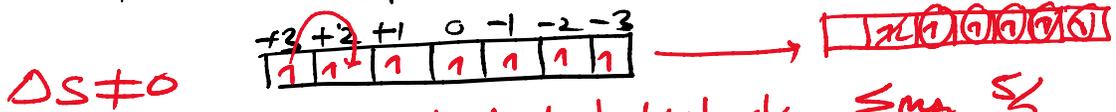
F-f transition gives shape band



In Lanthanide element

Spin-orbital coupling is most Imp

Ln⁺³ element not depend on ligand field strength



Spin forbidden

$$\sum m_s = +\frac{1}{2} + \frac{1}{2} + \frac{1}{2} + \frac{1}{2} + \frac{1}{2} + \frac{1}{2} + \frac{1}{2} = 3.5 @ \frac{7}{2}$$

4f⁰, 4f⁷, 4f¹⁴ ⇒ ΔS ≠ 0

4f¹, 4f², 4f³, 4f⁴ ⇒ ΔS = 0

F-f = [Shape band]

Spin only magnetic moment is less Imp

Electronic spectra lanthanoids:

1. Spectra of Ln^{3+} ions often contain large numbers of absorptions
2. the 4f electrons are well shielded and not affected by the environment of the ion, bands arising from f-f transitions are sharp (rather than broad like d-d absorptions) and their positions in the spectrum are little affected by complex formation.
3. In the lanthanides spin orbit coupling is more important than crystal field splitting

In the spectra of transition metals, crystal field splitting is of

Ln^{3+} elements generally form high coordination comp.
greater than 6

In the spectra of transition metals, crystal field splitting is of major importance. All but one of the lanthanide ions show absorptions in the visible or near-UV region of the spectrum.

4. Many trivalent lanthanide ions are strikingly coloured both in the solid state and in aqueous solution,

1. The colour seems to depend on the number of unpaired f electrons.

1. Elements with $(n) f$ electrons often have a similar colour to those with $(14 - n) f$ electrons.

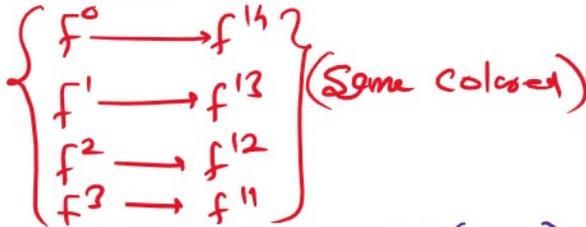


Table Colour of Ln³⁺ ions (aq) (solution)

	No of 4f electron	Colour	No of 4f electrons	Colour
1 f^0	0	Colourless	14	Colourless
2 f^1	1	Colourless	13	Colourless
3 f^2	2	Green	12	Pale Green
4 f^3	3	Lilac	11	Pink
5 f^4	4	Pink	10	Pale Yellow
6 f^5	5	Yellow	9	Yellow
7 f^6	6	Pale Pink	8	Pale Pink
7 f^7	7	Colourless	7	Colourless

$\Delta S \neq 0$ (Forbidden)
 $\Delta S = 0$ (Forbidden)
 electronic transition in U.V region

(LMCT) $MnO_4^- \rightarrow T_d d^0 \Rightarrow$ Pink (visible)
 $RuO_4^- \rightarrow T_g d^0 \Rightarrow$ Colourless (UV)

$[RuCl_4]^- \rightarrow Tg d^- \rightarrow (colours)$
UV

f-f transition \Rightarrow Sharp band

$\Delta S = 0$
 $\Delta L \neq \pm 1$

f^1

f^2, f^3, f^4, f^5

f^6, f^7

$f^8, f^9, f^{10}, f^{11}, f^{12}, f^{13}$

Ce^{+3}

Sharp band

Tm^{+3}

Sharp band

Broad Band

$\Delta L = \pm 1$

$\Delta S = 0$

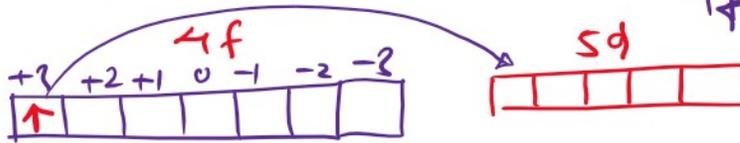
Broad Band

$\Delta L = \pm 1$

$\Delta S = 0$

$Ce^{+3} [Xe]_{54} 4f^1 5d^0 6s^0$

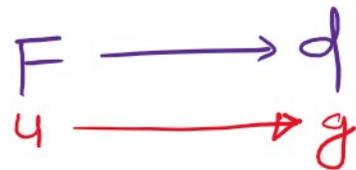
$Ce^{+4} \rightarrow Ce^{+3}$
 $4f^0 \rightarrow 4f^1$



Laporte allowed
 $[\Delta L = \pm 1]$

* $(g-u)(u-g)$
 \neq

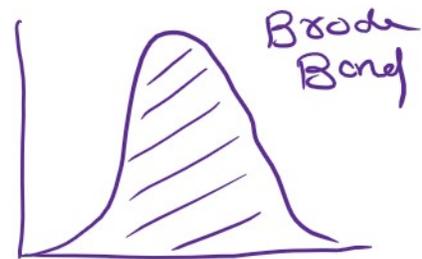
Laporte allowed



$L=3$

$L=2$

$[3-2] = \Delta L = (\pm 1)$



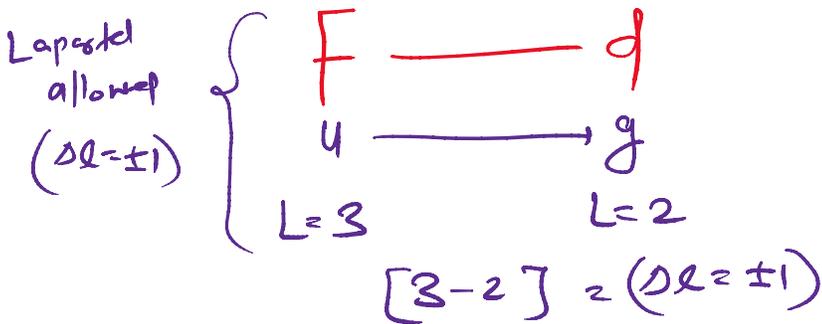
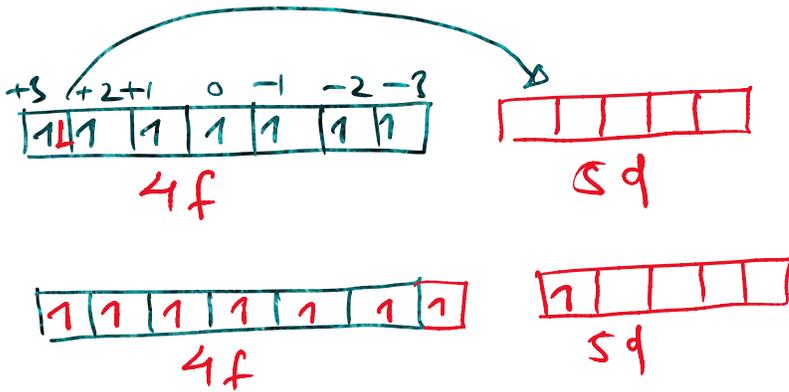
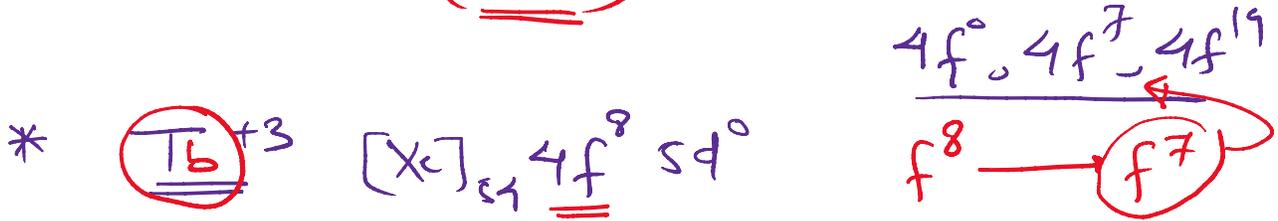
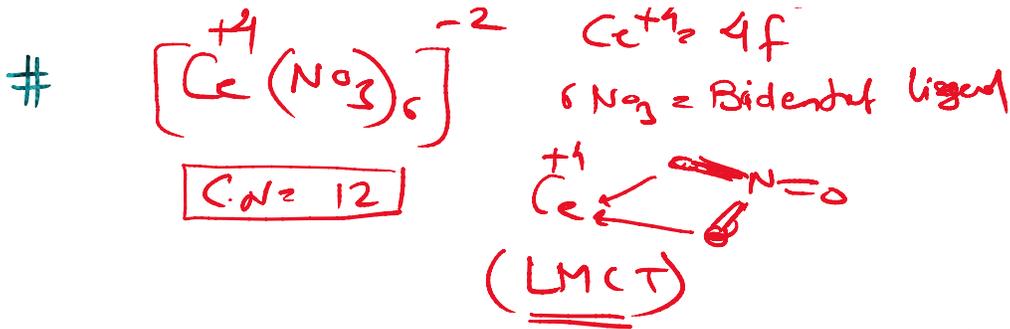
(Max Separation)

$\Delta S = 0$
 $\Delta L = \pm 1$

\Downarrow

[Charge Transfer transition]

$[Ce(NO_2)_6]^{3-}$ $Ce^{+4} 4f^0$
 (No. = Bridged ligand)

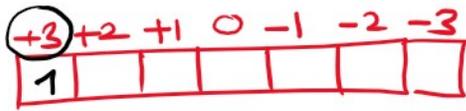


Ce^{+3} & Tb^{+3} generally show Brode Band
 Because of $f-d$ transition

All L_n^{+3} element shows $f-f$ transition
 Except $4f^0, 4f^7, 4f^9$
 Ce^{+3} Tb^{+3}
 f^1 f^8
 (Brode band)

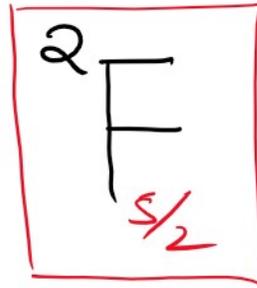
Imp

$f-f$ transition = Sharpe band



$\Sigma m_s = +\frac{1}{2}$ ($S = \frac{1}{2}$)

$L = 3$



Ground Term Symbol

$(2S+1) = (2 \times \frac{1}{2} + 1) = \boxed{2}$

L-value = $\boxed{+3}$

J-value Less than half filled

$$\begin{aligned} J &= (L - S) \\ &= (3 - \frac{1}{2}) \\ &= \frac{5}{2} \end{aligned}$$



possible J-values = $L - S$ to $L + S$
 $= (3 - \frac{1}{2})$ to $(3 + \frac{1}{2})$
 $= \frac{5}{2}$ to $\frac{7}{2}$

Microstates of Ce⁺³ :

$$\begin{aligned} \frac{N!}{(N-r)! \times r!} &= \frac{14!}{(14-1) \times 1!} \\ &= \frac{14 \times 13!}{13! \times 1!} \end{aligned}$$



Microstates = 14

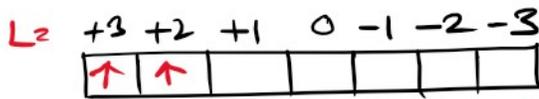
$$M_s = (2S+1) \times (2L+1)$$

$$= (2 \times \frac{1}{2} + 1) \times (2 \times 3 + 1)$$

$$= 2 \times 7 = \underline{14}$$



- * Ground Term Symbol
- * Microstate
- * possible J-values
- * total possible Term



L=0	1	2	3	4	5
S	P	D	F	G	H

① $\Sigma m_s = +\frac{1}{2} + \frac{1}{2} = \textcircled{1} [S = \frac{1}{2}]$

② $(2S+1) = (2 \times \frac{1}{2} + 1) = \textcircled{3}$



③ L-values $+3 + 2 = +5$

④ Less than half filled

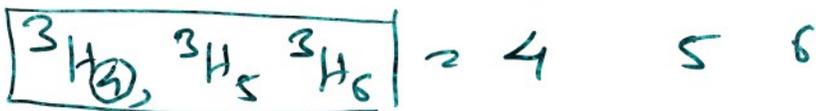
$J = L - S$

$J = 5 - \frac{1}{2} = 4\frac{1}{2}$

⑤ possible J-values $[L-S \text{ to } L+S]$
 $= [5 - \frac{1}{2} \text{ to } 5 + \frac{1}{2}]$



$= 4 \text{ to } 6$



② Microstate:

$$\frac{N!}{n_1! n_2! \dots n_i!} = \frac{14!}{(14! - 2!) \times 2!}$$



$$\frac{1^4}{(N! - r!) \times r!} = \frac{1}{(14! - 2!) \times 2!}$$

$$= \frac{7 \cancel{14} \times 13 \times \cancel{12!}}{\cancel{12!} \times 2 \times 1!}$$

Microworld = 91

3H L=5
S=1 = (2S+1) * (2L+1)

$$= (2 \times 1 + 1) \times (2 \times 5 + 1)$$

$$= 3 \times 11$$

$$= \underline{\underline{33}}$$

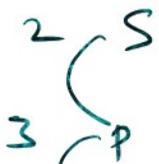
F²

F'	F'	3+3 = 6
L=3	L=3	3-3 = 0

s/L	6	5	4	3	2	1	0
S=0 <u>Singlet</u> <u>odd x</u>	<u>I</u>	H	<u>G</u>	F	<u>D</u>	P	<u>S</u>
S=1 <u>Triplet</u> <u>(even) x</u>	3I	<u>3H</u>	3G	<u>3F</u>	3D	<u>3P</u>	3S

<u>I_S</u>	1 x 1 = 1	}
<u>I_D</u>	1 x 5 = 5	
<u>I_G</u>	1 x 9 = 9	
<u>I_F</u>	1 x 13 = 13	

91



3 } p
5 } p
7 } p

36
33

69
22

85

1 } 1 x 13 = 13
3p } 3 x 3 = 9
3f } 3 x 7 = 21
3H } 3 x 11 = 33

Table-Ground term symbols for lanthanides:

	Ln^{III}	$4f^n, n =$	Ground term $2S+1L_J$	
F ¹	Ce	1	$2F_{5/2}$	$n=1$
F ²	Pr	2	$3H_4$	$n=2$
F ³	Nd	3	$4I_{9/2}$	$n=3$
F ⁴	Pm	4	$5I_4$	$n=4$
F ⁵	Sm	5	$6H_{5/2}$	$n=5$
F ⁶	Eu	6	$7F_0$	$n=6$
F ⁷	Gd	7	$8S_{7/2}$	$n=7$
F ⁸	Tb	8	$7F_6$	$n=6$
F ⁹	Dy	9	$6H_{15/2}$	$n=5$
F ¹⁰	Ho	10	$5I_8$	$n=4$
F ¹¹	Er	11	$4I_{15/2}$	$n=3$
F ¹²	Tm	12	$3H_6$	$n=2$
F ¹³	Yb	13	$2F_{7/2}$	$n=1$
F ¹⁴	Lu	14	$1S_0$	$n=0$

$J = L - S$
Less than half filled

paramagnetic

$J = L + S$
More than half filled

Diamagnetic

Thank you