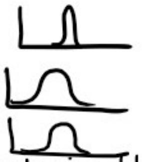
Summary:

* f-f transition
* d-d transition
* f-d transition



the spectra of the lanthanoid ions are normally characterized by the following

* properties:

1)Numerous absorptions due to the large number of microstates. $f^1 = 14$ $f^2 = 91$ $f^3 = 3003$

2) Weak absorptions due to lack of orbital mixing. Molar absorption coefficients(ε) are typically 1=10 dm3 mol–1 cm–1 compared with d metals (close to 100 dm3 mol–1 cm–1). [F−d]

3)Sharp absorptions due to the weak interaction of the f orbitals with the ligand vibrations.

4) Spectra that are to a large degree independent of the ligand type and coordination number

$\underline{> 6}$

$\underline{Nd^{+3}}$ $[Xe]_{54} 4f^3 5d^0 6s^0$

+3	+2	+1	0	−1	−2	−3
↑	↑	↑				

① $\sum m_s = +\frac{1}{2} + \frac{1}{2} + \frac{1}{2} = +\frac{3}{2}$ $\boxed{S = \frac{3}{2}}$

② $(2S+1) = (\cancel{2} \times \frac{3}{\cancel{2}} + 1) = 4$

③ L-value +3 +2 +1 ⇒ 6

L = 6 $^{4}I_{9/2}$ ⇒ paramagnetic

④ J = Less than half field =

\# $J = L - S$ to $L + S$

$= 6 - \frac{3}{2}$ to $6 + \frac{3}{2}$

$= \frac{9}{2}$ to $\frac{15}{2}$

$= {}^{4}I_{9/2}$ ${}^{4}I_{11/2}$ ${}^{4}I_{13/2}$ ${}^{4}I_{15/2}$

② J = Less then half filled =

$J = L - S$

$J = 6 - 3/2 \Rightarrow \boxed{9/2}$

Table-Ground term symbols for lanthanides:

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

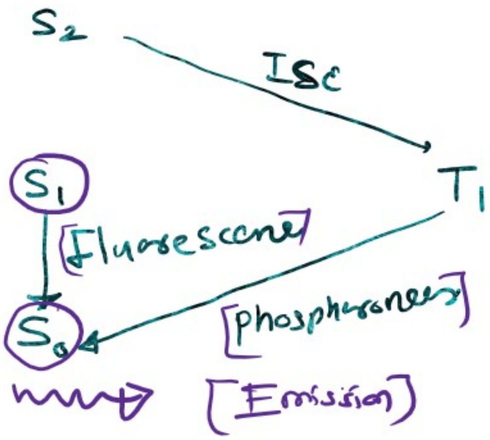
Hunds Rule ⇒

① High spin multiplicity act as ground Term

② High L-value act as a ground Term (lower Energy)

③ J = [L − S] less than half filled

J = (L + S) more than half filled



$S_0 \rightarrow S_1$ absorption

$S_1 \rightarrow S_0$ Emission

$La^{+3} = f^0$ $\xrightarrow{} {}^1S_0$

$L = 0$

$S = 0$

Emission spectra and fluorescence

1)All the lanthanoid ions except La^{3+} (f^0) and Lu^{3+} (f^{14}) show luminescence

Ln^{+3}, $\underbrace{f^1, f^2, f^3, f^4, f^5, f^6}_{\boxed{\Delta S = 0}}$, f^7, $\underbrace{f^8, f^9, f^{10}}_{\boxed{\Delta S = 0}}$ Spin-allowed

2) Eu3+ (f6) and Tb3+ (f8) being particularly strong.

$f^0, f^7, f^{14} \Rightarrow$ Spin-forbidden

If No of Unpaired e^- ↑

Strong Emission spectra

Eu^{+3}

f^6

+3	+2	+1	0	-1	-2	-3
↑	↑	↑	↑	↑	↑	

$\boxed{n = 6}$

Tb^{+3}

f^8

+3	+2	+1	0	-1	-2	-3
↑↓	↑	↑	↑	↑	↑	↑

$\boxed{n = 6}$

f° $\boxed{n=6}$

① $\Sigma m_s = \boxed{S=3}$

② $(2S+1) = (2\times3+1) = 7$

③ L-value = 3 $\boxed{{}^7F_0}$

④ $J = [L-S]$

$= 3-3 = 0$

⑤ $J = L-S$ to $L+S$

$J = 3-3$ to $3+3$

$= \boxed{0\ 1\ 2\ 3\ 4\ 5\ 6}$

f

① $\Sigma m_s = \boxed{S=3}$

② $(2S+1) = (2\times3+1) = 7$

② L-value = 3

$\boxed{{}^7F_0}$

④ $J = \boxed{7}$

ground state ⟸ $[{}^7F_0\ \ {}^7F_1\ \ {}^7F_2\ \ {}^7F_3\ \ {}^7F_4\ \ {}^7F_5\ \ {}^7F_6]$ → Excited state

3)the strong luminescence is due to the large number of excited states that exist, which increases the probability of intersystem crossing

La^{+3} $\boxed{{}^1S_0}$

Lu^{+3} $\boxed{{}^1S_0}$

} No Luminescence

→ No change in Spin multiplicity

1. fluorescence colours given in column A with lanthanide ions given in column B

Column A	ColumnB
(i) Pink	**(a) Sm(III)**
(ii) Red	**(b) Eu(III)**
(iii) Green	**(c) Tb(III)**
(iv) Blue	**(d) Tm(III)**

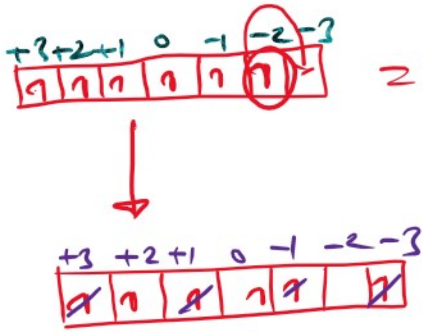
} Larger Number of Excited state

⇓

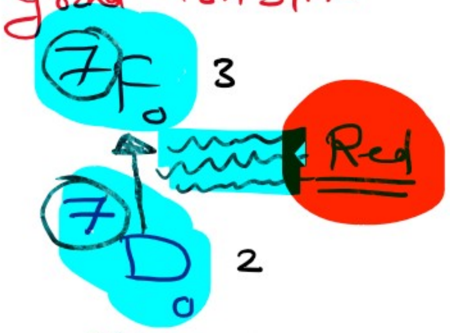
Strong Luminescence

Eu^{+3} f^6 $\begin{array}{|c|c|c|c|c|c|c|} +3 & +2 & +1 & 0 & -1 & -2 & -3 \\ \hline 1 & 1 & 1 & 1 & 1 & 1 & \\ \hline \end{array}$ = ground Term Symbol

Eu^{+3} f^6



= grand Term Symb



${}^{7}F_{0}$

${}^{7}D_{0}$

allowed

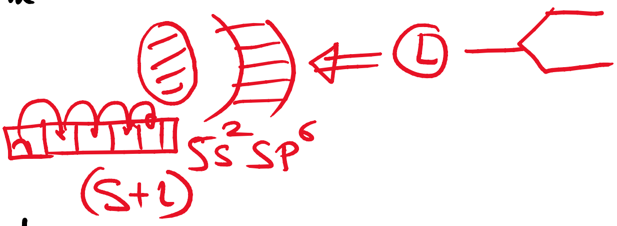
$\boxed{L = 2}$

$J = L - S$
$= 3 - 3 = 0$

$\boxed{\Delta S = 0}$
$\boxed{\Delta l = \pm 1}$
} allowed

Magnetic properties

① In Ln^{+3} Spin-orbital coupling is more Imp than Crystal field splitting



Spin only magnetic moment

La^{+3} f^0 $n=0$

Gd^{+3} f^7 $n=7$ half filled

Lu^{+3} f^{14} $n=14$ full filled

Spin only magnetic

$\boxed{\Delta S \neq 0}$

f-f ✗

$$\mu_{eff} = \sqrt{4S(S+1) + \underline{L(L+1)}}$$

or

$$= \sqrt{4S(S+1)}$$

or

=

Spin only magnetic $= \sqrt{n(n+2)}$ B.M

La^{+3} $n=0$ 0 B.M

Gd^{+3} $\boxed{n=7}$

Lu^{+3} $n=0$ 0 B.M

$$Gd^{+3} = \sqrt{7(7+2)} \text{ B.M}$$

$$= \sqrt{7(9)}$$

$$= 7.9 \text{ B.M}$$

Spin only magnetic moment not applicable for all Ln^{+3}

Except La^{+3} Gd^{+3} Lu^{+3}

$$\boxed{\mu_{eff} = g\sqrt{J(J+1)}}$$

this formula applicable for Ln^{+3} elements

Except

$$\boxed{\underline{\underline{g}} = 1 + \frac{S(S+1) - L(L+1) + J(J+1)}{2J(J+1)}}$$

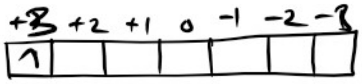
Ln^{+3} elements

Except

$\underline{\underline{La^{+3}, Lu^{+3}, Gd^{+3}}}$

* Ce^{+3} $[Xe]_{54}\, 4f^{1}$

[effective magnetic moment of Ce^{+3}]



① $\boxed{S = 1/2}$

② $(2S+1) = (2\times 1/2 + 1) = 2$

③ $\boxed{L\text{-value} = 3}$

④ $J = [L - S]$

$J = 3 - 1/2$

$\boxed{J = 5/2}$

$$\mu_{eff} = \bigcirc\!\!\!\!g\, \sqrt{J(J+1)}$$

$$\boxed{g} = 1 + \frac{S(S+1) - L(L+1) + J(J+1)}{2J(J+1)}$$

$$g = 1 + \frac{1/2\,(1/2+1) - 3(3+1) + 5/2\,(5/2+1)}{2\times 5/2\,(5/2+1)}$$

$$= 1 + \frac{1/2\,(3/2) - 3(4) + 5/2\,(7/2)}{2\times 5/2\,(7/2)}$$

$$\boxed{g = \frac{6}{7}}$$

$$\boxed{g = 0.85}$$

0 7

$\boxed{g = 0.85}$

$\mu_{eff} = g\sqrt{J(J+1)}$

$= \frac{6}{7}\sqrt{\frac{5}{2}\left(\frac{5}{2}+1\right)}$

$= \frac{6}{7}\sqrt{\frac{5}{2}\left(\frac{7}{2}\right)}$

$\boxed{\mu_{eff} = 2.54 \text{ BM}}$

* $\underline{Pr^{+3}}$ $[Xe]_{54}\, 4f^{2}$

ⓧ+3	+2	+1	0	-1	-2	-3
↿	↿					

① $S = \boxed{1}$

② $(2S+1) = (2\times1+1) = 3$

③ $\boxed{\text{L-value} = +5}$

④ $J = [L - S]$

$J = 5 - 1 = \boxed{4}$

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

$$= 1 + \frac{1(1+1) - 5(5+1) + 4(4+1)}{2\times4(4+1)}$$

$$= 1 + \frac{1\times2 - 5(6) + 4(5)}{8(5)}$$

$$= 1 + \frac{2 - 30 + 20}{40}$$

$\mu_{eff} = g\sqrt{J(J+1)}$

$= \frac{4}{5}\sqrt{4(4+1)}$

$$= 1 + \frac{2 - 30 + 20}{40}$$

$$= 1 + \frac{-8}{40}$$

$$= 1 + (-0.2)$$

$$\boxed{g = 0.8}$$

$$\boxed{g = \frac{4}{5}}$$

$$= \frac{4}{5}\sqrt{4(4+1)}$$

$$= \frac{4}{5}\sqrt{20}$$

$$= 0.8 \times \sqrt{20}$$

$$\underbrace{\mu_{eff} = 3.60.}_{\text{Spin-orbital coupling}}$$

*****

Spin only Magnetic moment less than Spin-orbital Magnetic moment

Table : Magnetism & Spectra

Ln	Ln^{3+} Configuration	Ground State	No. of Unpaired e-	Colour	$g_J\sqrt{J(J+1)}$	Observed μ_{eff}/μ_s
La	$4f^0$	$^1S_0$	0	Colorless	0	0
Ce	$4f^1$	$^2F_{5/2}$	1	Colorless	2.54	2.3-2.5
Pr	$4f^2$	$^3H_4$	2	Green	3.58	3.4-3.6
Nd	$4f^3$	$^4I_{9/2}$	3	Lilac	3.62	3.5-3.6
Pm	$4f^4$	$^5I_4$	4	Pink	2.68	-
Sm	$4f^5$	$^6H_{5/2}$	5	Yellow	0.85	1.4-1.7
Eu	$4f^6$	$^7F_0$	6	Pale pink	0	3.3-3.5
Gd	$4f^7$	$^8S_{7/2}$	7	Colorless	7.94	7.9-8.0
Tb	$4f^8$	$^7F_6$	6	Pale pink	9.72	9.5-9.8
Dy	$4f^9$	$^6H_{15/2}$	5	Yellow	10.65	10.4-10.6
Ho	$4f^{10}$	$^5I_8$	4	Yellow	10.6	10.4-10.7
Er	$4f^{11}$	$^4I_{15/2}$	3	Rose-pink	9.58	9.4-9.6
Tm	$4f^{12}$	$^3H_6$	2	Pale green	7.56	7.1-7.6
Yb	$4f^{13}$	$^2F_{7/2}$	1	Colorless	4.54	4.3-4.9
Lu	$4f^{14}$	$^1S_0$	0	colorless	0	0

Spin-only magnetic moment

$\mu_{eff} = g\sqrt{J(J+1)}$

[Larger deviation]

Same magnetic moment

S+L

S+L

Sm^{+3} = Cal = 0.85

Sm^{+3} = Cal = $\boxed{0.85}$

$\boxed{Eu^{+3} \quad \text{Cal} = \boxed{0}}$

(at low temp)

$$\left.\begin{array}{ll} f^{1} & Ce^{+3} \Rightarrow n = 1 \\ f^{13} & Yb^{+3} = n = 1 \end{array}\right\}$$

Colorless

⇓

absorption in

Ultraviolet region

1. The calculated and observed magnetic moments (in B.M.) of aqua complex of a lanthanide ion are 0 and ~3.5, respectively. The lanthanide ion is:

1. Pm^{3+} 2. Pr^{3+}
[✓ 3. Eu^{3+}] 4. Sm^{3+}

Eu^{+3} = Cal = 0
obs → $\underline{\underline{3.5}}$
(at low temp)

2. The actual magnetic moment shows a large deviation from the spin-only formula in the case of:

(1) Ti^{3+} (2) V^{3+}
(3) Gd^{3+} [✓ (4) Sm^{3+}]

{Cal = 0.85
obs = $\underline{\underline{3.4}}$}

Eu^{+3}
Sm^{+3}

3. Which of the following compounds show a charge-transfer band?
(1) Lanthanum nitrate La^{III}
[✓ (2) Ceric ammonium nitrate]
(3) Manganese (II) acetate Mn^{II}
(4) Copper (II) sulphate pentahydrate
Cu^{II}

Common o.s = $\underline{\underline{+3}}$

$\boxed{+4}$
$[Ce(NO_3)_6]^{-2}$

$[Ce(NO_3)_6]$

f^0 $\overset{+4}{Ce} \leftarrow NO_3$

(LMCT)

4. Match lanthanides in Column I with their properties in Column II:

Column I			Column II
a.	Lu	(i)	Reagent in oxidation state IV
b.	Eu	(ii)	MI_2 of metallic lustre
c.	Ce	(iii)	Diamagnetic M(III)
d.	Tb	(iv)	Pink in oxidation state III

$4f^{14}$ Lu^{+3} ⇒ Diamagn.

$4f^0$ Ce^{+4} ⇒ oxidising agent

$4f^8$ Tb^{+3} ⇒ Pink

$4f^7$ EuI_2 ⇒ Metallic lustre

Correct match is:

1. a-(iii); b-(ii); c-(i); d-(iv)
2. a-(ii); b-(iii); c-(iv); d-(i)
3. a-(iv); b-(ii); c-(i); d-(iii)
4. a-(iii); b-(ii); c-(iv); d-(i)

5. Which of the following statements are TRUE for the lanthanides?

(A) The observed magnetic moment of Eu^{3+} at room temperature is higher than that calculated from spin-orbit coupling

(B) Lanthanide oxides are predominantly acidic in nature

(C) The stability of Sm(II) is due to its half-filled sub-shell

1. A only   2. A and B

3. A and C   4. B and C

Eu^{+3} $4f^6$ obs = 3.5

(C) The stability of Sm(II) is due to its half-filled sub-shell

1. A only
2. A and B
3. A and C
4. B and C

Eu^{+3} $4f^{0}$ Obs = 3.5

Cal = 0

$Ln \xrightarrow{O_2} LnO_2$

Electropositive Basic

$Sm^{III} = 4f^{5}$

+3	+2	+1	0	-1	-2	-3
↿	↿	↿	↿	↿		

Less than half filled

6. Consider following lanthanide (III) ions

(1) Nd(III) (2) Gd(III) (3) Dy(III)

The magnetic moment closest to the spin only value is(are) for:

(1) B only (2) A and B only

(3) A and C only (4) B and C only

$Gd^{III} = 4f^{7} = 7.9$ B.M $\leftarrow \sqrt{n(n+2)}$ ✗

$= g\left(\sqrt{J(J+1)}\right)$ ✓

7. Consider the ions Eu(III), Gd(III), Sm(II) and Lu(III). The observed and calculated magnetic moment values are closest for the pair:

(a) Gd(III), Lu(III) (b) Eu(III), Lu(III)

(c) Sm(III), Gd(III) (d) Sm(III), Eu(III)

Eu^{III} =	0	3.5
Sm^{III} =	0.85	3.4
Lu^{III} =	0	0
Gd^{III} =	7.9	7.92

Large Deviation

Gd^{III} = 7.9 7.92

8. The difference in the ~~measured~~ measured and calculated magnetic moment (based on spin-orbit coupling) is observed for

(1) Pm^{3+}

[✓ (2) Eu^{3+}]

(3) Dy^{3+}

(4) Lu^{3+}

Eu^{+3} = obs cal

$3.5 \longleftrightarrow 0$

Max different

9. The calculated and observed magnetic moments differ considerably for an aqua complex of a Lanthanide (III) ion as a result of low-lying states of high J. The ion, among the following, is

(1) Ce^{3+}

(2) Pr^{3+}

[✓ (3) Eu^{3+}]

(4) Yb^{3+}

Eu^{+3} = obs cal

3.5 0

high J

$$\left[{}^7F_0 \quad {}^7F_1 \quad {}^7F_2 \quad {}^7F_3 \quad {}^7F_4 \quad {}^7F_5 \quad {}^7F_6 \right]$$

J = 0

10. The lanthanide ion the exhibits color in aqueous solution is

(1) La(III)

(2) Eu(III)

(1) La(III)
(2) Eu(III)
(3) Gd(III)
(4) Lu(III)

La^{III} $4f^0$ Colorles $\boxed{n=0}$

Spin-allowed ⇐ Eu^{III} $4f^6$ $\boxed{\text{pink}}$ $n=6$

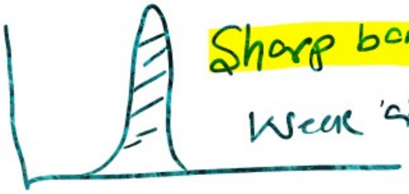
Spin forbidden ⇐ Gd^{III} $4f^7$ $\boxed{\text{Colorles}}$ $\boxed{n=7}$

$\boxed{\Delta S \neq 0}$

Lu^{III} $4f^{14}$ Colorless $\boxed{n=0}$

11. Generally, the coordination number and the nature of the electronic absorption band {*f* →*f* transition} of lanthanide (III) ion in their complexes are, respectively

[✓ (1) greater than 6 and sharp]
(2) 6 and broad
(3) less than 6 and sharp
(4) greater than 6 and broad



Sharp band
Weak absorption

$\boxed{F—F}$

$\boxed{\text{Thank you}}$