OR

: Lanthanides Series :

DR. ANIMESH PATRA
Assistant Professor
Department of Chemistry (UG & PG)
Midnapore College (Autonomous)
Midnapore 721101

Name	Electronic configaration	Ground State symbole of M^{+3}	unpaired electrons in M^{+3} state	Calculated Value $M_{eff} = g\sqrt{J(J+1)}$ BM	Experimental value M_{eff} in BM
Lanthanum 57 (La)	$[Xe]\,5d^1\,6s^2$	$^1S_0$	0	0	0
Cerium (Ce) 58	$[Xe]\,4f^1\,5d^1\,6s^2$	$^2F_{5/2}$	1	2·54	2·3 – 2·5
Praseodymium (Pr) 59	$[Xe]\,4f^3\,6s^2$	$^3H_4$	2	3·58	3·4 – 3·6
Neodymium (Nd) 60	$[Xe]\,4f^4\,6s^2$	$^4I_{9/2}$	3	3·62	3·5 – 3·6
Promethium (Pm) 61	$[Xe]\,4f^5\,6s^2$	$^5I_4$	4	2·68	–
Samarium (Sm) 62	$[Xe]\,4f^6\,6s^2$	$^6H_{5/2}$	5	0·84	1·5 – 1·6
Europium (Eu) 63	$[Xe]\,4f^7\,6s^2$	$^7F_0$	6	0	3·4 – 3·6
Gadolinium (Gd) 64	$[Xe]\,4f^7\,5d^1\,6s^2$	$^8S_{7/2}$	7	7·94	7·8 – 8·0
Terbium (Tb) 65	$[Xe]\,4f^9\,6s^2$	$^7F_0$	6	9·72	9·4 – 9·6
Dysprosium 66 (Dy)	$[Xe]\,4f^{10}\,6s^2$	$^6H_{5/2}$	5	10·63	10·4 – 10·5
Holmium 67 (Ho)	$[Xe]\,4f^{11}\,6s^2$	$^5I_8$	4	10·60	10·3 – 10·5
Erbium (Er) 68	$[Xe]\,4f^{12}\,6s^2$	$^4I_{15/2}$	3	9·57	9·4 – 9·6
Thulium (Tm) 69	$[Xe]\,4f^{13}\,6s^2$	$^3H_6$	2	7·63	7·1 – 7·4
ytterbium 70 (Yb)	$[Xe]\,4f^{14}\,6s^2$	$^2F_{7/2}$	1	4·50	4·4 – 4·9
Lutetium 71 (Lu)	$[Xe]\,4f^{14}\,5d^1\,6s^2$	$^1S_0$	0	0	0

In ce, the increase in Z_{eff} is not sufficient to stabilise the $4f^2\,5d^0$ electronic configaration, compared to $4f^1\,5d^1$. The nuclear charge is insufficient to construnt the 4f orbital and lower their energy well below the 5d-orbital.

Gd has the $4f^7\,5d^1$ configaration, consistant with the exchange energy stabilisation for a half-filled f-shell.

Lu has $4f^{14}\,5d^1$ configaration, where the last electron is enter to the capacity of the 4f-shell.

Lanthanide contraction:

The element cerium to Lutetium of atomic number 58-71 are called Lanthanides. They are so similar in properties with lanthanum (57) that they may be considered as a single element and so that they should be placed along with lanthanum in the same place of the periodic table.

On moving from left to right across a period the size of the atom of the element decreases due to increase in nuclear charge & introduction of electron in the same outer shell (4f) decrease in size also occurs among the 14 Lanthanides. The contraction in size from one element to another is fairly small, additive effect of the 14 elements becomes about 0·2 Å unit and this contraction in size is known as Lanthanides contraction.

Cause of Lanthanide Contraction:

We have already seen that in lanthanides the additional electrons enters into 4f-subshell not in the valence-shell namely sixth shell. The shielding effect in 4f-electrons are very little, because of the diffused shape of the f-subshell. The nuclear charge increases by unity at each step. Thus the nuclear charge increases at each step, while there is no comparable increase in the mutual shielding in 4f electrons. As a result electrons in the outermost shell experience increasing nuclear attraction from the growing nucleus. For this reason the atomic size go on decreasing as we move from ${}_{57}La \longrightarrow {}_{71}Lu$.

The valence-shell electronic configaration of Lanthanides can be represented as: $4f^{0,2\cdots14}$, $5d^{0,1}$, $6s^2$

The complete electronic configaration of Lanthanides is $1s^2\ 2s^2 2p^6\ 3s^2 3p^6 3d^{10}\ 4s^2 4p^6 4d^{10} 4f^{0,2-14}\ 5s^2 5p^6 5d^{0,1}\ 6s^2$

Complex Formation: All Lanthanides ions are form stable complexes with chelating ligands such as EDTA. Those ions at the righ hand side of lanthanides series such as Lu^{+3} form strongest complexes as they have the smallest size. If some acid is added, the least stable EDTA complexes are dissociated. give ions at the left hand side of the series Ce^{+3}, Pr^{+3}, Nd^{+3}.

oxalates of the lanthanides are insoluble. but left hand is side of Lanthanides are ppted as the oxalates.

Pr (IV) and Tb (IV):

These exist only in oxides and Fluorides. The oxides are very common & non stoichiometsic.

$Tb_2O_3 \xrightarrow[{[O]}]{450^\circ C} Tb_2O_2$ $NaPrF_5$, Na_2PrF_6

$Pr_2O_3 \xrightarrow[air]{500^\circ C} PrO_2$

$Tb^{+4} \rightarrow 4f^7$ $Dy^{+4} \rightarrow 4f^8$

$Pr^{+4} \rightarrow 4f^1$

M+2:

$Eu^{+2} \rightarrow [Xe]\,4f^7$

$Yb^{+2} \rightarrow [Xe]\,4f^{14}$

⊛ Aqueous chemistry of Ce(IV) :

In Lanthanides, only aq. chemistry of Ce^{+4} is exist. The high charge of ion leads easily hydrated. Except ($HClO_4$) in strong acidic sol^n, the hydrated Ce^{+4} is hydrolysed giving the polymeric specis and H^+ ion.

Preparation: Aq. Ce(IV) can be prepared by oxidising a Ce(III) solution with very strong oxidising agent e.g.- Ammonium peroxodisulphate, $(NH_4)_2S_2O_8$

Use:

⟨i⟩ Ce(IV) is used to oxidised alcohol, aldehyde & ketone at the α- carbon atom.

⟨ii⟩ Ce(IV) is used in the volumetric titration which can be used as a oxidising agent like $K_2Cr_2O_7$ & $KMnO_4$.

⊛ Ce and Eu are quite different from the rest of the Lanthanides - justify.

Except Ce & Eu, all the lanthanides show stable +3 oxidation state. But Ce is stable in +4 state (f^0) and Eu is a stable in +2 state (f^7). Hence as the properties are determind by size and charge of metal ions, so it is easily understood that the size of Ce(IV) & Eu(+2) are quite $diff^t$ so their properties are quite different from the rest of lanthanides.

Eu^{+2} reacts with H_2SO_4 to give $EuSO_4$ which is insoluble in water. but other Lanthanide sulfates are soluble in H_2O.

The magnetic moment of 1st row transition elements may be calculated from the equation:

$$\mu_{(S+L)} = \sqrt{4S(S+1) + \sqrt{L(L+1)}} \quad BM$$

where S = Resultant spin quantum number

L = Resultant orbital quantum number

For transition elements, the orbital contribution is usually quenched out by interaction with the electric fields of the ligands in its environment. Thus the magnetic moment can be calculated using the simple spin only formula i,e,

$$\mu_S = \sqrt{4S(S+1)} \quad BM \qquad \text{where } S = n/2$$

$$= \sqrt{n(n+2)} \quad BM \qquad n = \text{number of unpaired electrons.}$$

This simple relationship works with La^{+3}, Ce^{+4} (f^0), Gd^{+3} (f^7) and Lu^{+3} (f^{14}).

La^{+3}, Ce^{+4} have f^0 and Lu^{+3} has an f^{14} configaration; thus these are diamagnetic and other f-states contain unpaired electrons and are therefore paramagnetic.

The 4f electrons of Lanthanide ions are deeply inside the atom. Thus they are largly shielded from external fields by the overlapping 5S and 5P electrons. As a result, Spin-orbit Coupling is much larger than the crystal field (of the order of 2000 cm^{-1} compared to 100 cm^{-1}) and must be considered. But the reverse situations is occur in the d-block elements where the d-electrons are exposed directly to the influence of neighbouring groups and the crystal field is therefore much greater than the spin-orbit coupling.

Thus the magnetic effect of the motion of the electron in its orbital is not quenched out. The magnetic moment must be calculated from unpaired electron spins and that from the orbital motion. This also happens with the second and third row transition elements.

$$\mu = g\sqrt{J(J+1)}\ \text{BM}$$

g = Lande splitting factor

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

$$\begin{array}{cccccccc} L \rightarrow & 0 & 1 & 2 & 3 & 4 & 5 & 6 \\ & \downarrow & \downarrow & \downarrow & \downarrow & \downarrow & \downarrow & \downarrow \\ & S & P & D & F & G & H & I \end{array}$$

In the Lanthanides the spin contribution 'S' and orbital contribution 'L' couple together to give a new quantum number J.

$J = L - S$ when the shell is less than ~~fat~~ half full

$J = L + S$ when the shell is more than half full.

J can take the values |L

$J = |L+S|, |L+S-1|, |L+S-2| \ldots\ldots\ldots |L-S|$.

Thus the magnetic moment μ is calculated in Bohr magneton by

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

$$g = 3/2 + \frac{S(S+1) - L(L+1)}{2J(J+1)}$$

For most of the Lanthanides there is excellent agreement between the calculated values using the coupled spin and orbital momentum formula and experimental values measured at 300 K.

The agreement for Eu^{+3} is poor, and that for Sm^{+3} is not very good. The reason is that with Eu^{+3} the spin orbit coupling constant is only about 300 cm^{-1}. This means that the difference in energy between the ground state and next state is small. Thus the energy of thermal motion is sufficient to promote some electrons and partially populate the higher state. Because of this the magnetic properties are not solely determind by the ground stat configaration. At low temparature, measuring the magnetic moment prevents the population of higher energy level For this reason, at low temparature the magnetic moment of Eu^{+3} is close to zero.

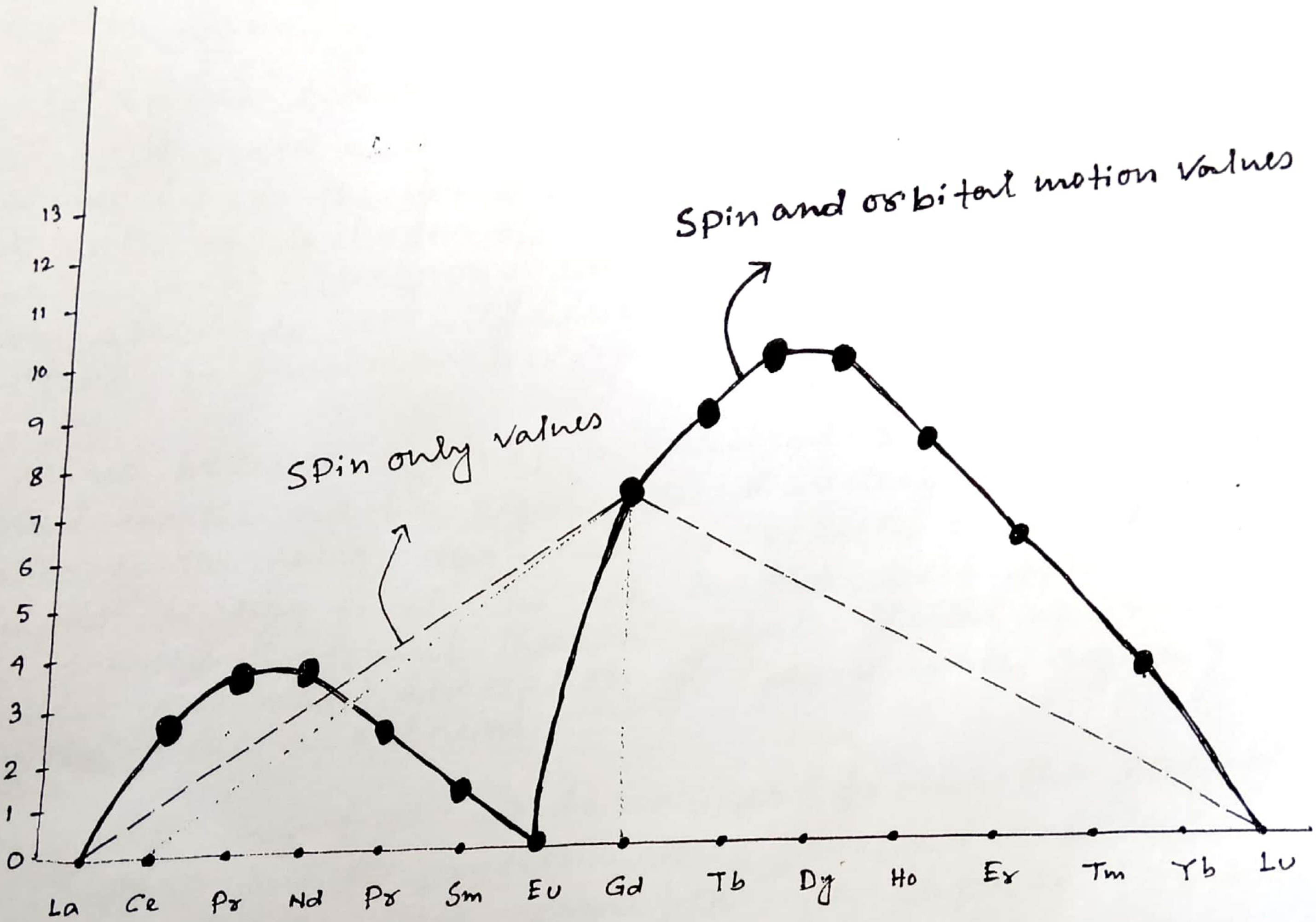

Fig: Paramagnetic moments of Ln^{3+} Lanthanide ions at 300K.

Colour and Spectra:

Many trivalent lanthanides ions are distinct coloured in both solid state and in aqueous solution. The colour seems to depend on the number of unpaired f-electrons. The elements with nf electrons often have a similar colour to a those with (14-n) f electrons. However, the elements in other oxidation states do not all have colours similar to their isoelectronic 3+ counterparts.

Colour arises because light of a particular wavelength is absorbed in the visible region. The wavelength absorbed corresponds to the energy required to promote an electron to a higher energy level. In the lanthanides spin-orbit coupling is more important than crystal field splitting. Lanthanides ions show absorption in the visible region or UV-region of the spectrum.

In Ln^{3+} ion, the excited state arises from the ground state of $4f^n$. Thus the transitions are involved mainly 'f-f' transitions. Strictly these transitions are Laporte forbidden ($\Delta l=0$). Thus the colours are pale because they depend on relaxation of the rule. The f-orbitals are deeply inside the atom. Thus they are largely shielded from environmental factors such as nature and number of ligands and from vibrations of the ligands. The 4f level is much deep-seated and least affected by crystal field and M-L bond vibration. Thus the position of the absorption band (i.e. colour) does not change with different ligands.

	f-electron	Colour		f-electron	Colour
La^{+3}	0	Colourless	Lu^{+3}	14	Colourless
Ce^{+3}	1	Colourless	Yb^{+3}	13	Colourless
Pr^{+3}	2	Green	Tm^{+3}	12	Green
Nd^{+3}	3	Pink	Er^{+3}	11	Pink
Pm^{+3}	4	Pink yellow	Ho^{+3}	10	Pink yellow
Sm^{+3}	5	yellow	Dy^{+3}	9	yellow
Eu^{+3}	6	Pale Pink	Tb^{+3}	8	Pale Pink
Gd^{+3}	7	Colourless	Gd^{+3}	7	Colourless

Q. Why Ce^{+3} and Tb^{+3} are colourless?

Ans: Ce^{+3} and Tb^{+3} are colourless because they do not absorb in the visible region. However they show exceptionally strong absorption in UV region, because of transitions from 4f to 5d orbital, thus lapport allowed transition $(\delta l = 1)$ & gives stronger absorption than forbidden f-f transition.
The electronic configuration of Ce^{+3} is f^1 & Tb^{+3} is f^8, thus loss of one electron gives the extra stability of an empty and half-filled shell.

● Charge Transfer transition:

Charge transfer spectra are possible due to transfer of an electron from ligand to metal. This transition is possible if metal is very high oxidation state or the ligand has reducing properties. CT usually produces more intense colour. The yellow colour of Ce^{+4} solution arises from CT rather than 'f-f' transition.
The blood-red colour of Sm^{+3} is due to CT transition.

● Lanthanides elements give sharp peak whereas transition elements give broad peak - Explain.

(i) The f-orbitals are deep inside the atom. Thus they are largly shielded from environmental factors such as the nature & number of ligands which form the complexes, and from vibration of the ligands.
But d-orbitals in transition elements are weakly shielded from environmental factors.

(ii) For lanthanides the spin-orbit coupling become more pronounced than crystal field strength and different states of J values are sufficiently apart in energy.
But for transition element Russel-saunder states are close to each other.

(iii) For an f-electron the subsidiary quantum number $l = 3$ so me may have values +3, +2, +1, 0, -1, -2 & -3. Thus a large number of transitions are possible. But for transition element the number of possible transition is less.

Colour: The colour of Lanthanides due to transition of electrons from ground state to excited state & absorption must be occurs in visible region.

The colour of f^n & f^{14-n} show similar colour —

The transition of Lanthanides mainly f-f transition which are forbidden like d-d transition.

For transition metal, relaxation is available in d-d transition due to distortion & CF splitting is more pronounced.

For Lanthanides, CF splitting is less pronounced due to deeply-seated 4f orbitals. Hence colour of Ln^{+3} ions are less intense.

Spin-orbit coupling become more pronounced than CF strength & dif^t states of J value are sufficiently apart in energy; electronic transition between them gives rise to sharp bands.

For Lanthanides, $l = 3$ & $m_l = \pm 3, \pm 2\ \pm 1$ & 0. thus large number of transitions are possible.

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Assistant Professor
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Midnapore College (Autonomous)
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