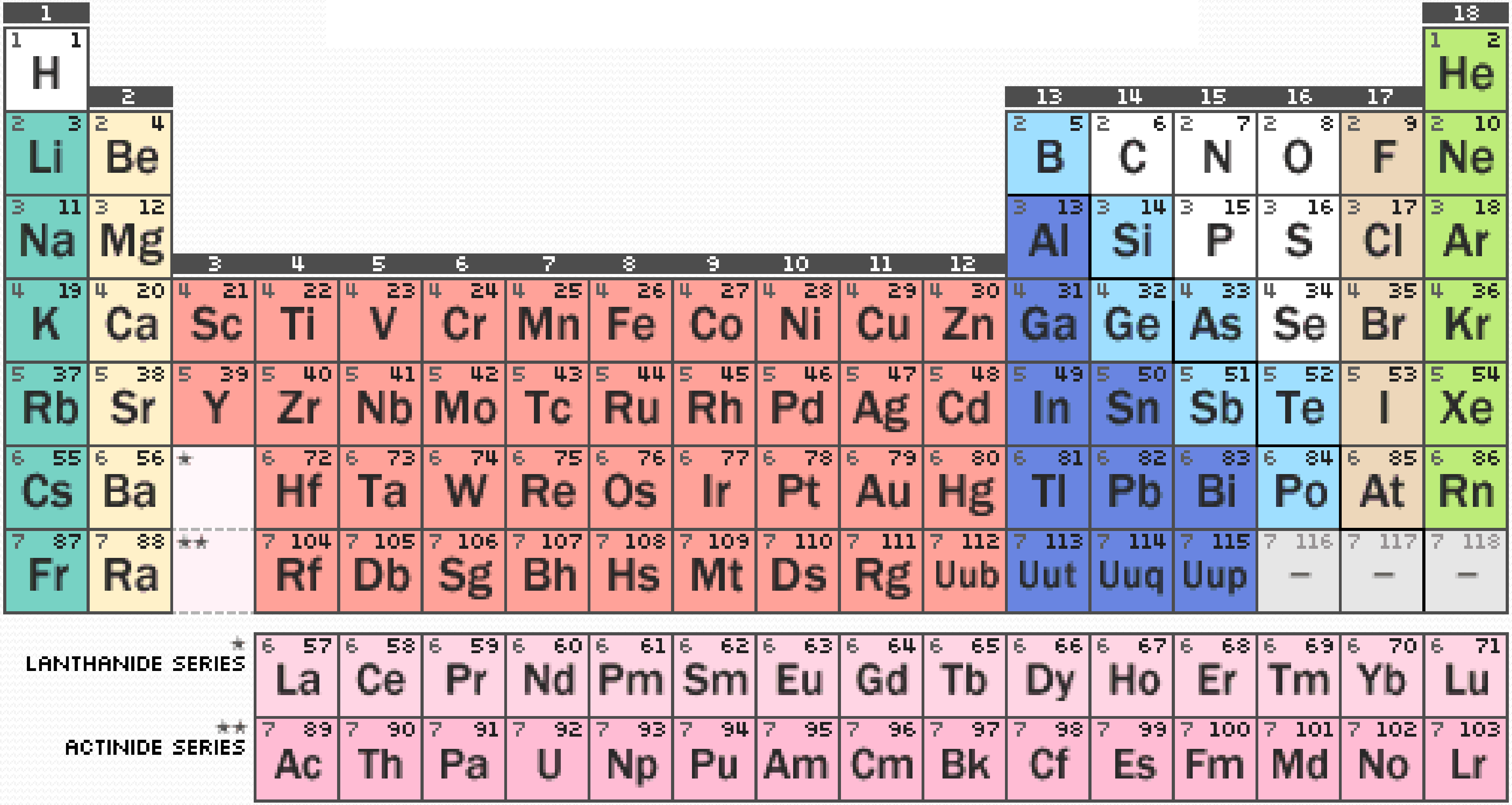
LANTHANIDES



1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
1 1 H																	1 2 He
2 3 Li	2 4 Be											2 5 B	2 6 C	2 7 N	2 8 O	2 9 F	2 10 Ne
3 11 Na	3 12 Mg											3 13 Al	3 14 Si	3 15 P	3 16 S	3 17 Cl	3 18 Ar
4 19 K	4 20 Ca	4 21 Sc	4 22 Ti	4 23 V	4 24 Cr	4 25 Mn	4 26 Fe	4 27 Co	4 28 Ni	4 29 Cu	4 30 Zn	4 31 Ga	4 32 Ge	4 33 As	4 34 Se	4 35 Br	4 36 Kr
5 37 Rb	5 38 Sr	5 39 Y	5 40 Zr	5 41 Nb	5 42 Mo	5 43 Tc	5 44 Ru	5 45 Rh	5 46 Pd	5 47 Ag	5 48 Cd	5 49 In	5 50 Sn	5 51 Sb	5 52 Te	5 53 I	5 54 Xe
6 55 Cs	6 56 Ba	*	6 72 Hf	6 73 Ta	6 74 W	6 75 Re	6 76 Os	6 77 Ir	6 78 Pt	6 79 Au	6 80 Hg	6 81 Tl	6 82 Pb	6 83 Bi	6 84 Po	6 85 At	6 86 Rn
7 87 Fr	7 88 Ra	**	7 104 Rf	7 105 Db	7 106 Sg	7 107 Bh	7 108 Hs	7 109 Mt	7 110 Ds	7 111 Rg	7 112 Uub	7 113 Uut	7 114 Uuq	7 115 Uup	7 116 –	7 117 –	7 118 –
* LANTHANIDE SERIES			6 57 La	6 58 Ce	6 59 Pr	6 60 Nd	6 61 Pm	6 62 Sm	6 63 Eu	6 64 Gd	6 65 Tb	6 66 Dy	6 67 Ho	6 68 Er	6 69 Tm	6 70 Yb	6 71 Lu
** ACTINIDE SERIES			7 89 Ac	7 90 Th	7 91 Pa	7 92 U	7 93 Np	7 94 Pu	7 95 Am	7 96 Cm	7 97 Bk	7 98 Cf	7 99 Es	7 100 Fm	7 101 Md	7 102 No	7 103 Lr

Lanthanides ,also called rare earth elements comprise of a group of 15 elements of which only one, promethium (Pm) does not occur naturally in the earths crust while the other fourteen are relatively abundant in rocks and soils. "**The series of fifteen metallic elements from lanthanum to lutetium are called lanthanides. In these elements the differentiating electron enters 4f-orbitals.** The name lanthanides has been derived from lanthanum (La) element which is the prototype of lanthanides

Position in Periodic table – In 6th period after La the incoming electron enters the 4f orbital and the following 14 elements are called Lanthanide/Lanthanones. Placed outside the body of main periodic table as they resemble each other very closely and keeping them inside the main table will over rule periodic law.

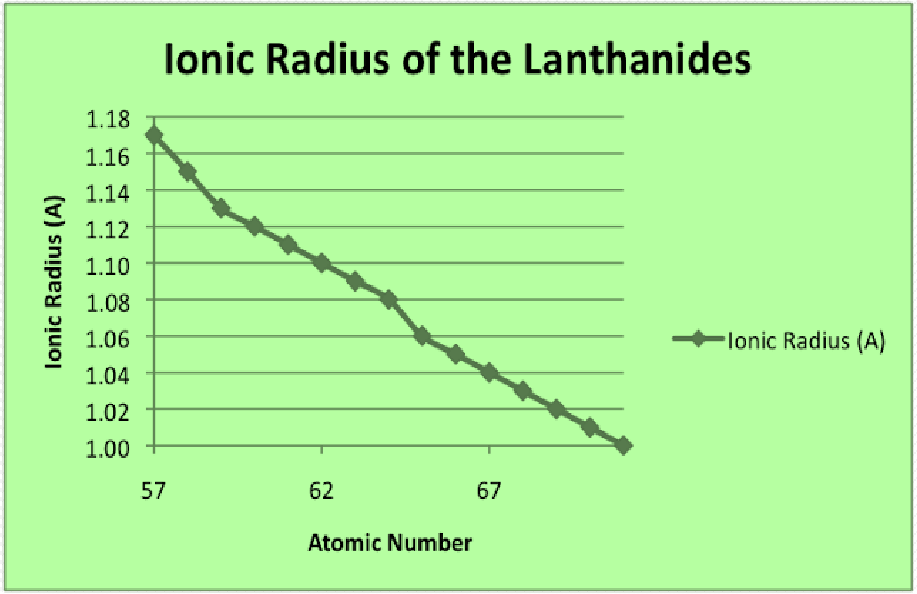
Electronic configuration - **The general electronic configuration of these elements is ns^2 $(n\text{-}1)d^{0\text{-}1}$ $(n\text{-}2)f^{1\text{-}14}$.** They resemble each other very closely as they have same electronic configuration in nth and (n-1) valency shell. Their most common oxidation state is +3 involving only $5d^1$ and $6s^2$ electrons.
An alternate electronic configuration is also suggested that after Ce, the d electron also shifts to 4f orbital, except for those elements where it will disturb **f^1 or f^{14} configuration.**

1.Electronic configuration

Element name	**Symbol**	**Ln**		**Ln^{3+}**	**Radius**
		I	**II**		**Ln^{3+}/ pm**
Lanthanum 57 **116**	**La**	$[Xe]\ 4f^{0}6s^{2}5d^{1}$	$[Xe]\ 4f^{0}6s^{2}5d^{1}$	$[Xe]4f^{0}$	
Cerium 58	**Ce**	$[Xe]\ 4f^{1}6s^{2}5d^{1}$	$[Xe]4f^{1}6s^{2}5d^{1}$	$[Xe]4f^{1}$	**114**
Praseodymium	59Pr	$[Xe]\ 4f^{2}6s^{2}5d^{1}$	$[Xe]4f^{3}6s^{2}$	$[Xe]4f^{2}$	113
Neodymium 60	Nd	$[Xe]\ 4f^{3}6s^{2}5d^{1}$	$[Xe]4f^{4}6s^{2}$	$[Xe]4f^{3}$	111
Promethium 61	Pm	$[Xe]\ 4f^{4}6s^{2}5d^{1}$	$[Xe]4f^{5}6s^{2}$	$[Xe]4f^{4}$	109
Samarium 62	Sm	$[Xe]\ 4f^{5}6s^{2}5d^{1}$	$[Xe]4f^{6}6s^{2}$	$[Xe]4f^{5}$	108
Europium 63	Eu	$[Xe]\ 4f^{6}6s^{2}5d^{1}$	$[Xe]4f^{7}6s^{2}$	$[Xe]4f^{6}$	107
Gadolinium 64	**Eu**	$[Xe]\ 4f^{7}6s^{2}5d^{1}$	$[Xe]4f^{7}6s^{2}5d^{1}$	$[Xe]4f^{7}$	**105**
Terbium 65	Tb	$[Xe]\ 4f^{8}6s^{2}5d^{1}$	$[Xe]\ 4f^{9}6s^{2}$	$[Xe]4f^{8}$	104
Dysprosium 66	Dy	$[Xe]\ 4f^{9}6s^{2}5d^{1}$	$[Xe]\ 4f^{10}6s^{2}$	$[Xe]4f^{9}$	103
Holmium 67	Ho	$[Xe]\ 4f^{10}6s^{2}5d^{1}$	$[Xe]\ 4f^{11}6s^{2}$	$[Xe]4f^{10}$	102
Erbium 68	Er	$[Xe]\ 4f^{11}6s^{2}5d^{1}$	$[Xe]\ 4f^{12}6s^{2}$	$[Xe]4f^{11}$	100
Thulium 60	Tm	$[Xe]\ 4f^{12}6s^{2}5d^{1}$	$[Xe]\ 4f^{13}6s^{2}$	$[Xe]4f^{12}$	99
Ytterbium 70	Yb	$[Xe]\ 4f^{13}6s^{2}5d^{1}$	$[Xe]\ 4f^{14}6s^{2}$	$[Xe]4f^{13}$	99
Lutetium 71	**Lu**	$[Xe]\ 4f^{14}6s^{2}5d^{1}$	$[Xe]\ 4f^{14}6s^{2}5d^{1}$	$[Xe]4f^{14}$	**98**

2. Lanthanide Contraction

Definition - The steady **decrease in the size of the atoms and ions** of the rare-earth elements **with increasing atomic number** from lanthanum (atomic number 57) through lutetium (atomic number 71) is known as the lanthanide contraction. For each consecutive atom the nuclear charge increases by one unit, accompanied by a corresponding increase in the number of electrons present in the 4f orbitals.



Cause – The new electrons enter the 4f orbital which have very poor shielding effect due to their diffused shape, as a result nuclear attraction increases and electron shells contract.

Consequences –

1. **Among the lanthanides**
2. **Post Lanthanides**

Consequences –

I Among Lanthanides –

1. **Basicity** of ions- decreases from La $^{3+}$ to Lu^{3+} so their oxides and hydroxides are less basic
2. As the atomic size decreases across the series –
   - a) The ionisation potential increases
   - b) Metallic nature decreases
   - c) Electropositivity decreases
   - d) Electronegativity Increseases
   - e) Tendency to form complexes increases

II Post Lanthanides –

i) Occurrence of elements as pairs – Due to similar size of 4d and 5d in a group, they have similar physical and chemical properties and their separation becomes very difficult. Zr/Hf, Nb/Ta, Mo/W

ii)**Densities** – 5d elements have very high densities as down the group there is large increase in mass but no increase in volume.

III -Occurrence of Yttrium along with heavier lanthanides –

yttrium has similar charge and size to Ho^{3+} & Er^{3+}

3. Oxidation States

Symbol	Idealized	Observed	M^{3+}	M^{2+}	M^{4+}	At. Radii A*	N0. of f-electron
La	[Xe] $4f^0 5d^1 6s^2$	[Xe] $4f^0 5d^1 6s^2$	[Xe]	-		1.88	0
Ce	[Xe]$4f^1 5d^1 6s^2$	[Xe]$4f^2 5d^0 6s^2$	4f1	$4f^2$	[Xe]	1.82	1
Pr	[Xe]$4f^2 5d^1 6s^2$	[Xe]$4f^3 5d^0 6s^2$	$4f^2$	-	$4f^1$	1.83	2
Nd	[Xe]$4f^3 5d^1 6s^2$	[Xe]$4f^4$ $6s^2$	$4f^3$	$4f^4$	$4f^2$	1.82	3
Pm	[Xe]$4f^4 5d^1 6s^2$	[Xe]$4f^5$ $6s^2$	$4f^4$	-	-		4
Sm	[Xe]$4f^5 5d^1 6s^2$	[Xe]$4f^6$ $6s^2$	$4f^5$	$4f^6$	-	1.80	5
Eu	[Xe]$4f^6 5d^1 6s^2$	[Xe]$4f^7$ $6s^2$	$4f^6$	$4f^7$	-	2.04	6
Gd	[Xe]$4f^7 5d^1 6s^2$	[Xe]$4f^7 5d^1 6s^2$	$4f^7$	-	-	1.80	7
Tb	[Xe]$4f^8 5d^1 6s^2$	[Xe]$4f^9$ $6s^2$	$4f^8$	-	$4f^7$	1.78	8
Dy	[Xe]$4f^9 5d^1 6s^2$	[Xe]$4f^{10}$ $6s^2$	$4f^9$	-	$4f^8$	1.77	9
Ho	[Xe]$4f^{10} 5d^1 6s^2$	[Xe]$4f^{11}$ $6s^2$	$4f^{10}$	-	-	1.77	10
Er	[Xe]$4f^{11} 5d^1 6s^2$	[Xe]$4f^{12}$ $6s^2$	$4f^{11}$	-	-	1.76	11
Tm	[Xe]$4f^{12} 5d^1 6s^2$	[Xe]$4f^{13}$ $6s^2$	$4f^{12}$	$4f^{13}$	-	1.75	12
Yb	[Xe]$4f^{13} 5d^1 6s^2$	[Xe]$4f^{14}$ $6s^2$	$4f^{13}$	$4f^{14}$	-	1.94	13
Lu	[Xe]$4f^{14} 5d^1 6s^2$	[Xe]$4f^{14} 5d^1 6s^2$	$4f^{14}$	-	-	1.73	14

Oxidation States

- The configuration of La $^{3+}$ ion, is that of xenon which is highly stable. So, it is not possible to have a La+4 ion.

- In the same way Ga, Lu also form only +3 ions, because the removal of three electrons give stable half filled $4f^7$ configuration for Gd $^{3+}$ ion and in completely filled 4f1-4 configuration for Lu $^{3+}$ ions.

- In other Lanthanides, +2 and +4 oxidations states also occur but these are always less table than the +3 oxidation state which is characteristic of this family

- The +2 and +4 oxidation states are shown by those elements which will attain **f^{0}, f^{7} and f^{14}** configurations by doing so

- For eg . Ce $^{4+}$, Eu $^{2+}$ are $4f^{7}$, Tb $^{4+}$ - $4f^{7}$, Yb $^{2+}$ – $4f^{14}$

extra stability is associated with f^{0}, f^{7}, f^{14} configurations.

4. Magnetic Behaviour

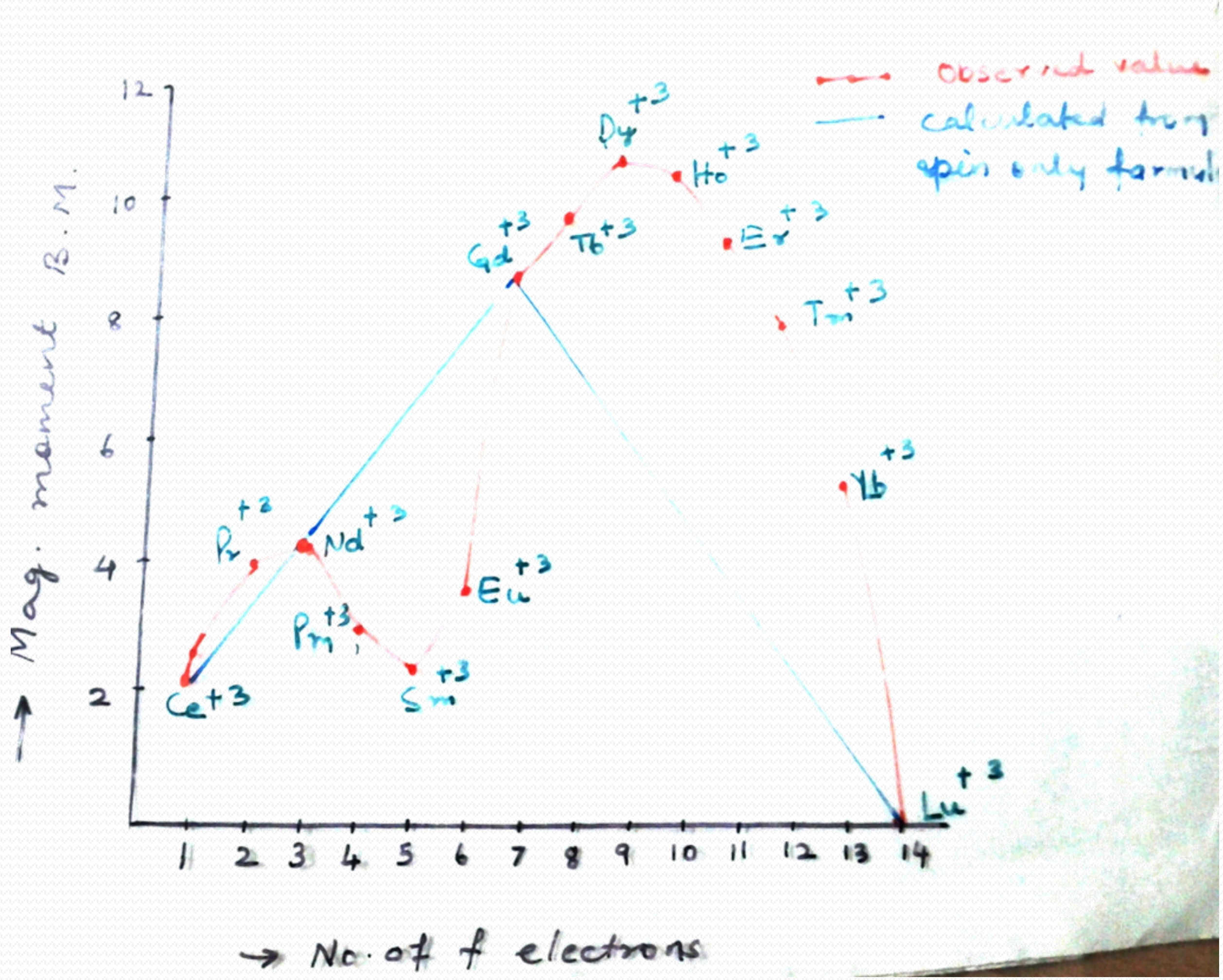
❖ La+3 and Lu+3 do not contain any unpaired electrons, so they do not show paramagnetism. **All other tri positive ions of lanthanides are paramagnetic**.

❖ the 4f electrons are **deep inside** the ion and are well shielded from the quenching effect of the environment. The 4f-orbitals are **well shielded** from the surroundings by the overlying 5s and 5p- orbitals . As a result, the electric field of the ligands surrounding the ion **does not restrict the orbital motion of the electron**. So, in this case the observed paramagnetism is due to both factors – the electron spin and orbital motion.

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

S- spin contribution, L – Orbital contribution

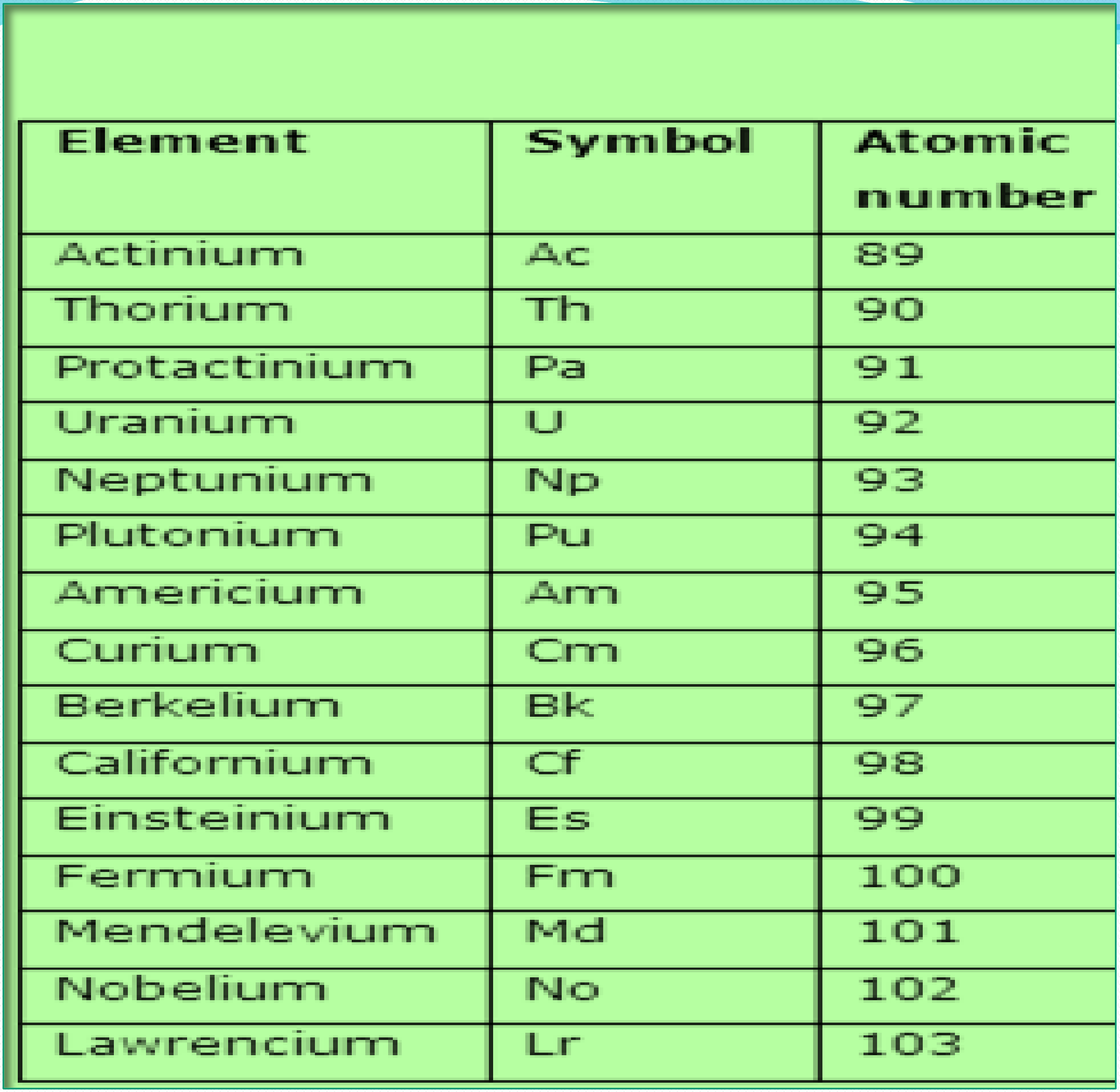
❖The magnetic moments of tri positive lanthanide ions are plotted against their respective atomic number .The value increases up to Nd+3 and then drops to (1.47) sm+3. it raises again and becomes maximum Dy+3 and starts dropping to zero for Lu+3 (f14) which is diamagnetic.


observed value
calculated from
spin only formul
Mag. moment B.M.
12
10
8
6
4
2
No. of f electrons
1
2
3
4
5
6
7
8
9
10
11
12
13
14
Ce+3
Pr+3
Nd+3
Pm+3
Sm+3
Eu+3
Gd+3
Tb+3
Dy+3
Ho+3
Er+3
Tm+3
Yb+3
Lu+3

5. Colour - The colour of the Ln $^{3+}$cations to a large extent depend upon the electronic configuration. For eg. **La $^{3+}$($4f^0$), Gd $^{3+}$($4f^7$) and Lu $^{3+}$ ($4f^{14}$)** are colourless. The colour is due to **f—f transitions i.e.** transition of the electrons from the **lower energy f-orbitals to the higher energy f orbital**. The colour of ion having n no. of f- electron is same as that of element having (14 – n) no.

6. Complexes -Lanthanides are **moderate** in their complex forming ability which increases to the right . Although tripositive cations have a high charge equal to +3 on them, their size is so large, their **charge to radius ratio becomes so small** that these ions have less tendency to form complexes, eg: Stable complexes are known with chelating oxygen containing ligands like EDTA, oxalic acid, acetylacetone, . There is a general decrease in complex formation with a specific ligands from **Ln $^{4+}$> Ln $^{3+}$>Ln $^{2+}$ as charge decreases**

Actinides



Element	Symbol	Atomic number
Actinium	Ac	89
Thorium	Th	90
Protactinium	Pa	91
Uranium	U	92
Neptunium	Np	93
Plutonium	Pu	94
Americium	Am	95
Curium	Cm	96
Berkelium	Bk	97
Californium	Cf	98
Einsteinium	Es	99
Fermium	Fm	100
Mendelevium	Md	101
Nobelium	No	102
Lawrencium	Lr	103

Electronic Configuration

Element	Seaborg view	Dawson View	Oxidation States
Ac	[Rd] $5f^0\ 6d^1\ 7s^2$	[Rd] $5f^0\ 6d^1\ 7s^2$	+3, +2
Th	[Rd] $5f^1\ 6d^1\ 7s^2$	[Rd] $5f^0\ 6d^2\ 7s^2$	+4
Pa	[Rd] $5f^2\ 6d^1\ 7s^2$	[Rd] $5f^0\ 6d^3\ 7s^2$	+4, +5
U	[Rd] $5f^3\ 6d^1\ 7s^2$	[Rd] $5f^0\ 6d^4\ 7s^2$	+4, +5, +6
Np	[Rd] $5f^4\ 6d^1\ 7s^2$	[Rd] $5f^4\ 6d^1\ 7s^2$	+4, +5, +6, +7
Pu	[Rd] $5f^5\ 6d^1\ 7s^2$	[Rd] $5f^5\ 6d^1\ 7s^2$	+4 , +5 , +6
Am	[Rd] $5f^6\ 6d^1\ 7s^2$	[Rd] $5f^6\ 6d^1\ 7s^2$	+3, +4, +5, +6
Cm	[Rd] $5f^7\ 6d^1\ 7s^2$	[Rd] $5f^7\ 6d^1\ 7s^2$	+3
Bk	[Rd] $5f^8\ 6d^1\ 7s^2$	[Rd] $5f^8\ 6d^1\ 7s^2$	+3
Cf	[Rd] $5f^9\ 6d^1\ 7s^2$	[Rd] $5f^9\ 6d^1\ 7s^2$	+3
Es	[Rd] $5f^{10}\ 6d^1\ 7s^2$	[Rd] $5f^{10}\ 6d^1\ 7s^2$	+3
Fm	[Rd] $5f^{11}\ 6d^1\ 7s^2$	[Rd] $5f^{11}\ 6d^1\ 7s^2$	+3
Md	[Rd] $5f^{12}\ 6d^1\ 7s^2$	[Rd] $5f^{12}\ 6d^1\ 7s^2$	+3
No	[Rd] $5f^{13}\ 6d^1\ 7s^2$	[Rd] $5f^{13}\ 6d^1\ 7s^2$	+2 (f^{14})
Lr	[Rd] $5f^{14}\ 6d^1\ 7s^2$	[Rd] $5f^{14}\ 6d^1\ 7s^2$	+3

1.Atomic Radii –

Steady **decrease from Ac to Lr** due to imperfect shielding by f- orbitals due to their diffused shape is known as Actinide contraction.

2. Oxidation States –

1. +3 is most common stable O.S.
2. Higher oxidation states are more common for elements upto Np.
3. O. S. upto **+6** are stable.

3. Colour :

- ✓ Metals, ions are **coloured** due to **f-f transitions** and intense change transfer transitions.
- ✓ **f^o, f^7, f^{14} –ions are colour less.**

4. Complex formations:

Far greater tendency than Lanthanides due to high charge and small size.

(i) M^{4+} shows greatest tendency

(ii) $M^{4+} > MO_2{}^{2+}$ $M^{3+} > MO_2{}^{+}$

(iii) High coordn. Nos., upto 8, 9 are common

(iv) Adducts are formed with alkali metal halides.

$ThCl_4 + MCl \rightarrow MThCl_5$, $M_2\ ThCl_2$ etc

(v) Many complexes are formed with chelating agents viz oxine, EDTA, acetyl acetone

(vi) Complexes are formed with ʎ - ligands also viz Thioether, phosphine

(vii) Stability with singly charged ions follows the trend

$F^- > NO_3{}^- > Cl^-$ and

Doubly charged ions – $CO_3{}^{2-} > C2O4\ {}^{2-} > SO_4{}^{2-}$

Separation of Lanthanides

(i) Solvent extraction method

This method is based on the **difference in partition co-effecients** of lanthanide salts between water and organic solvents. The solvents employed in this method of extraction of the lanthanides are usually **tri n-butyl phosphate (TBP) and di (2-ethylhexy) phosphoric acid**. For eg. Gd(NO3)3 can be separated from La $(NO_3)_3$ by continuous extraction with water from a solution of these salts in TBP .

(ii) Ion exchange method:

A synthetic **ion-exchange resin** with functional groups like – COOH and – SO $_3$H is packed in a long column fixed in a vertical position.

The steady decrease in size and consequent decrease in basicity causes the steady increase the complexing ability with increasing atomic number of lanthanides. When an aqueous solution containing `the mixture of trivalent lanthanide ion M+3(aq) is passed through a column having synthetic cation-exchange resin (HR)solid, the **M+3 ions replace H+ ion** of the resin and thus get fixed on that

M+3 (aq) + 3 HR → MR3 (solid) + 3H+(aq)

Small Lu $^{3+}$ gets more hydrated than La $^{3+}$ and is bigger in size. So La(aq) $^{3+}$ gets strongly bound to the resin column than others.

In order to recover M3+ ions fixed on the resin, the column is eluted with a **citric acid – ammonium citrate solution (eluant).** During elution process **NH4+ ions replace M+3 ion** and M- citrate complexes are formed.

The bigger aquated ion is least strongly held and comes out first.

Other ions remain on the column and can be separated by repeated elution.

$$\mathbf{R - M^{3+} + NH_4^+ \longrightarrow R - NH_4^+ + M^{3+} - citrate}$$