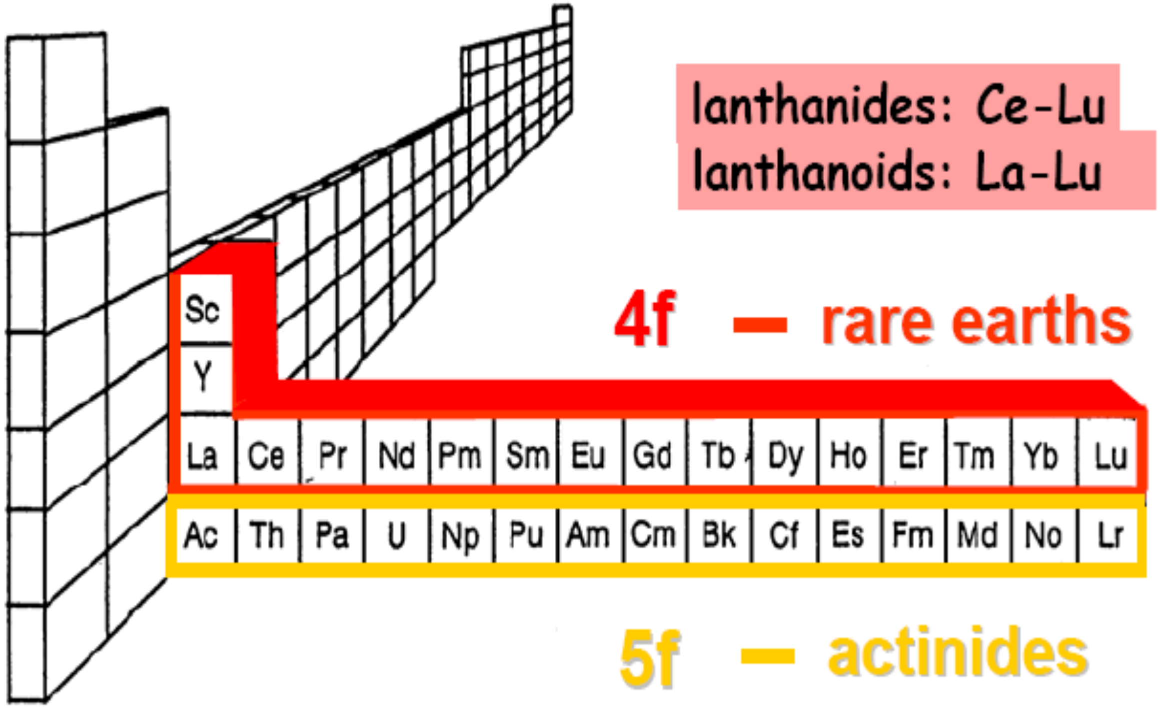
Coordination Chemistry and Reactivity of f Elements

Marinella Mazzanti
Coordination Chemistry Group



lanthanides: Ce-Lu
lanthanoids: La-Lu

4f — rare earths

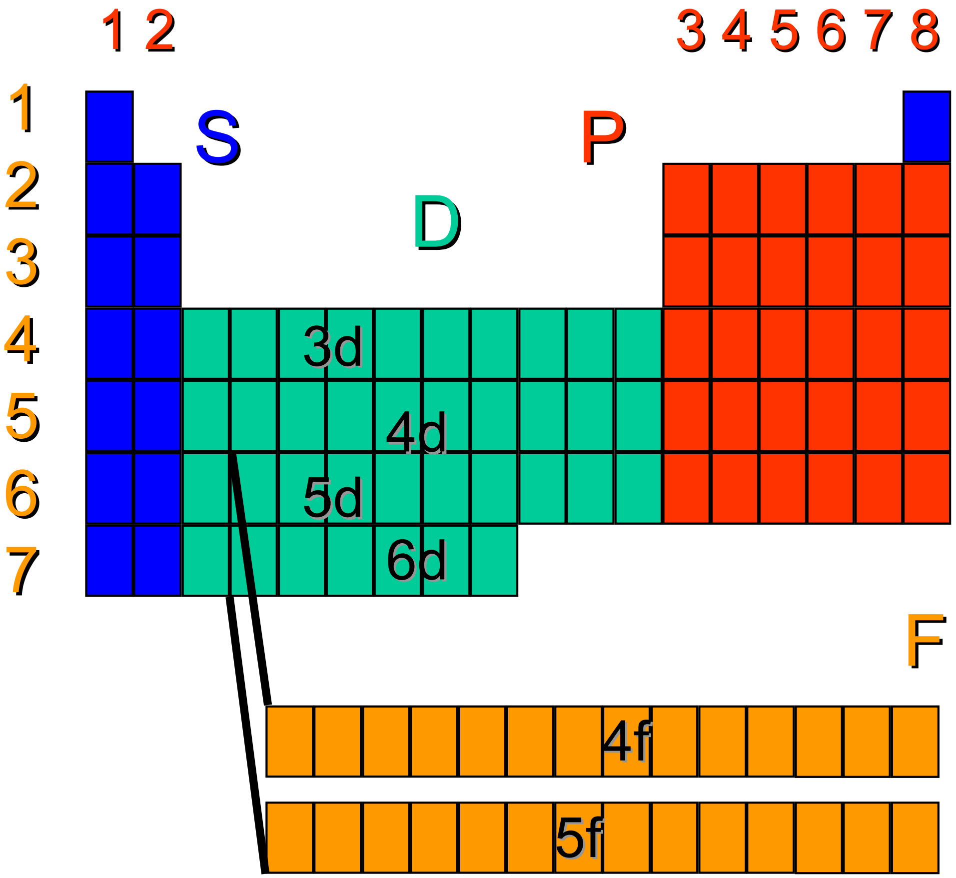
5f — actinides

Pedagogical objective

- Overview of f-elements properties, their fundamental properties and their applications

Pre-requisites

Coordination chemistry

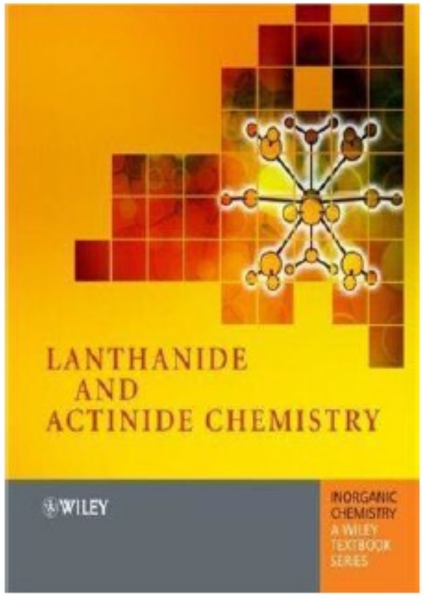


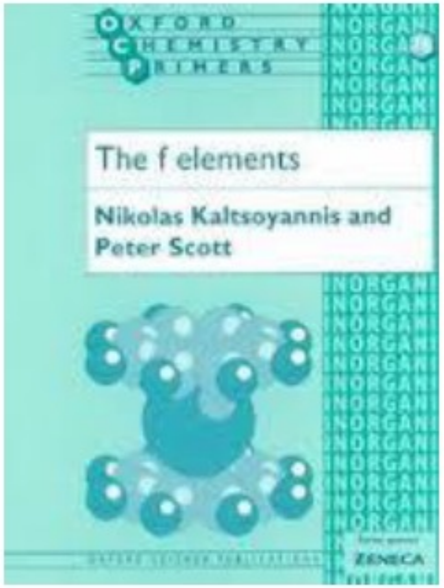
Schedule 2025

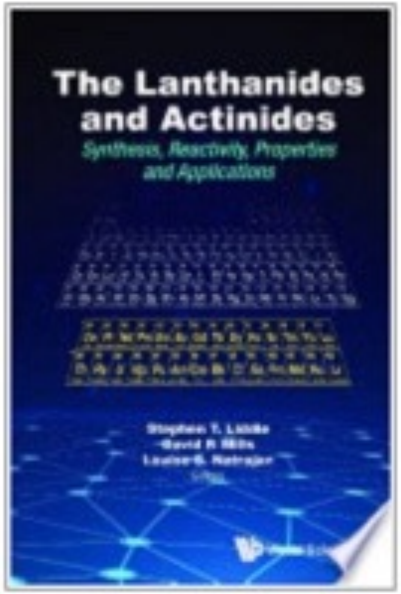
Cours 1 (19/02)	Definition, origins and basic properties of atoms and ions (Cotton Ch1-2)
Cours 2 (26/02)	Electronic spectroscopy, and magnetism of 4 f ions. MRI contrast agents (Cotton Ch 5)
Cours 3 (05/03)	TD1
Cours 4 (12/03)	MRI/Luminescence of 4f ions and its applications
Cours 5 (19/03)	TD 2/Luminescence
Cours 6 (26/03)	Coordination chemistry of 4 f elements (Ch4)
Cours 7 (02/04)	Coordination chemistry of 4 f elements (Ch4)
Cours 8 (09/04)	TD3
Cours 9 (16/04)	Basic properties , Spectroscopy, luminescence and magnetism of 5f elements (Cotton Ch 12)
Cours 10 (30/04)	TD4
Cours 11 (07/05)	Coordination Chemistry of 5 f Element (CH11)-
Cours 12 (14/05)	TD5
Cours 13 (21/05)	Organometallic chemistry (Cotton Ch 6 and 12)
Cour 14 (28/05)	Catalysis and small molecules activation(Ch8)/TD6

Changes in the specific program may occur during the year

Recommended Reading and References







Basic:

Lanthanide and Actinide Chemistry – Simon Cotton (Wiley)

The f-elements – Nikolas Kaltsoyannis and Peter Scott (OUP)

d- and f- block Chemistry – Chris Jones (RSC)

Advanced for those who want more:

The Lanthanides And Actinides: Synthesis, Reactivity, Properties And Applications (World Scientific)

Coordination Chemistry and Reactivity of f Elements

Cours 1 Definition, origins and basic properties of atoms and ions

Learning Outcomes

-Recognize the difference between f-orbitals and other orbitals
Can you remember what d orbitals look like?

-Relate the nature of f-orbitals to properties

-Identify electron configurations of Ln in their different oxidation states

-Assign Ln oxidation states and relate their stability to ionization energies

-Identify conditions stabilizing divalent oxidation state

-Explain lanthanide contraction and its consequences

-Recall the main applications of lanthanides

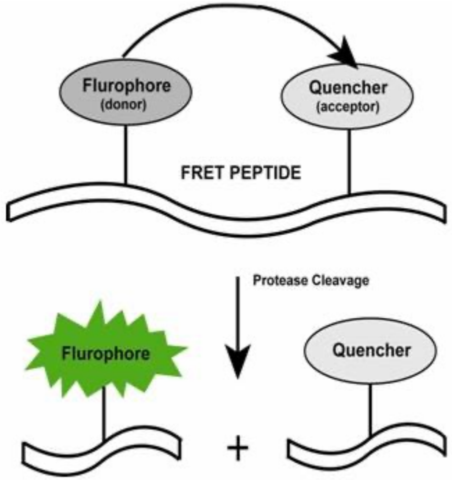
Applications of Lanthanide Ions

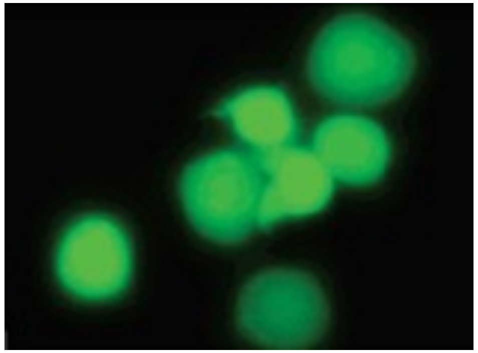
Engine catalysts, pigments, catalysts in organic synthesis

Lanthanide oxides used as chromophores
In fluorescent lights, LEDS, displays

Y_2O_3 :EuIII

First application of **lanthanide fluorescence**
Followed in 1970 by application of molecular compounds as stains in biological assays



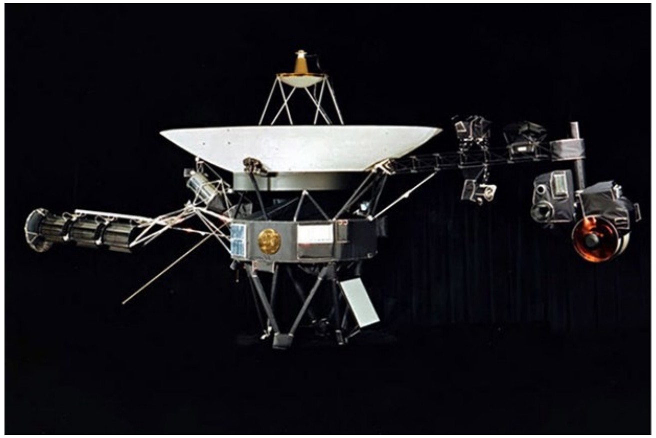


Responsive lanthanide complexes for imaging of key cell cycle regulators and inhibition of tumor cells

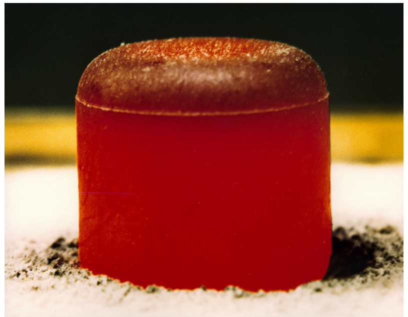
Actinides applications

Uranium and thorium nuclear energy production, U and Pu^{239} military applications and plutonium thermoelectric generator

In 2013 (2022) 36.4%
in Switzerland
Thorium for next generation ??



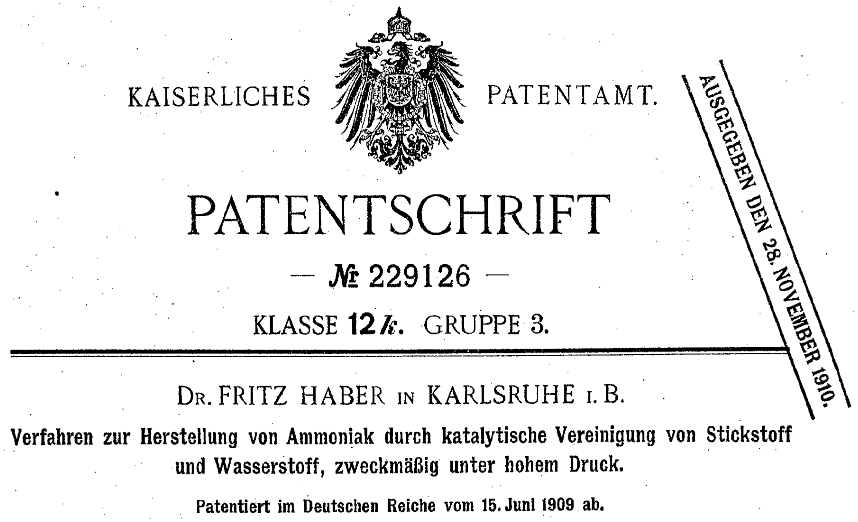
Voyager powered by Pu^{238}
Byproduct of bomb-grade Pu^{239} production



Plutonium pellets
Used to power batteries of Apollo 13

Potential applications of U and Th

Catalysis:
Uranium
Has better performance than iron in nitrogen conversion to NH_3



KAISERLICHES PATENTAMT.

AUSGEGEBEN DEN 28. NOVEMBER 1910.

PATENTSCHRIFT

— № 229126 —

KLASSE 12 k. GRUPPE 3.

Dr. FRITZ HABER in KARLSRUHE i. B.

Verfahren zur Herstellung von Ammoniak durch katalytische Vereinigung von Stickstoff und Wasserstoff, zweckmäßig unter hohem Druck.

Patentiert im Deutschen Reiche vom 15. Juni 1909 ab.

Definitions and discovery

La: $5d^16s^2$

Ce: $4f^1\ 5d^1\ 6s^2$

$4f^{14}5d^16s^2$

57 **La** Lanthanum 138.90547	58 **Ce** Cerium 140.116	59 **Pr** Praseodymium 140.90765	60 **Nd** Neodymium 144.242	61 **Pm** Promethium (145)	62 **Sm** Samarium 150.36	63 **Eu** Europium 151.964	64 **Gd** Gadolinium 157.25	65 **Tb** Terbium 158.92535	66 **Dy** Dysprosium 162.5	67 **Ho** Holmium 164.93032	68 **Er** Erbium 167.259	69 **Tm** Thulium 168.93421	70 **Yb** Ytterbium 173.054	71 **Lu** Lutetium 174.9668
89 **Ac** Actinium (227)	90 **Th** Thorium 232.03806	91 **Pa** Protactinium 231.03588	92 **U** Uranium 238.02891	93 **Np** Neptunium (237)	94 **Pu** Plutonium (244)	95 **Am** Americium (243)	96 **Cm** Curium (247)	97 **Bk** Berkelium (247)	98 **Cf** Californium (251)	99 **Es** Einsteinium (252)	100 **Fm** Fermium (257)	101 **Md** Mendelevium (258)	102 **No** Nobelium (259)	103 **Lr** Lawrencium (262)

$6d^1\ 7s^2$

$5f^{14}\ 7s^2\ 7p^1$

Lanthanides: 58-71 Ln

Actinides: 90-103 An

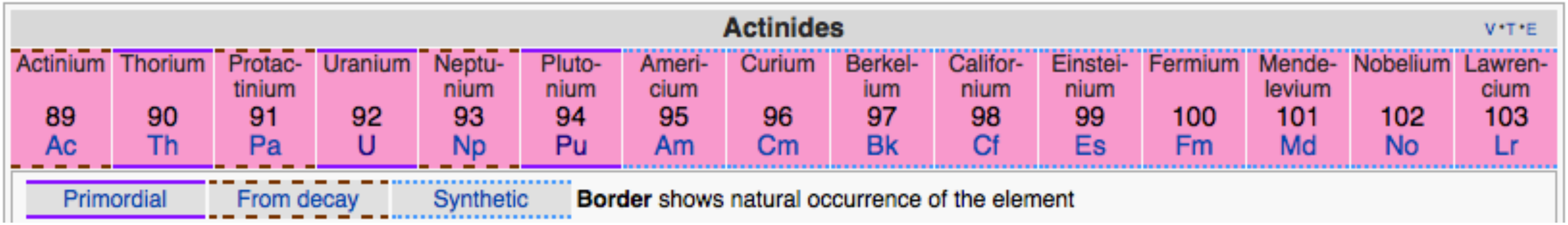
Parent elements La and Ac often included in Ln and An

All f elements are metallic

Rare earths: Sc, Y, La + Ce-Lu

Discovery of rare earths

1794 (Y) – 1947 (Pm)



Actinides V•T•E

Actinium	Thorium	Protac-tinium	Uranium	Neptu-nium	Pluto-nium	Ameri-cium	Curium	Berkel-ium	Califor-nium	Einstei-nium	Fermium	Mende-levium	Nobelium	Lawren-cium
89 Ac	90 Th	91 Pa	92 U	93 Np	94 Pu	95 Am	96 Cm	97 Bk	98 Cf	99 Es	100 Fm	101 Md	102 No	103 Lr

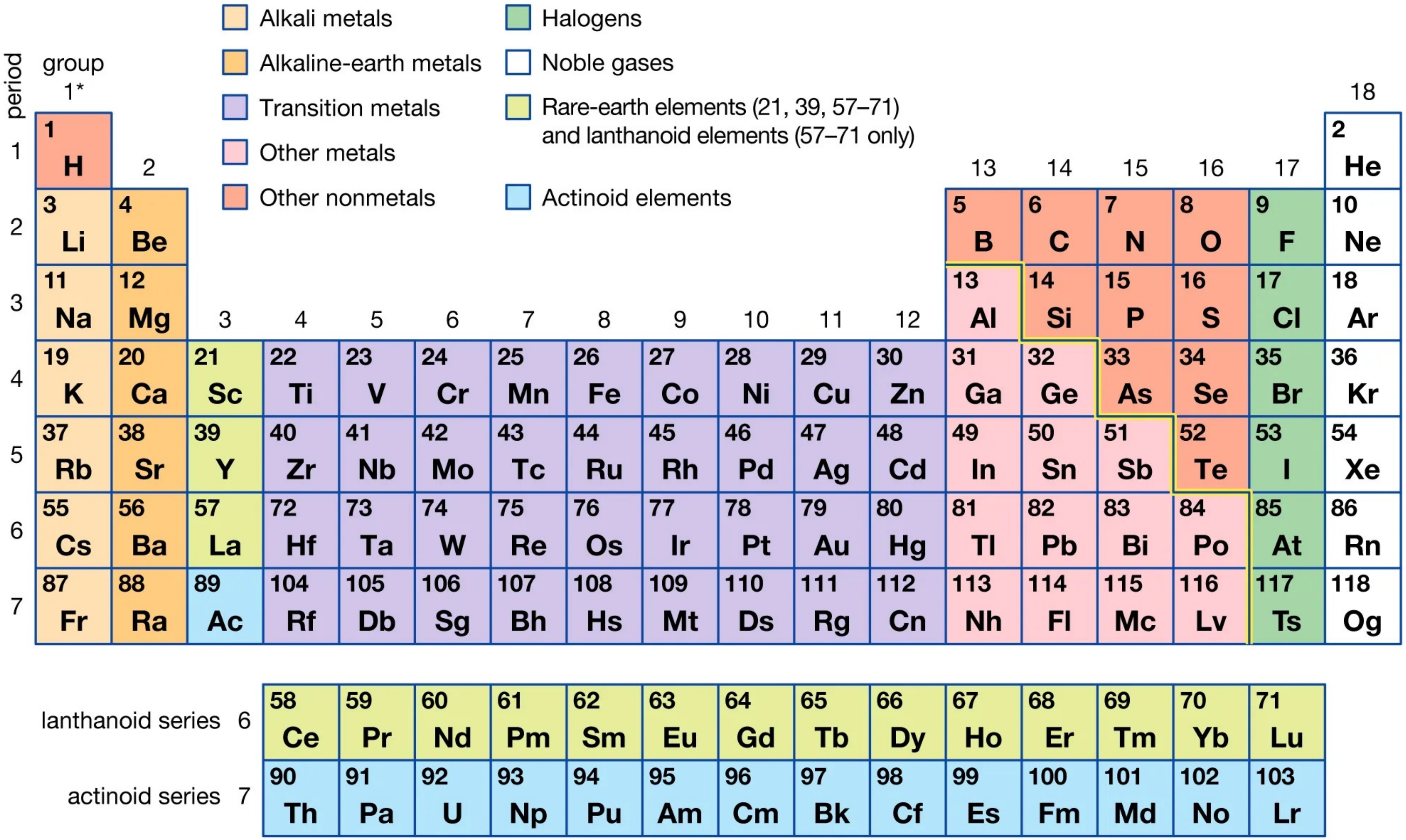
Primordial From decay Synthetic **Border** shows natural occurrence of the element

Discovery of actinides

1789 (U) – 1971 (Lr)

Naturally occurring: Th, Pa, U, Np, ^{244}Pu (^{239}Pu prepared in reactors from uranium)

Periodic table of the elements



🟨 Alkali metals
🟧 Alkaline-earth metals
🟪 Transition metals
▢ Other metals
🟥 Other nonmetals
🟩 Halogens
⬜ Noble gases
🟨 Rare-earth elements (21, 39, 57–71) and lanthanoid elements (57–71 only)
🟦 Actinoid elements

period	group 1*	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
1	1 H																	2 He
2	3 Li	4 Be											5 B	6 C	7 N	8 O	9 F	10 Ne
3	11 Na	12 Mg											13 Al	14 Si	15 P	16 S	17 Cl	18 Ar
4	19 K	20 Ca	21 Sc	22 Ti	23 V	24 Cr	25 Mn	26 Fe	27 Co	28 Ni	29 Cu	30 Zn	31 Ga	32 Ge	33 As	34 Se	35 Br	36 Kr
5	37 Rb	38 Sr	39 Y	40 Zr	41 Nb	42 Mo	43 Tc	44 Ru	45 Rh	46 Pd	47 Ag	48 Cd	49 In	50 Sn	51 Sb	52 Te	53 I	54 Xe
6	55 Cs	56 Ba	57 La	72 Hf	73 Ta	74 W	75 Re	76 Os	77 Ir	78 Pt	79 Au	80 Hg	81 Tl	82 Pb	83 Bi	84 Po	85 At	86 Rn
7	87 Fr	88 Ra	89 Ac	104 Rf	105 Db	106 Sg	107 Bh	108 Hs	109 Mt	110 Ds	111 Rg	112 Cn	113 Nh	114 Fl	115 Mc	116 Lv	117 Ts	118 Og

lanthanoid series 6	58 Ce	59 Pr	60 Nd	61 Pm	62 Sm	63 Eu	64 Gd	65 Tb	66 Dy	67 Ho	68 Er	69 Tm	70 Yb	71 Lu
actinoid series 7	90 Th	91 Pa	92 U	93 Np	94 Pu	95 Am	96 Cm	97 Bk	98 Cf	99 Es	100 Fm	101 Md	102 No	103 Lr

*Numbering system adopted by the International Union of Pure and Applied Chemistry (IUPAC).

History

1789 – Klaproth isolated Uranium from Pitchblende

1794 - J. Gadolin isolated *yttria* from a mineral discovered at Ytterby. Oxides of Y, Tb, Er, Yb, Sc, Ho, Tm, Gd, Dy and Lu

1803 – isolation of Cerite by Klaproth, Berzelius and Hisinger. Oxides of Ce, La, Pr, Nd, Sm and Eu

1828 – isolation of Th from thoria

1913 – discovery of ^{234}Pa ($t_{1/2}$ = 6.7 hr)

1916 – discovery of ^{231}Pa ($t_{1/2}$ = 32 760 hr) decay of ^{235}U

1940 – synthesis of Np and Pu from ^{238}U with ^{1}n

1944 – synthesis of Am and Cm from ^{239}Pu

Seabourg (1951 Nobel)

1947 – observation of Pm in decay of ^{235}U

1949 – synthesis of Bk

1955 – identification of Es and Fm in debris of thermonuclear explosions

1961–71 Synthesis of No and Lr by bombardment of $_{95}$Am or $_{98}$Cf

1996 – 2012 Reports of the synthesis of elements 112 – 118 ($_{114}$Fl and $_{116}$Lv named 30/05/12)

Definitions and discovery

1794 J. Gadolin (1760-1852) studies the mineral and publishes a 19-page report in 1794 in the Proceedings of the Royal Swedish Academy of Sciences, concluding to the presence of a new “earth”, which he names yttrium.

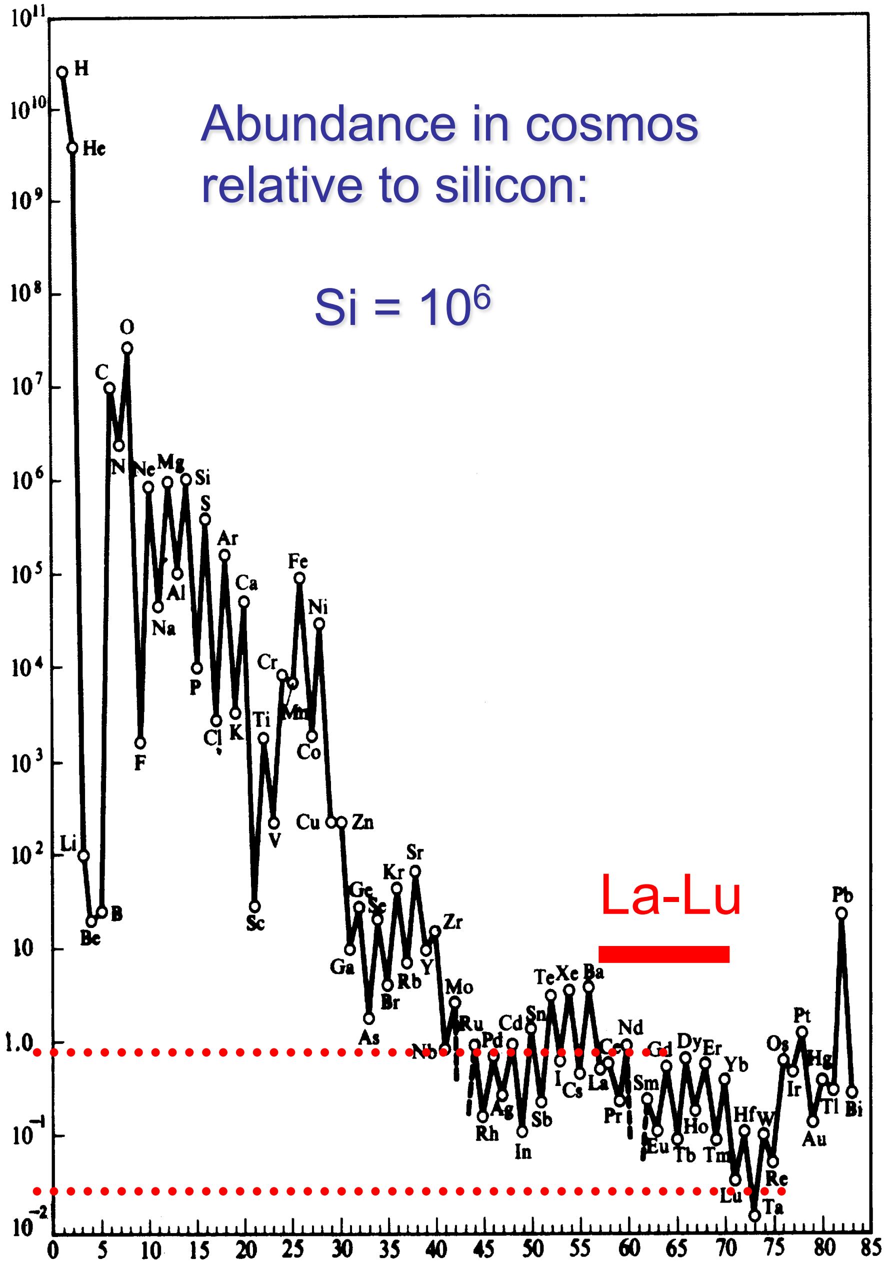
Subsequent work (using fractional precipitation and crystallisation techniques) revealed that yttrium contained the oxides of 10 other elements.

1803 W. Hisinger and J. J. Berzelius analyse this stone and find it contains an unknown “earth” they name ceria after the recently discovered planet Ceres. Their finding is published in 1804 in a 24-page report and confirmed by the German chemist Klaproth. It was shown later to contain six elements.

Occurrence of 4f elements

The elements are “rare” but not rarer than many others, such as Au, Pt, Pd, Rh, for instance

Cerium is the 26 most abundant element
Nd more than gold
Thulium more than iodine



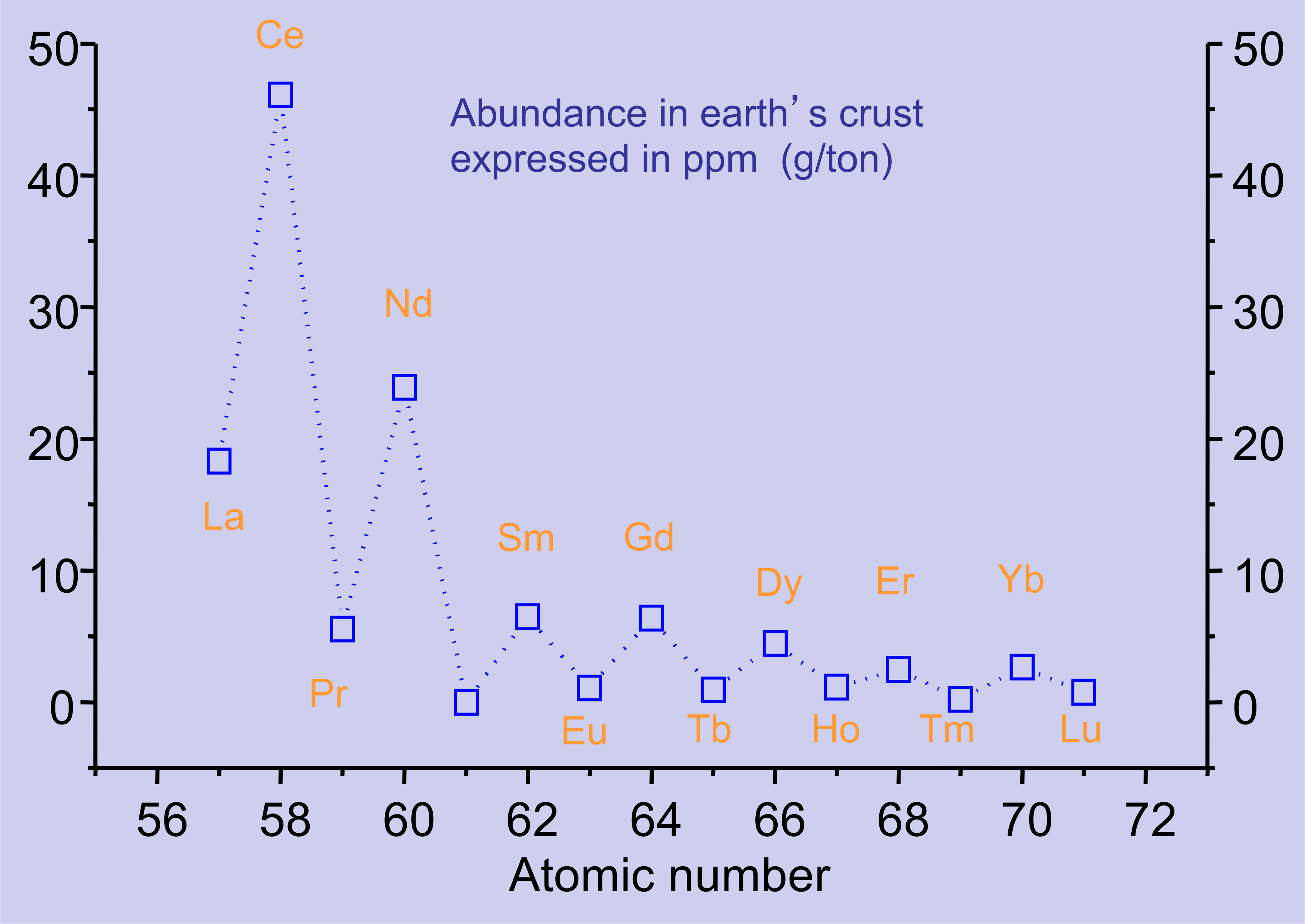
Abundance in cosmos relative to silicon:

Si = 10^6

La-Lu

Natural abundance

Oddo-Harkins Rule : Even atomic numbers more prevalent than odd atomic numbers



Lanthanide containing minerals

Cerium group (lighter elements)

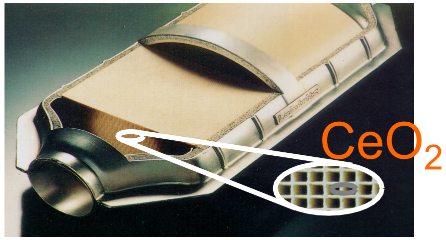
Bastnasite	$Ln(CO_3)F$	65-70%
Monazite	$LnPO_4$	50-75%
Cerite	$(Ce,La)_3M^{II}H_3Si_3O_{13}$	50-70%

Yttrium group (heavier elements)

Xenotime	$LnPO_4$	55-65%
Gadolinite	$Ln_2M_3Si_2O_{10}$	35-50%
Euxenite	$Ln(Nb,Ta)TiO_6xH_2O$	15-35%

Main ressources in China (50%) and Russia (25%) followed by USA (10%)

Applications of 4f-elements



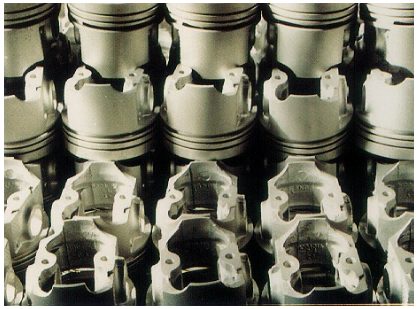
- Catalysts

- cracking of hydrocarbons
- conversion of exhaust gases, minimizes CO emission (diesel) CeO_2

$$2\,CeO_2 + CO \longrightarrow Ce_2O_3 + CO_2$$

$$2\,Ce_2O_3 + O_2 \longrightarrow 4\,CeO_2$$

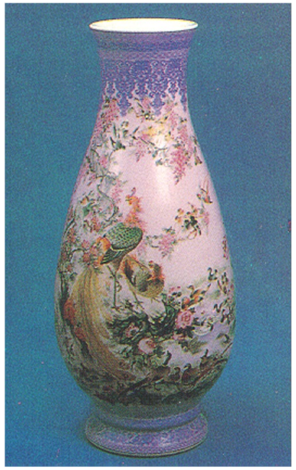
- Metallurgy
  - Steel production (removal of O, S)
  - Nodular graphite
  - Hardener (*e.g.* in magnesium)



Reinforced
cast Al pistons

- Materials
  - High temperature superconducting ceramics
  - Electronic devices (capacitors, O_2-sensors)
  - Magnets (Sm_5Co, Nd_5Fe)
  - Neutron moderators in nuclear reactors
  - Hydrogen storage with metal hydrides

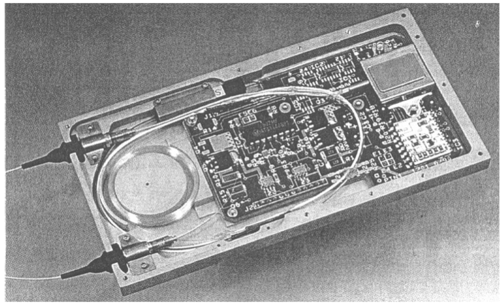
Applications of 4f-elements



Pigments
Ln sulfides

- Medicine
  - Seasickness (Ce oxalate), thromboses (Nd oxalate)
  - Renal insufficiency ($La_2(CO_3)_3 \cdot 4H_2O$)
  - X-ray intensifying screens
  - NMR imaging
  - Cancer radio- and photo-therapy
  - Laser surgery (Nd YAG ($Nd:Y_3Al_5O_{12}$) laser)
  - Luminescent immunoassays

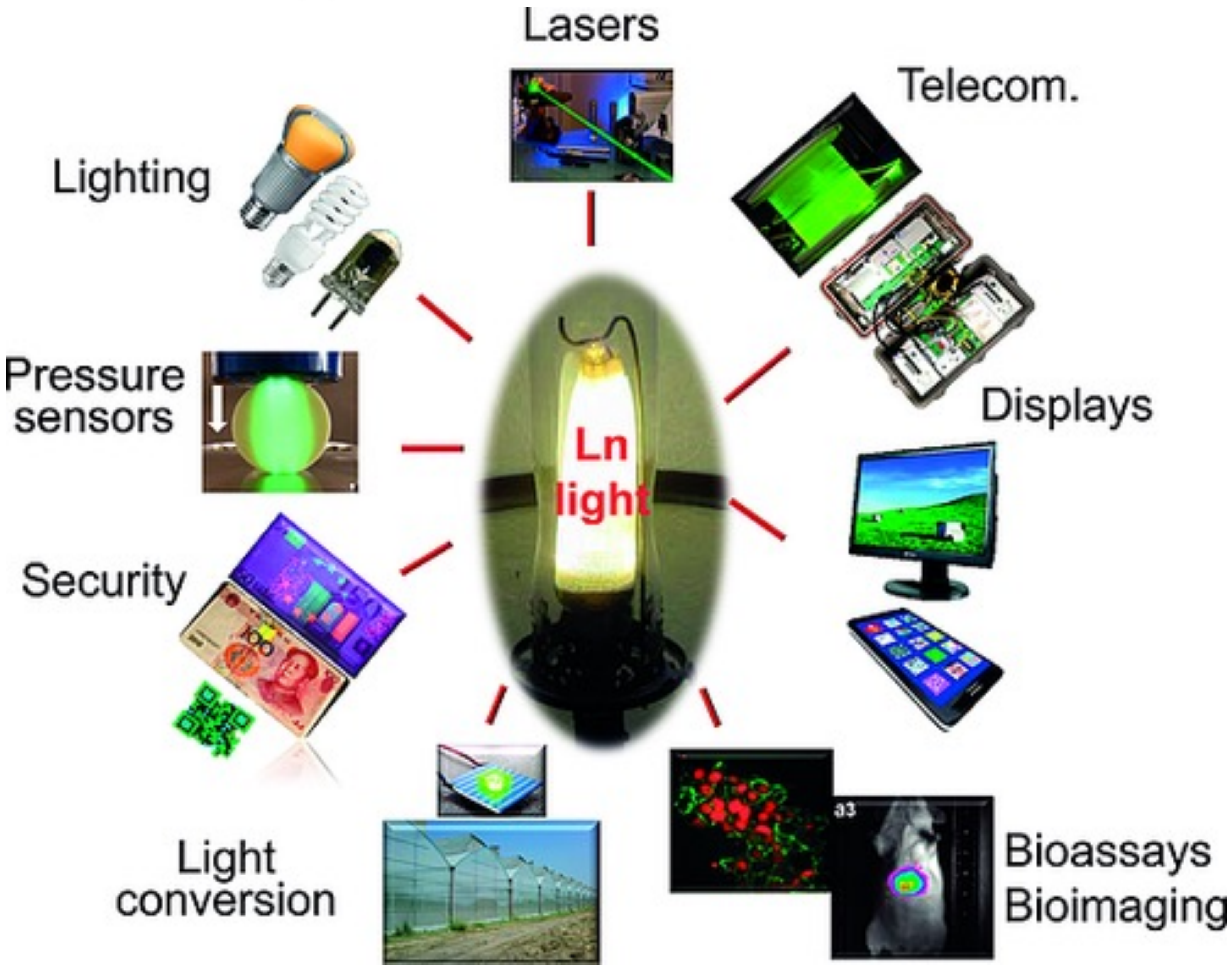
- Science
  - Shift reagents, luminescent and magnetic probes
  - Catalysts for organic chemistry



Er amplifier
for optical fibers

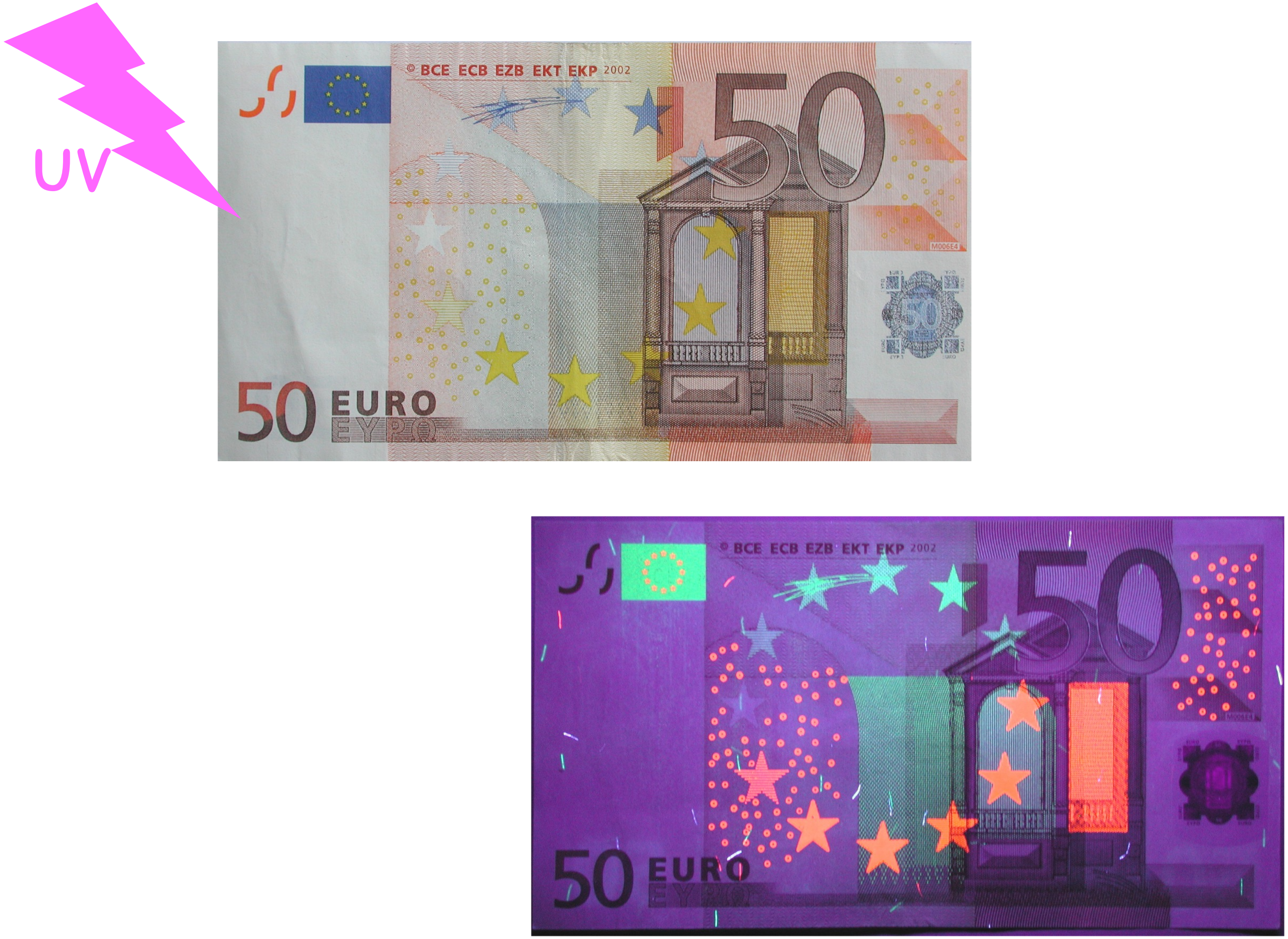
- Optics and lighting
  - Polishing powders
  - Protection against sun (sunglasses)
  - Lasers, particularly Nd YAG
  - Amplifiers
  - Phosphors for displays (incl. electrolumin. displays)
  - Fluorescent lamps
-

Applications of lanthanide luminescence



Eur. J. Inorg. Chem. 2017, 5058–5063

Applications of lanthanide complexes in security



Vibrator (magnets)
Neodymium
Praseodymium
Terbium
Dysprosium

Circuit board electronics
Neodymium
Praseodymium
Dysprosium
Lanthanum
Gadolinium

Color screen
Europium
Yttrium
Terbium
Lanthanum
Dysprosium
Praseodymiur
Gadolinium

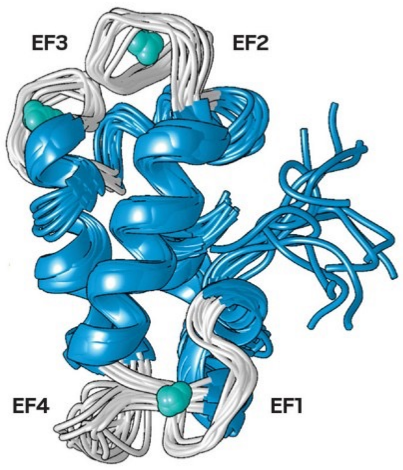
Speaker (magnets)
Neodymium
Praseodymium
Terbium
Dysprosium

Glass polishing
Cerium
Lanthanum
Praseodymium

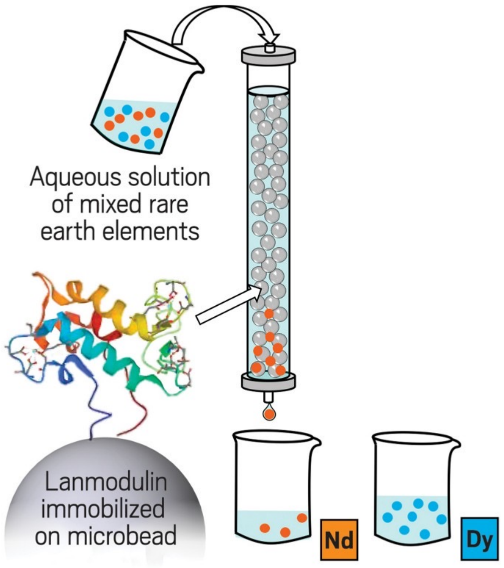
Biological relevance of lanthanides

In 2005 Arjan Pol a microbiologist
Fished from the volcanic crater in Naple
A bacterium that could not survive without lanthanides
Methylacidiphilum fumariolicum SolV
Microbiologists have now discovered many species that use a suite
of specialized molecules to bind, transport, and employ these elements:
lanthanome

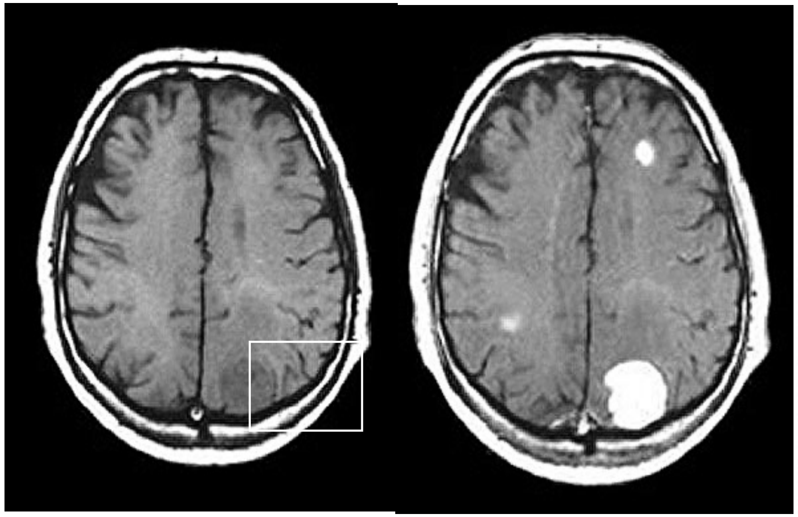
They could be used to identify lanthanide presence or to extract lanthanides
From ores



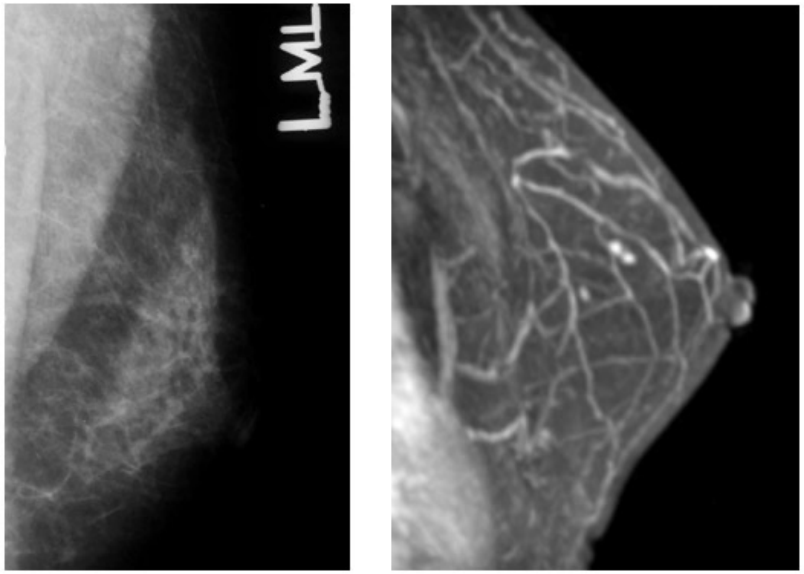
Lanmodulin can tightly bind three rare earth ions (turquoise; Y^{III} shown here)



Gd(III) Complexes as Magnetic Resonance Imaging (MRI) Contrast Agents

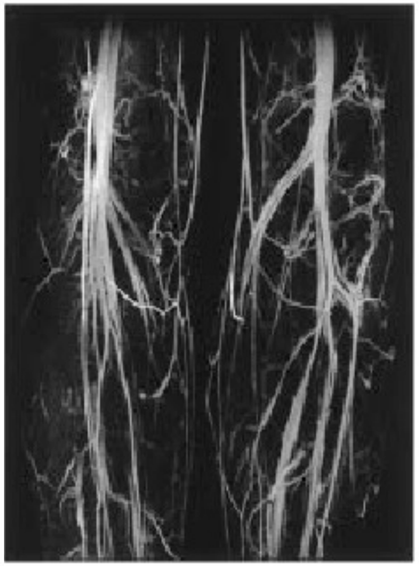


Pre-contrast 0.3mmol/Kg of CA



X-Ray MRI image

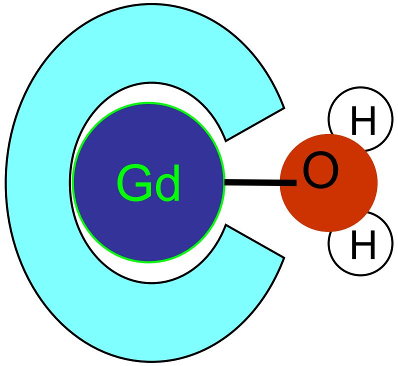
Early detection of Breast Cancer



Imaging of vascular systems

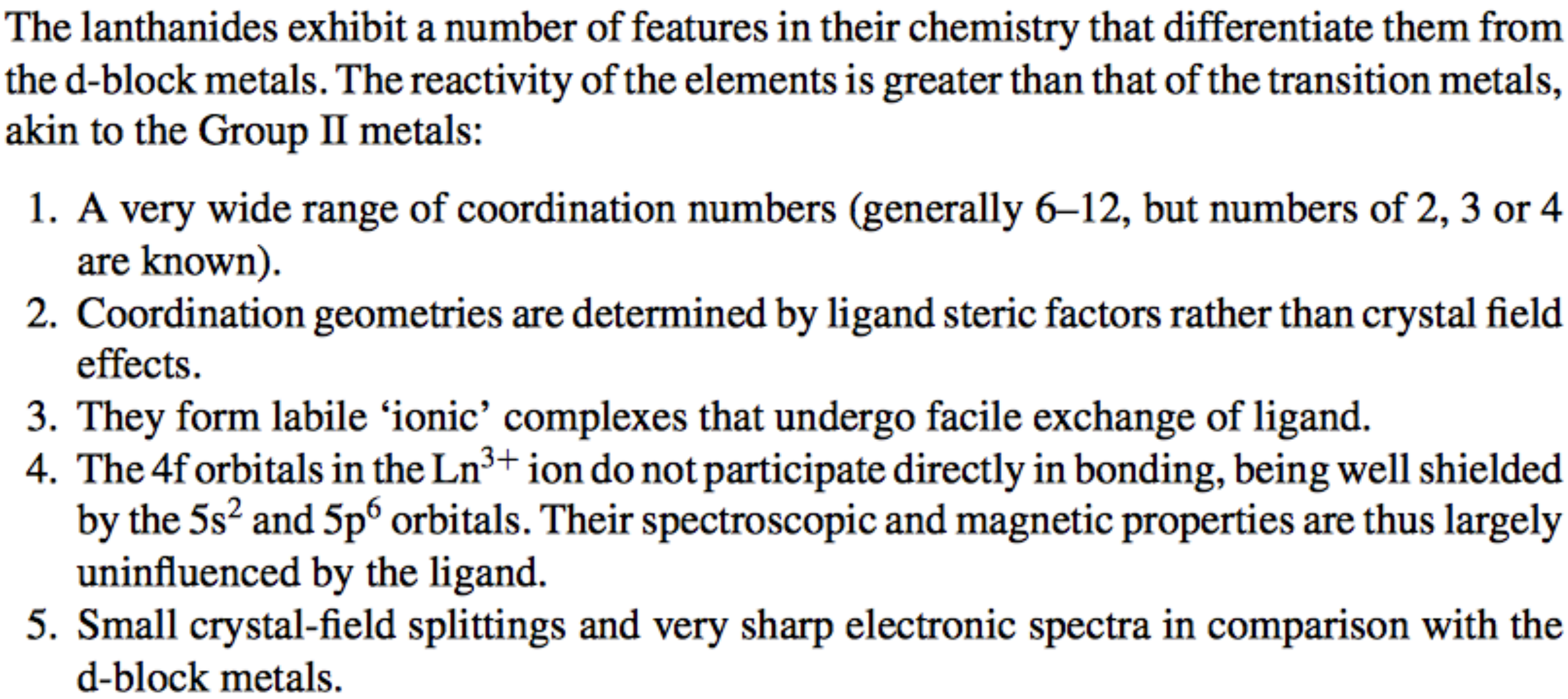
Gd^{3+} S = 7/2

Gadolinium complexes are used in 40% of MRI exams to enhance contrast .



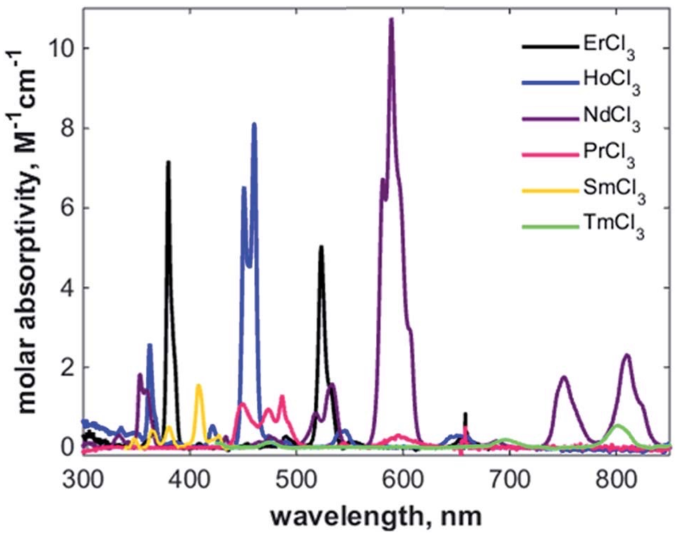
Gd increases the relaxation rate (1/T1) of water protons
The increase depends on the Gd concentration

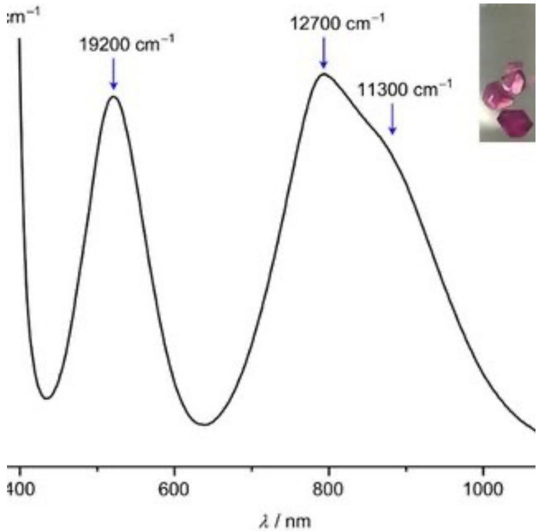
Key Characteristics of the Lanthanides



The lanthanides exhibit a number of features in their chemistry that differentiate them from the d-block metals. The reactivity of the elements is greater than that of the transition metals, akin to the Group II metals:

1. A very wide range of coordination numbers (generally 6–12, but numbers of 2, 3 or 4 are known).
2. Coordination geometries are determined by ligand steric factors rather than crystal field effects.
3. They form labile 'ionic' complexes that undergo facile exchange of ligand.
4. The 4f orbitals in the Ln^{3+} ion do not participate directly in bonding, being well shielded by the 5s^2 and 5p^6 orbitals. Their spectroscopic and magnetic properties are thus largely uninfluenced by the ligand.
5. Small crystal-field splittings and very sharp electronic spectra in comparison with the d-block metals.



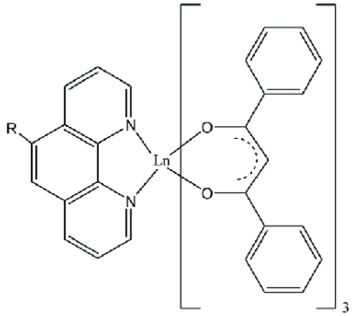


V(III) complex

Simon Cotton

Key Characteristics of the Lanthanides

6. They prefer anionic ligands with donor atoms of rather high electronegativity (e.g. O, F).



Complex used in oleds
Handling in air results in replacement of the bipy by H_2O molecules

7. They readily form hydrated complexes (on account of the high hydration energy of the small Ln^{3+} ion) and this can cause uncertainty in assigning coordination numbers.
8. Insoluble hydroxides precipitate at neutral pH unless complexing agents are present.
9. The chemistry is largely that of one (3+) oxidation state (certainly in aqueous solution).
10. They do not form Ln=O or Ln≡N multiple bonds of the type known for many transition metals and certain actinides.

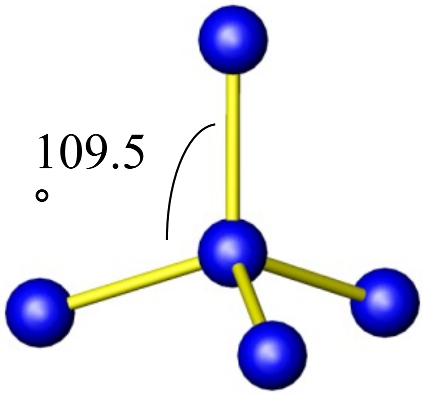
Multiple bonding requires orbital overlap

11. Unlike the transition metals, they do not form stable carbonyls and have (virtually) no chemistry in the 0 oxidation state.

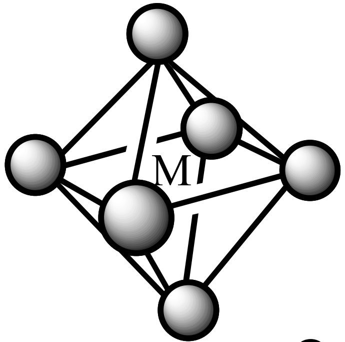
No access to backbonding interactions

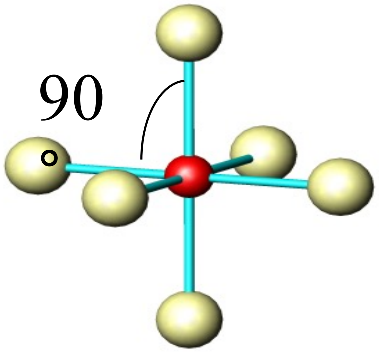
Simon Cotton

Most Common Geometries in Transition Metals



Tetrahedral



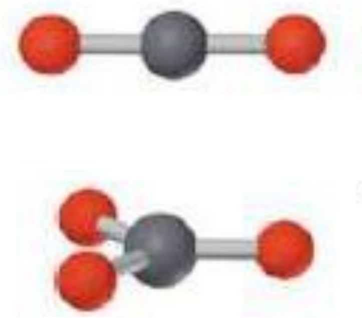


Octahedral

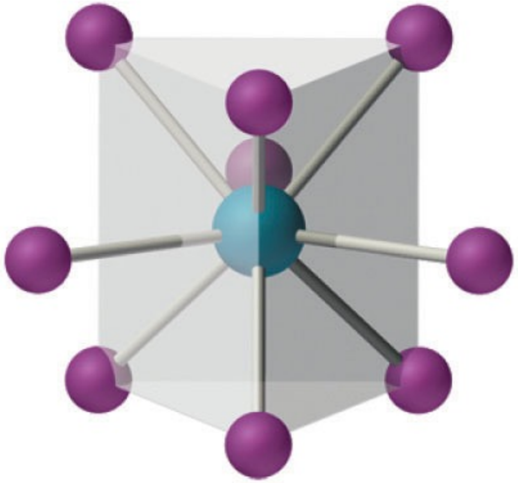
Square planar

Geometry is well defined due to strong Crystal field splitting

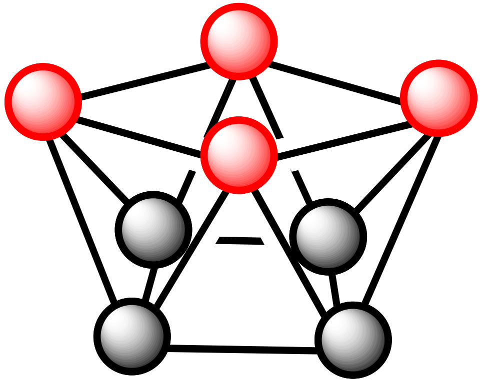
Linear and trigonal with bulky ligands (d^9 , d^{10} metals)



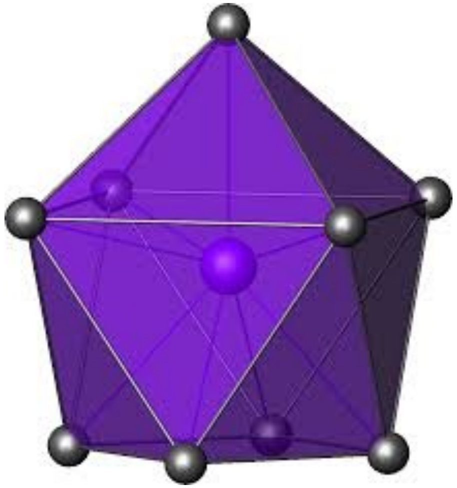
Most Common Geometries in Lanthanides for Coordination Numbers(NC) 8 and 9



Tricapped trigonal
Prism
CN 9



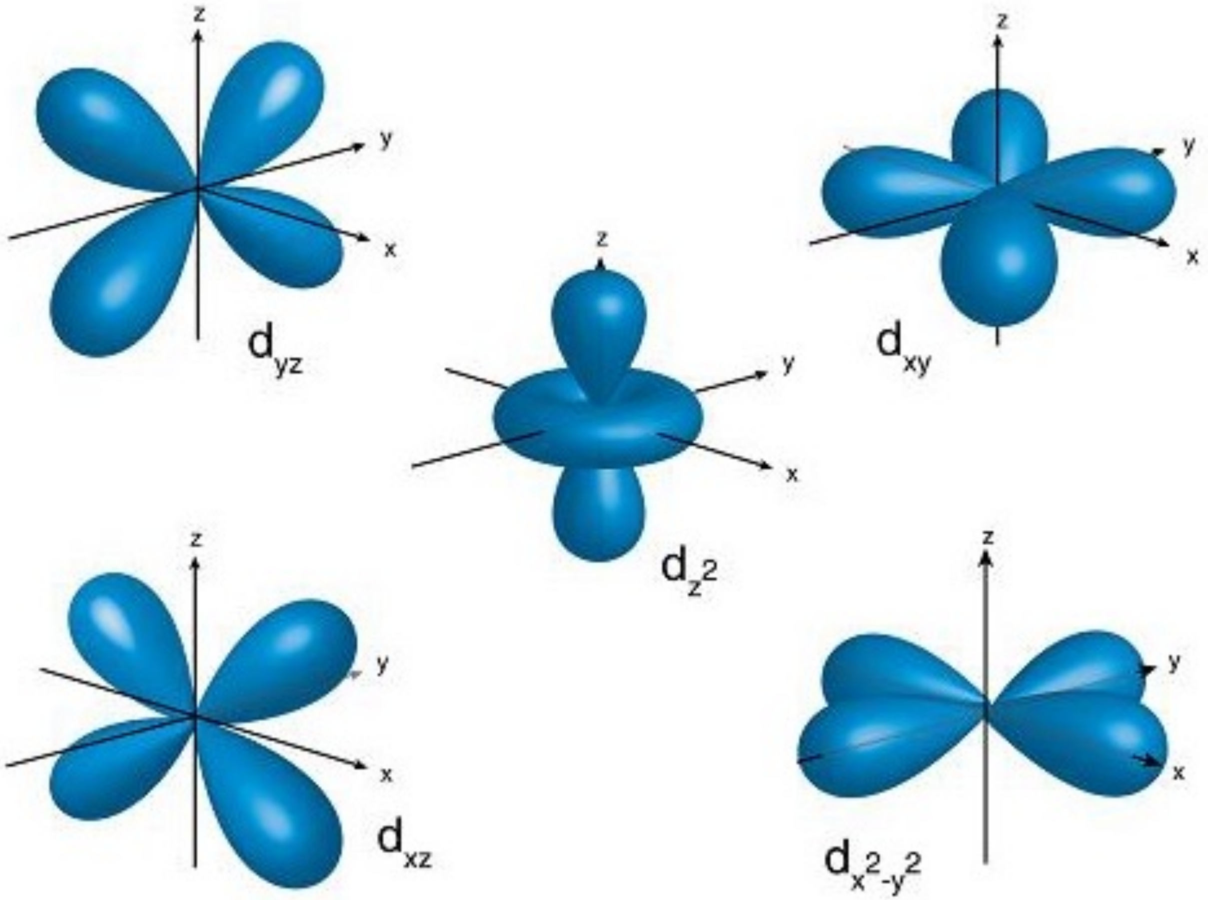
Square anti-prism
CN 8



Dodecahedron
CN 8

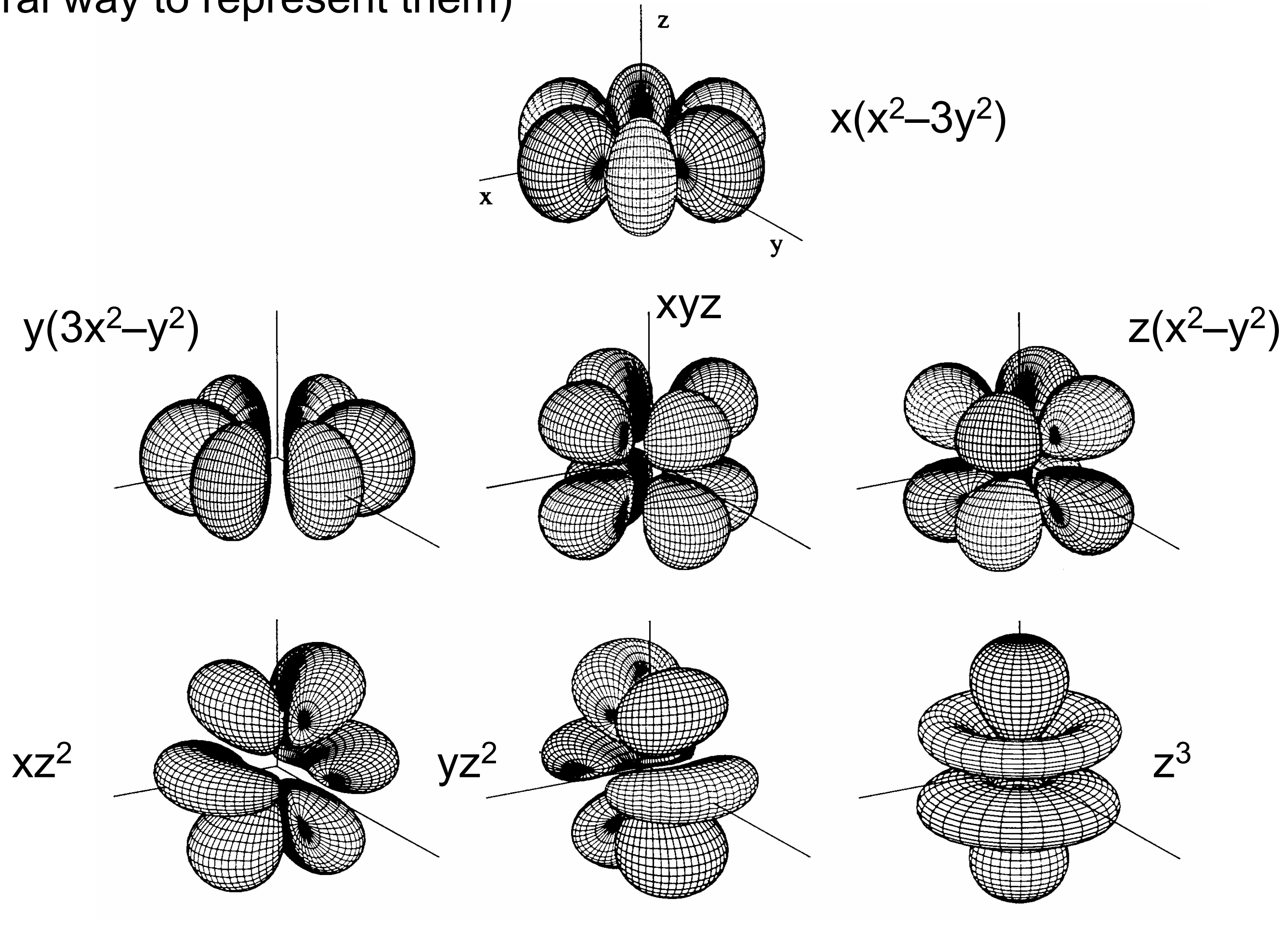
Lanthanides generally are large ions therefore high coordination numbers are common with small ligands such as Cl^- and polydentate ligands (up to 12)

d-ORBITALS

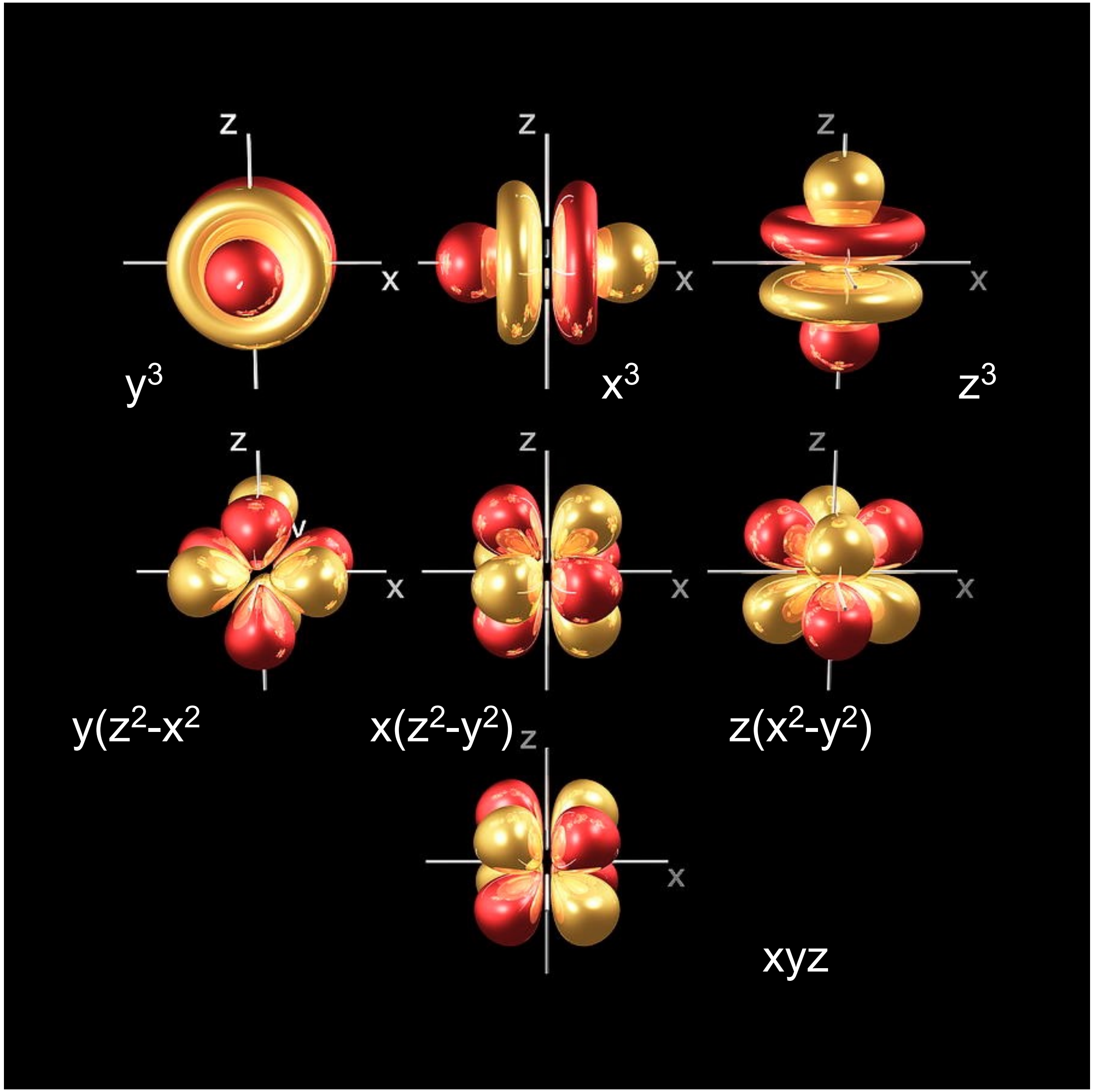


Electronic configuration

f-orbitals (several way to represent them)



f-orbitals cubic set (for molecules in Td and Oh groups)

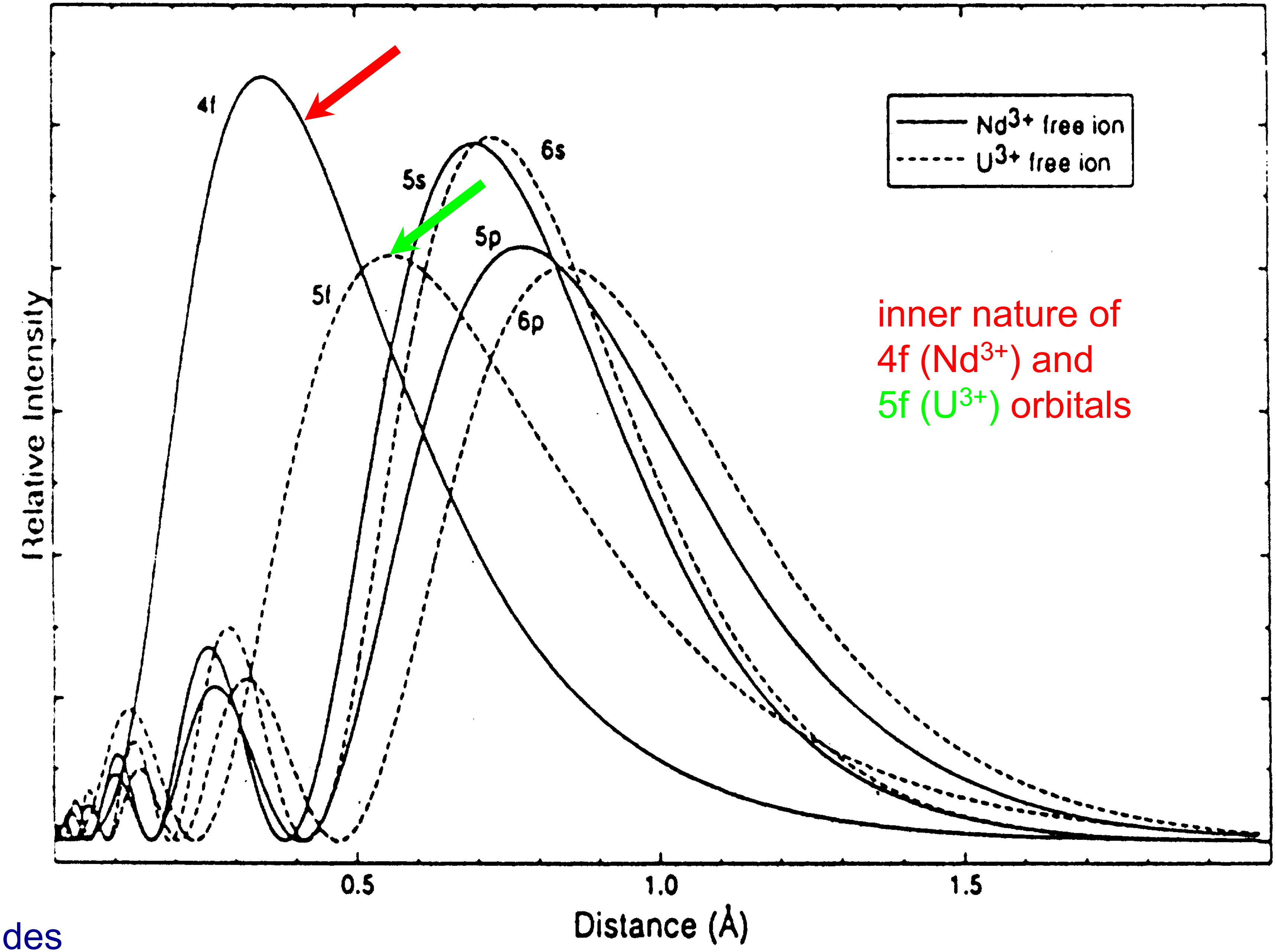


T_{1u}

T_{2u}

A_{2u}

f-orbitals radial extension



inner nature of 4f (Nd^{3+}) and 5f (U^{3+}) orbitals

Actinides

- the 5f orbitals are also “inner orbitals”

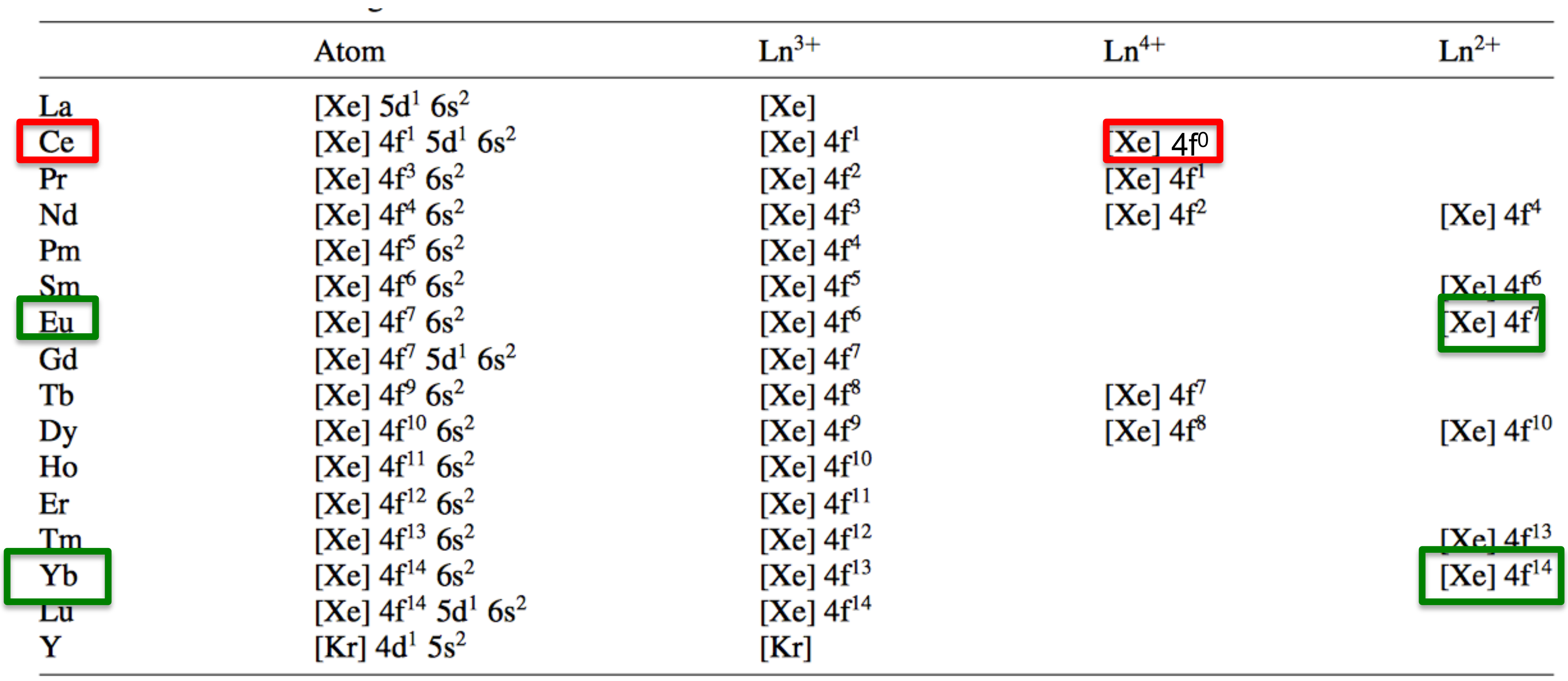
Electronic Configuration

Lanthanides

- Sc, Y and La introduce the 3d, 4d and 5d transition series: $nd^1(n+1)s^2$

n=3 (Sc), 4 (Y) and 5 (La)

- The energy of the 4f orbitals decreases abruptly beyond La: -0.95 eV for La, -5 eV for Nd ! which leads to the filling of the 4f shell



	Atom	Ln^{3+}	Ln^{4+}	Ln^{2+}
La	[Xe] $5d^1$ $6s^2$	[Xe]		
Ce	[Xe] $4f^1$ $5d^1$ $6s^2$	[Xe] $4f^1$	[Xe] $4f^0$	
Pr	[Xe] $4f^3$ $6s^2$	[Xe] $4f^2$	[Xe] $4f^1$	
Nd	[Xe] $4f^4$ $6s^2$	[Xe] $4f^3$	[Xe] $4f^2$	[Xe] $4f^4$
Pm	[Xe] $4f^5$ $6s^2$	[Xe] $4f^4$		
Sm	[Xe] $4f^6$ $6s^2$	[Xe] $4f^5$		[Xe] $4f^6$
Eu	[Xe] $4f^7$ $6s^2$	[Xe] $4f^6$		[Xe] $4f^7$
Gd	[Xe] $4f^7$ $5d^1$ $6s^2$	[Xe] $4f^7$		
Tb	[Xe] $4f^9$ $6s^2$	[Xe] $4f^8$	[Xe] $4f^7$	
Dy	[Xe] $4f^{10}$ $6s^2$	[Xe] $4f^9$	[Xe] $4f^8$	[Xe] $4f^{10}$
Ho	[Xe] $4f^{11}$ $6s^2$	[Xe] $4f^{10}$		
Er	[Xe] $4f^{12}$ $6s^2$	[Xe] $4f^{11}$		
Tm	[Xe] $4f^{13}$ $6s^2$	[Xe] $4f^{12}$		[Xe] $4f^{13}$
Yb	[Xe] $4f^{14}$ $6s^2$	[Xe] $4f^{13}$		[Xe] $4f^{14}$
Lu	[Xe] $4f^{14}$ $5d^1$ $6s^2$	[Xe] $4f^{14}$		
Y	[Kr] $4d^1$ $5s^2$	[Kr]		

Oxidation states of 4f elements

Ln^0 $4f^{N-1}\,5d^1\,6s^2$
La, Ce, Gd, Lu
$4f^N\,6s^2$
Pr-Eu,Tb-Yb

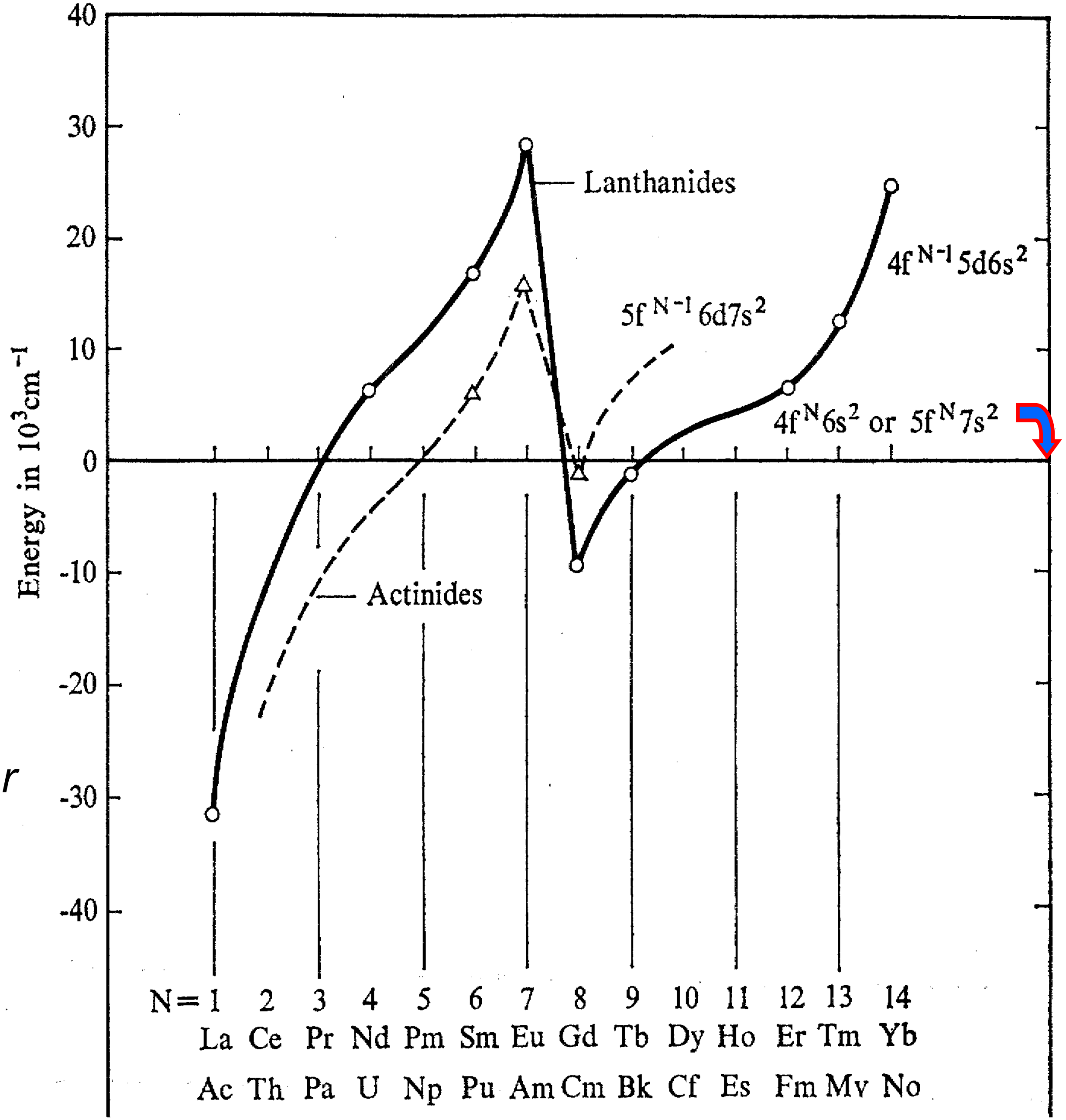
Ln^{II} $4f^{N-1}\,5d^1$
MX_2
La, Gd
$4f^N$
Ce-Eu, Tb-Y
$4f^{N-1}\,6s^1$Lu

electronic configuration crossover

Ln^{III} $4f^{N-1}$ (no exception)

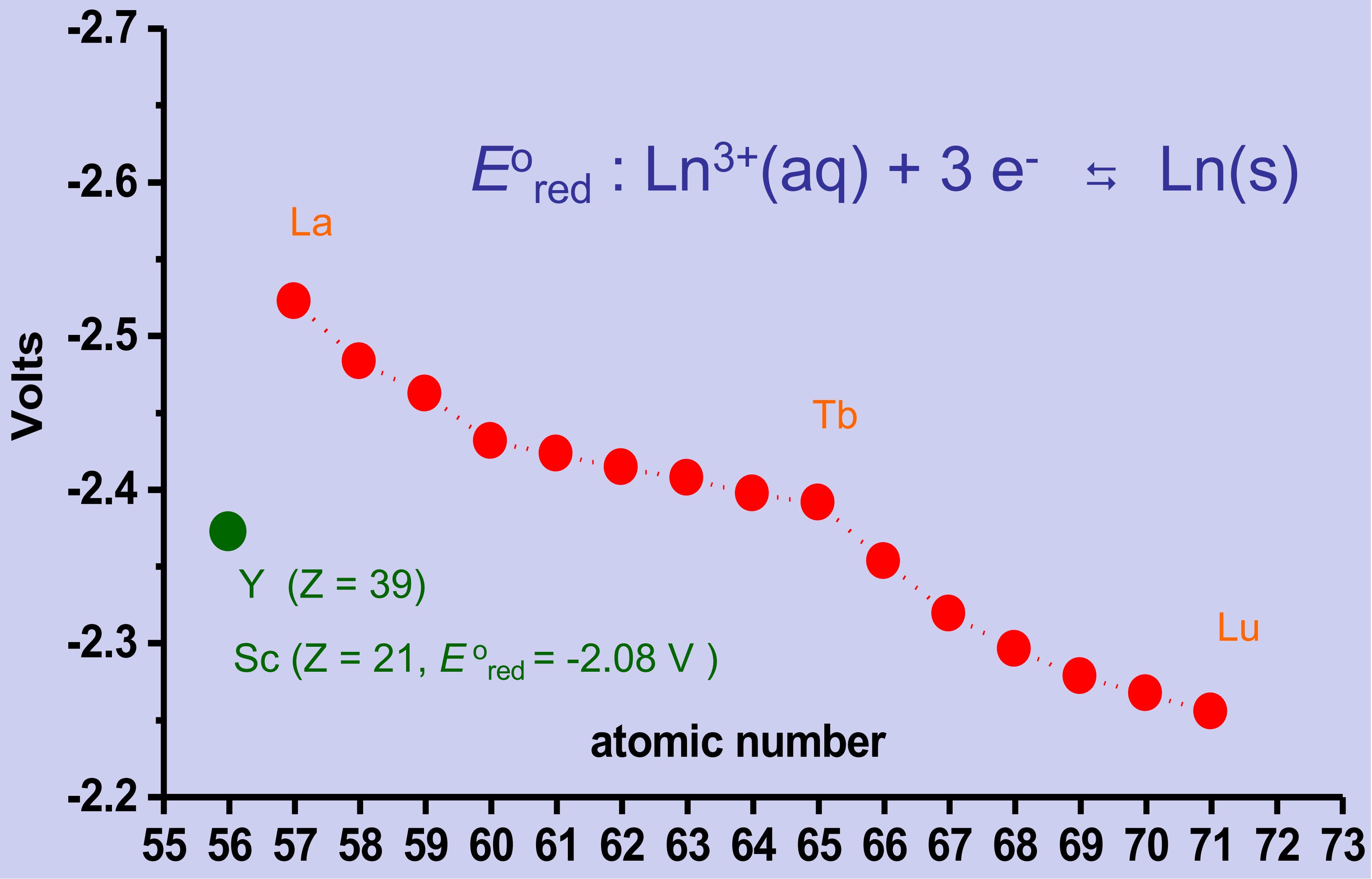
Ln^{IV} $4f^{N-2}$ (Ce, Pr, Tb)

Nd and Dy in oxides



Oxidation states of 4f elements

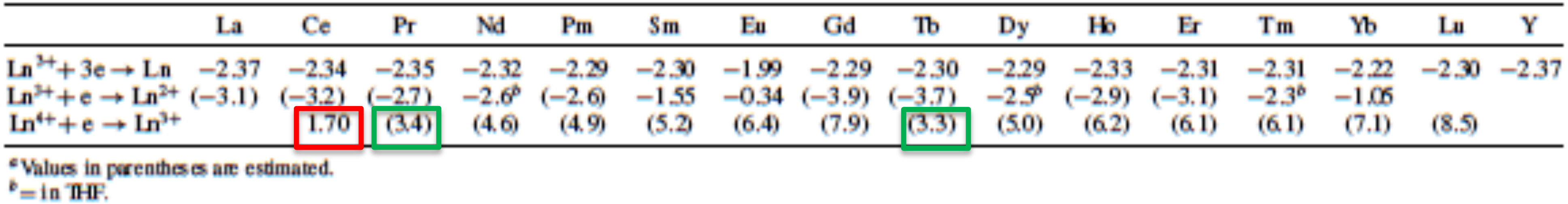
- The more stable oxidation state of Ln is +3



The more stable oxidation state of Ln is +3

Main reason: the fourth ionization energy is larger than the sum of the first three ones; this extra energy cannot, in most cases, be compensated by bond formation

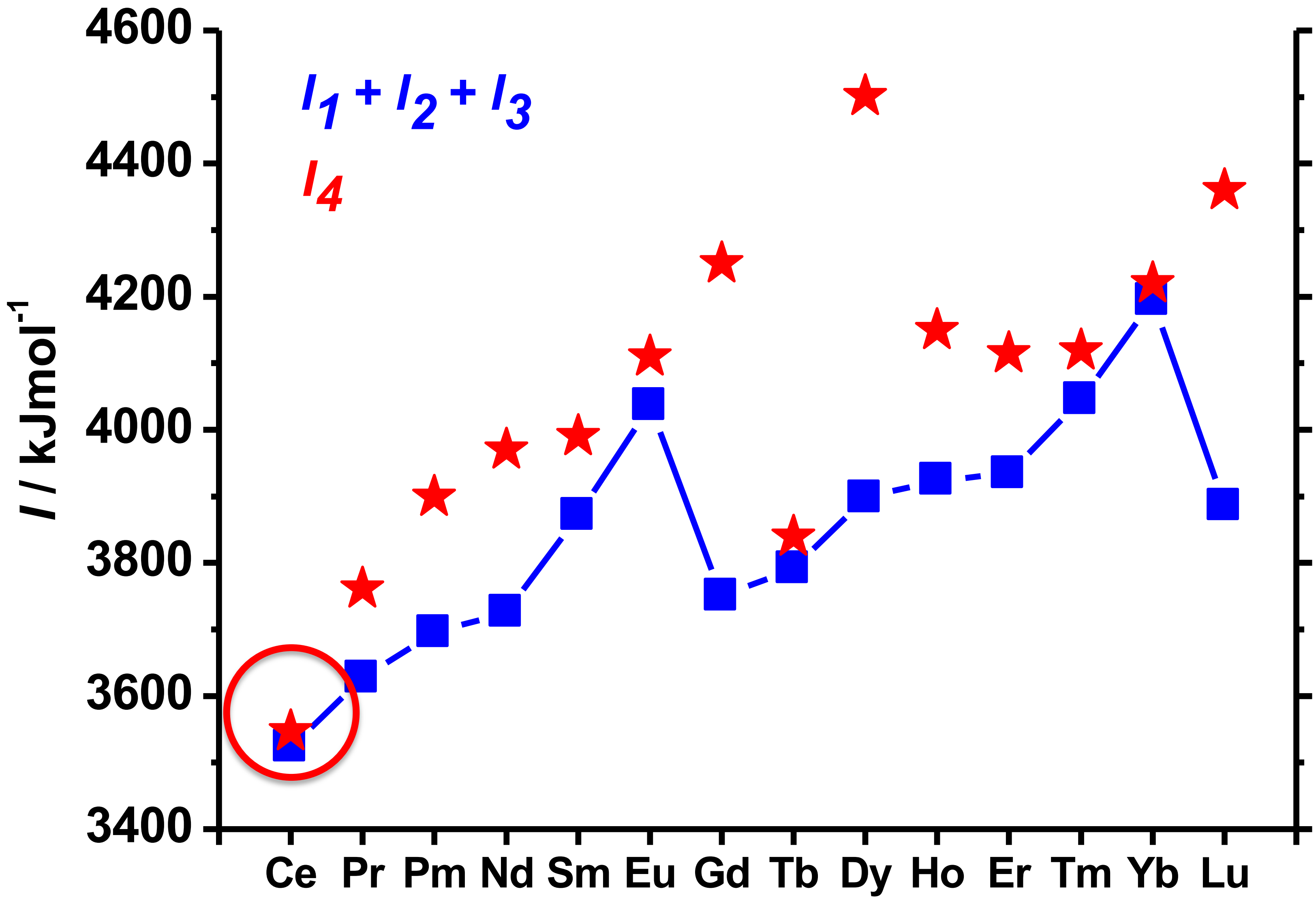
Explanation:
Upon ionization, all of the valence orbitals (4f, 5d, 6s) are stabilized, but to variable degrees.
4f orbitals are stabilized most and 6s least.
After removal of three electrons, the remaining are very tightly bound



	La	Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu	Y
$Ln^{3+} + 3e \rightarrow Ln$	−2.37	−2.34	−2.35	−2.32	−2.29	−2.30	−1.99	−2.29	−2.30	−2.29	−2.33	−2.31	−2.31	−2.22	−2.30	−2.37
$Ln^{3+} + e \rightarrow Ln^{2+}$	(−3.1)	(−3.2)	(−2.7)	−2.6[b]	(−2.6)	−1.55	−0.34	(−3.9)	(−3.7)	−2.5[b]	(−2.9)	(−3.1)	−2.3[b]	−1.06		
$Ln^{4+} + e \rightarrow Ln^{3+}$		1.70	(3.4)	(4.6)	(4.9)	(5.2)	(6.4)	(7.9)	(3.3)	(5.0)	(6.2)	(6.1)	(6.1)	(7.1)	(8.5)	

[a] Values in parentheses are estimated.
[b] = in THF.

Fourth ionization energy



Oxidation states of 4f elements

- **Ce**, Pr, and Tb may have +4 oxidation state

E^{0}_{red} for $Ln^{4+}(aq) + e^{-} \leftrightarrows Ln^{3+}(aq)$ in acidic solutions:

+1.72 V for Ce^{4+}, stable in water
+3.20 V for Pr^{4+}, oxidises water
+3.10 V for Tb^{4+}, oxidises water

- Sm, **Eu**, and Yb have a relatively stable +2 state

E^{0}_{red} for $Ln^{3+}(aq) + e^{-} \leftrightarrows Ln^{2+}(aq)$ in acidic solutions:

-0.35 V for Eu^{2+}, stable in water

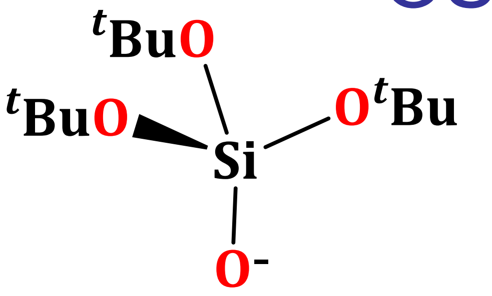
-1.15 V for Yb^{2+}, reduces water

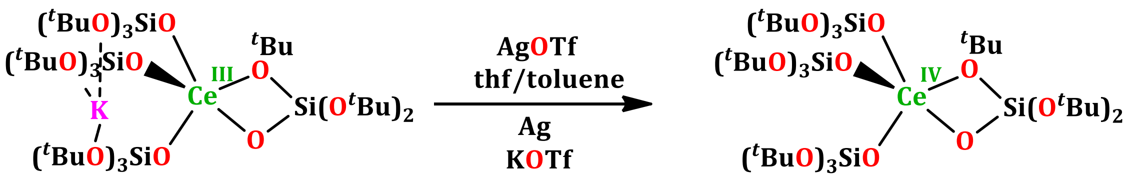
-1.56 V for Sm^{2+}, reduces water

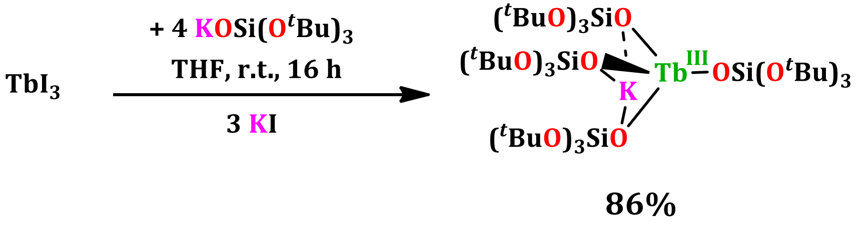
Ln^{2+} ions *reduce* water to hydrogen: $2Ln^{2+}_{(aq)} + 2H^{+}_{(aq)} \rightarrow 2Ln^{3+}_{(aq)} + H_{2(g)}$

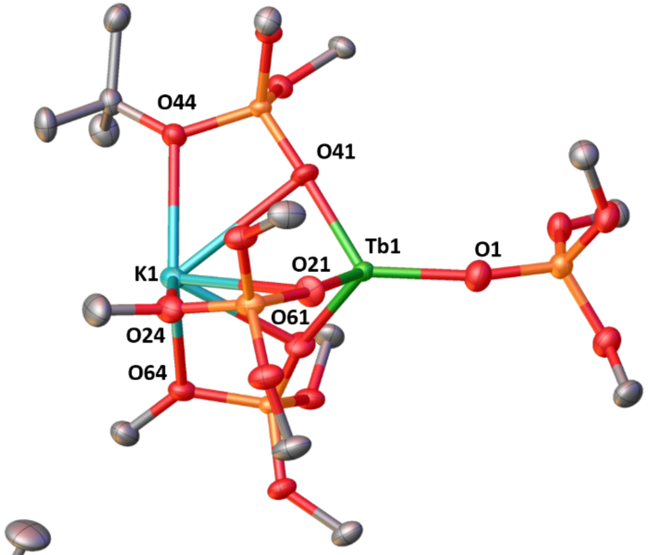
Ln^{4+} ions *oxidise* water to oxygen: $4Ln^{4+}_{(aq)} + 2H_2O_{(l)} \mapsto 4Ln^{3+}_{(aq)} + O_{2(g)} + 4H^{+}_{(aq)}$

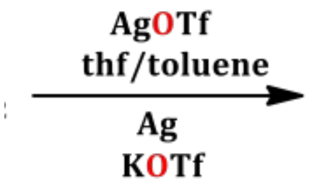
$OSi(O^tBu)_3$ Stabilizes Ce^{4+} and Tb^{4+}



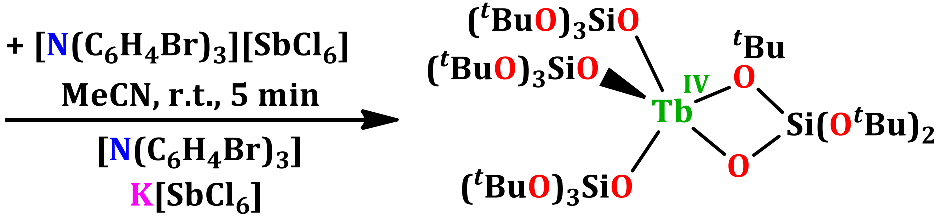


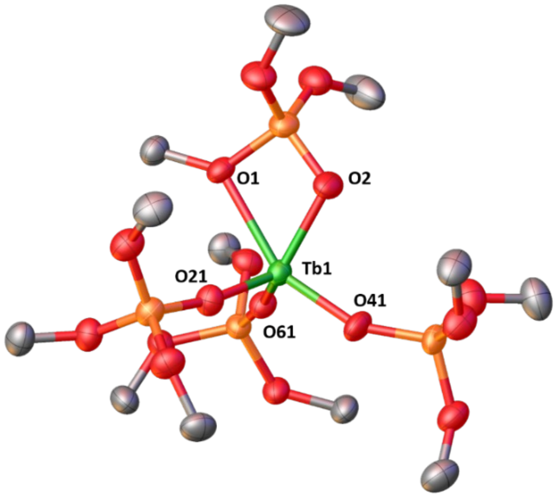






No reaction





Tb(IV): $4f^7$

$[N(C_6H_4Br)_3][SbCl_6]$

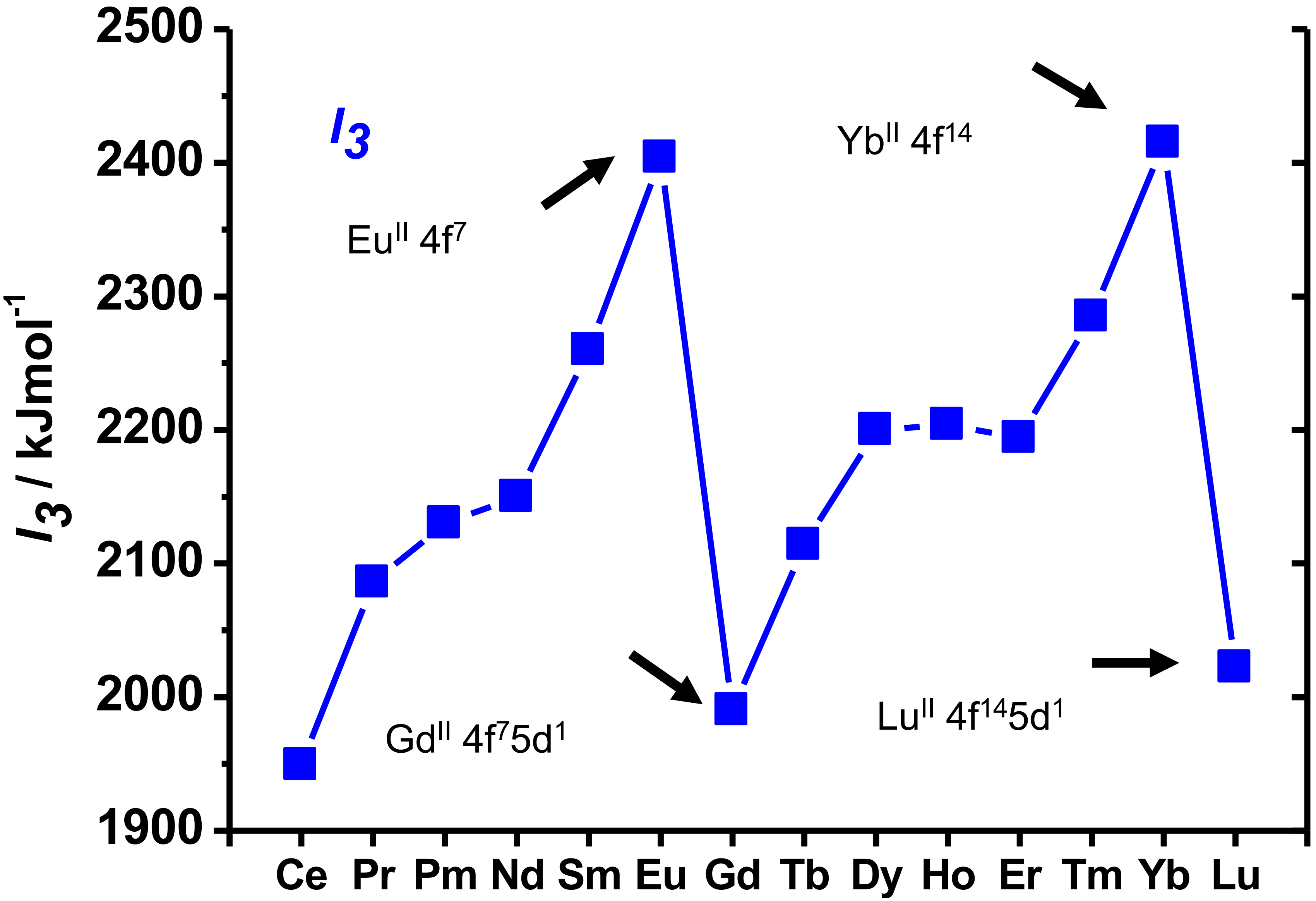
0.67 V vs Fc/Fc^+ in MeCN

Ag^+

0.04 V vs Fc/Fc^+ in MeCN

Palumbo, C. T; Zivkovic, I; Scopelliti, R.; Mazzanti, M. *J. Am. Chem. Soc.* **2019**, *141*, 9827-9831

Third ionization energy



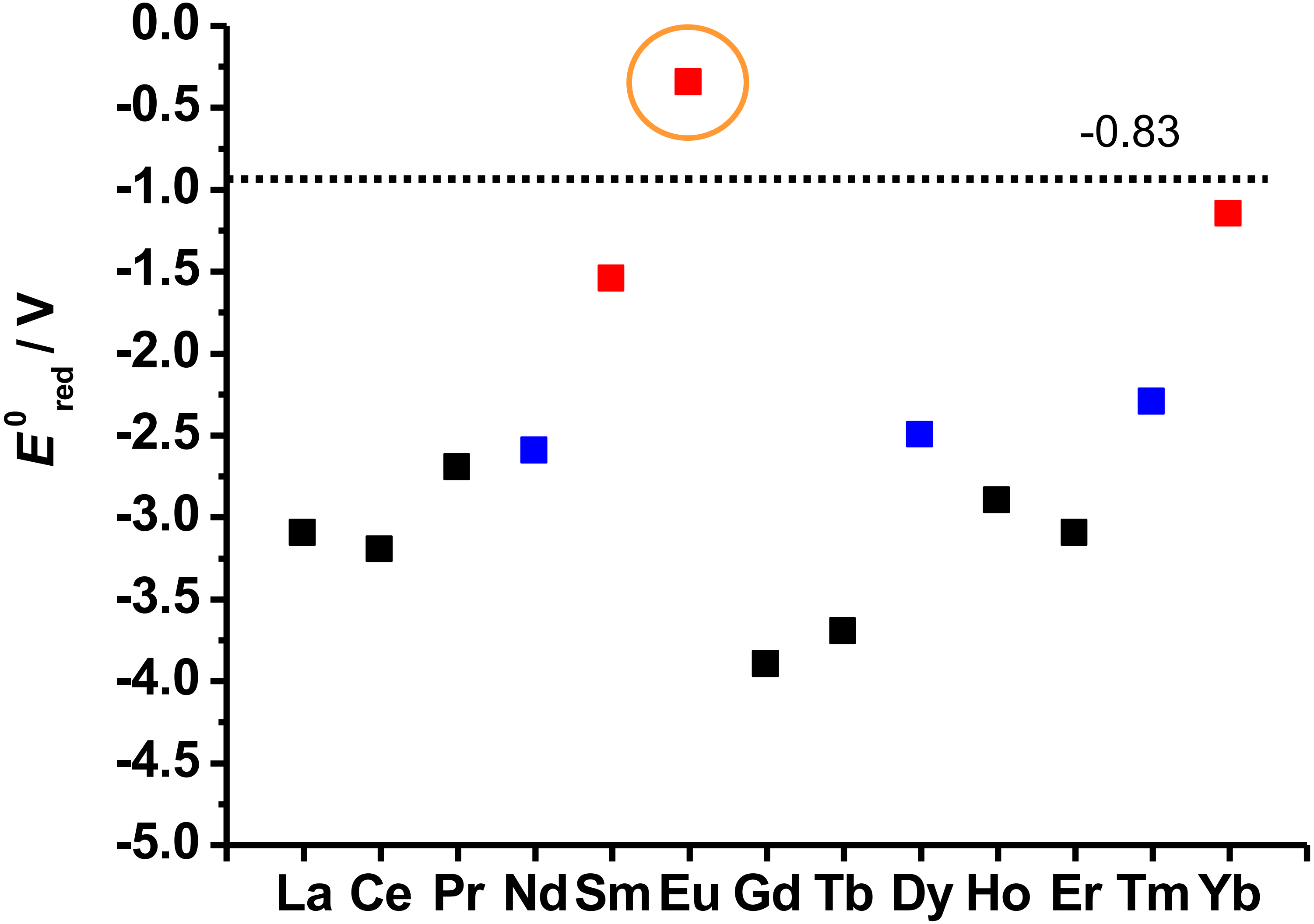
Oxidation states of 4f elements

$Ln^{3+} + e^- \leftrightarrows Ln^{2+}$

In water

In thf

Calculated



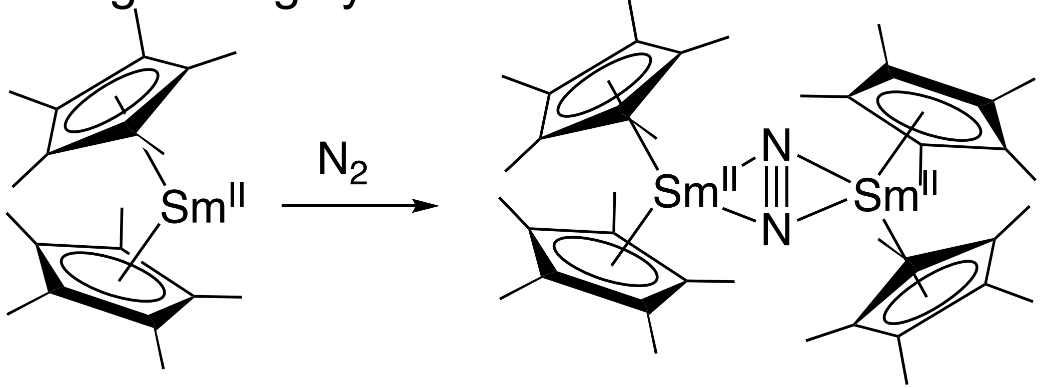
Divalent Lanthanides

In the late **1990s** three more lanthanide(II) complexes that incorporated thulium, neodymium, and dysprosium were isolated. Some of the chemistry could be rationalized by the ions having stabilizing electron configurations: Yb^{2+}, Tm^{2+}, Eu^{2+}, and Sm^{2+} have filled, nearly filled, half-filled, or nearly half-filled 4f orbitals.

But in 2008, University of Sussex chemistry professor
Michael F. Lappert and colleagues isolated lanthanum(II) and cerium(II) complexes
(*Angew. Chem. Int. Ed.,* 2008, 47, 1488 –1491
And finally in recent years, William Evans, and colleagues completed the series, synthesizing first holmium(II) and erbium(II) (*J. Am. Chem. Soc.*, **2012**, *134* , 8420–8423) complexes, then praseodymium(II), gadolinium(II), terbium(II), and lutetium(II)

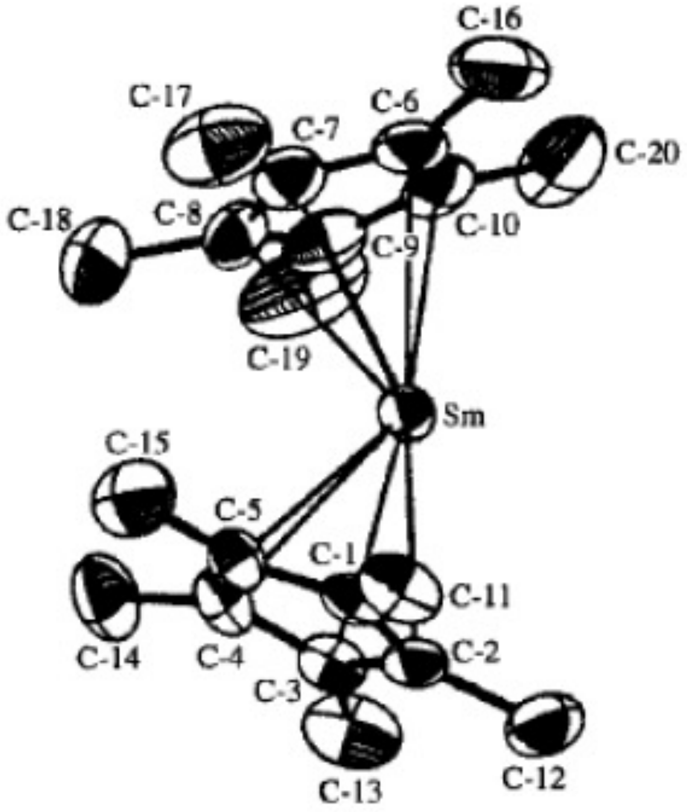
Nitrogen activation by a Sm(II) Organometallic Complex

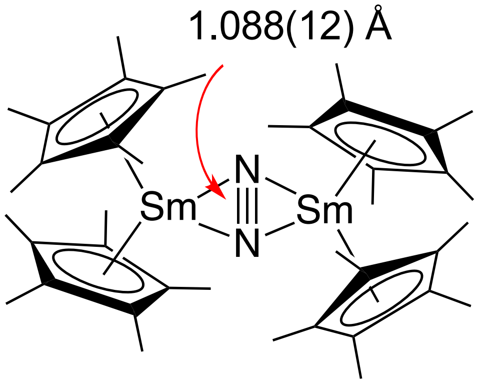
Redox couple (SmII/SmIII) enhanced in Cp^*_2Sm vs. SmI_2 → Cp^*_2Sm
Undergoes highly unusual reaction:

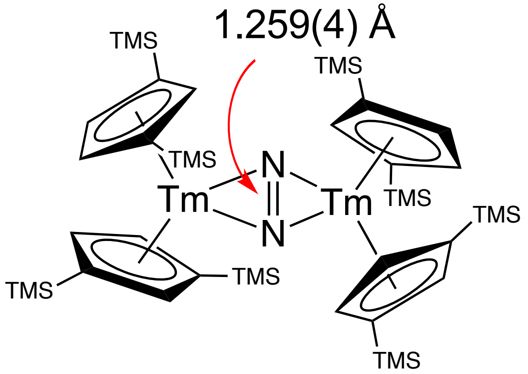


No reaction for $[Cp^*_2Sm(THF)]$

Cp^*_2Sm must be handled under Ar







Reaction with N_2 (d_{N2} = 1.0975Å)

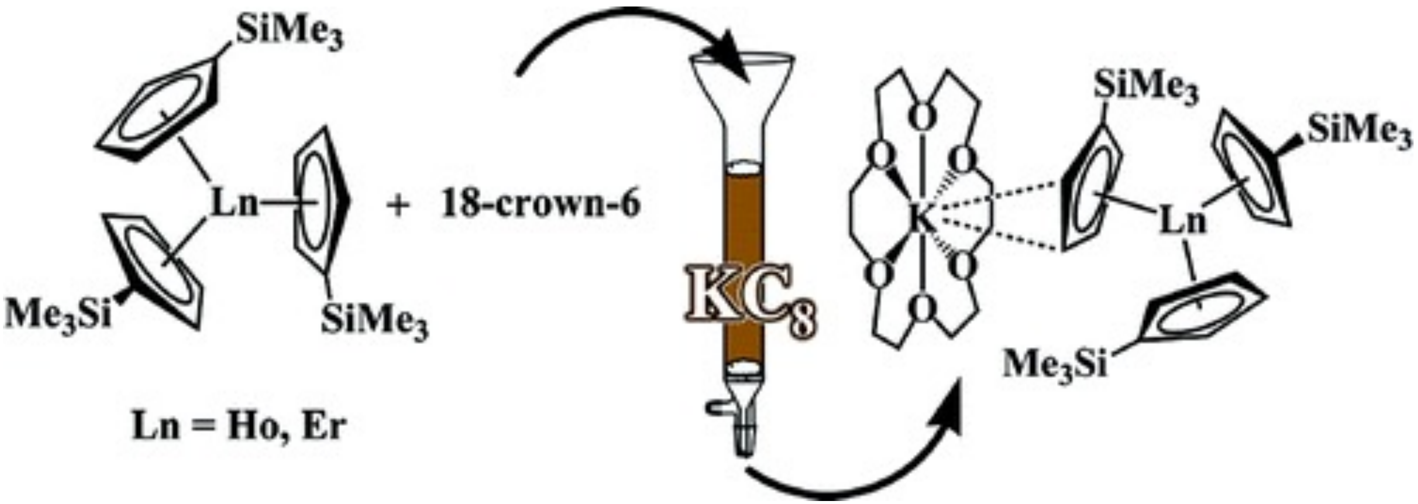
Tm N_2 has been reduced to N_2^{2-}

Reduction potentials (-2.3 V for Tm(II) and -1.5 V for Sm(II)).

Evans, Jacs 1988 and 2001

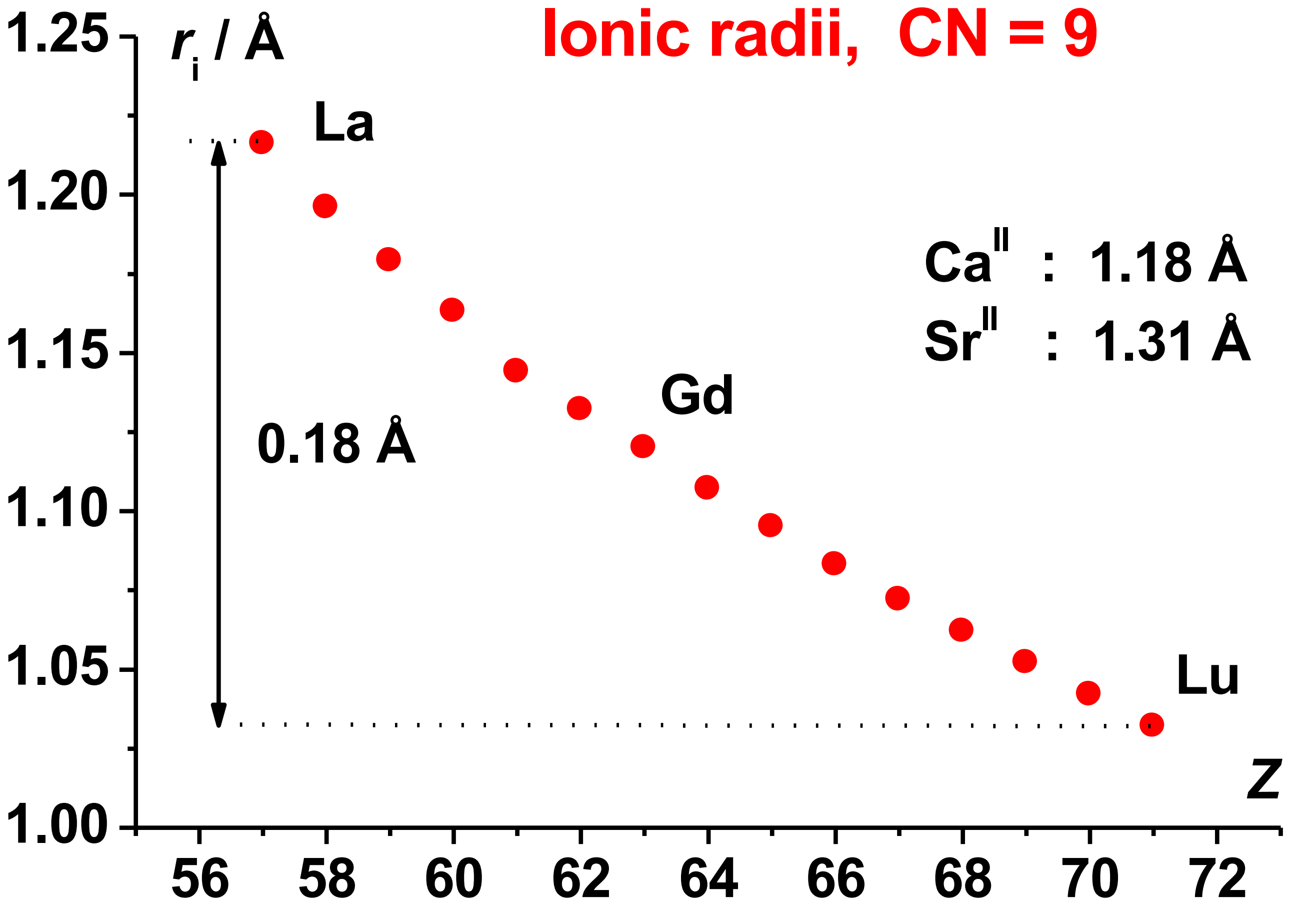
Divalent lanthanides

William Evans and cow;
J. Am. Chem. Soc., **2012**, *134* (20), pp 8420–8423
Expanding Rare-Earth Oxidation State Chemistry
to Molecular Complexes of Holmium(II) and Erbium(II)



The first molecular complexes of holmium and erbium in the +2 oxidation state have been generated by reducing Cp'_3Ln [$Cp' = C_5H_4SiMe_3$; Ln = Ho, Er with KC_8 in the presence of 18-crown-6 in Et_2O at −35 ° C under argon. Purification and crystallization below −35 ° C gave isomorphous [(18-crown-6)K][Cp'_3Ln] [Ln = Ho, Er].

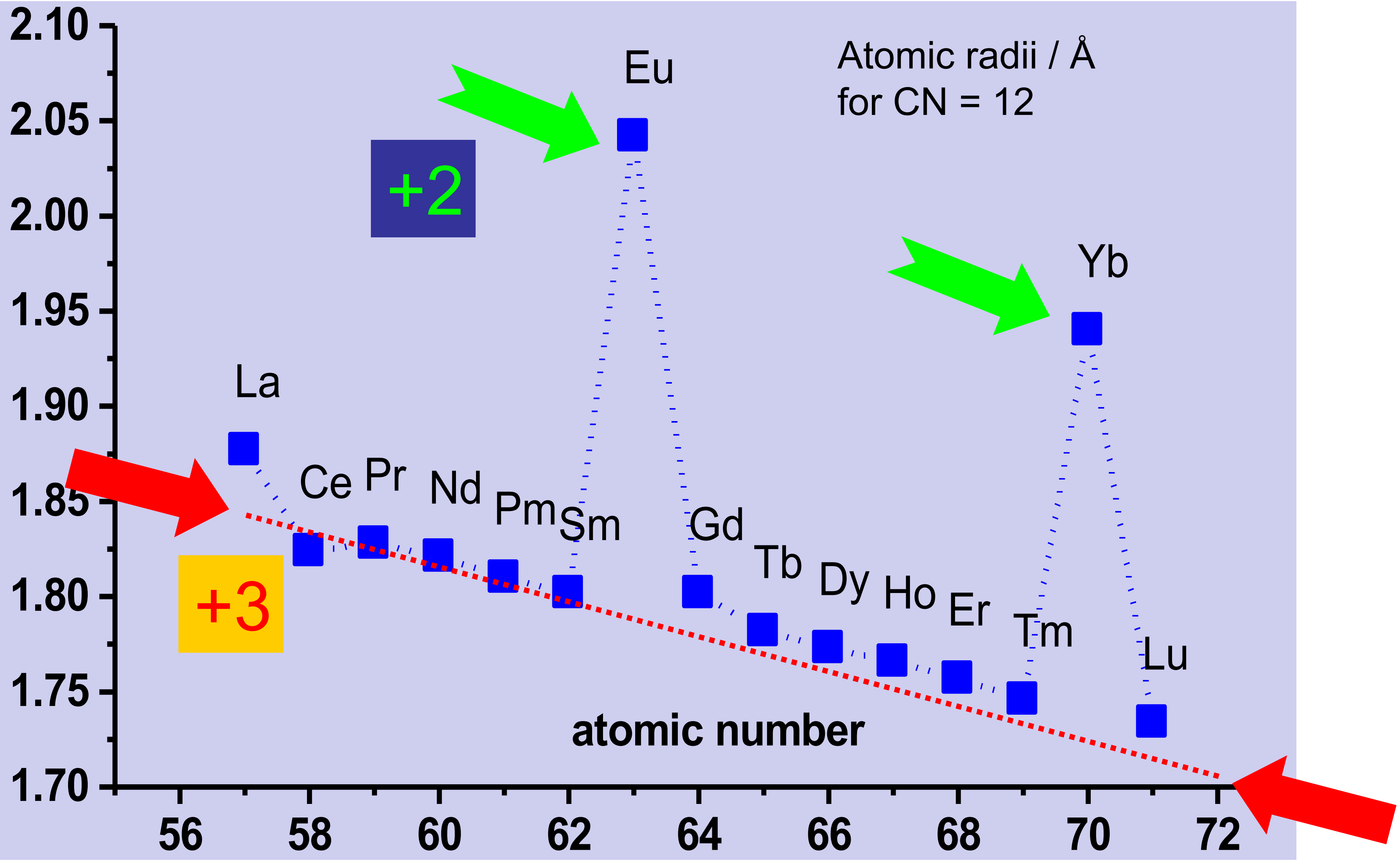
Ionic radii (Ln^{3+}) : lanthanide contraction



Lewis acidity increases along the series due to the increased charge/size ratio

Use of Ln(III) as Lewis acid catalysts in organic chemistry

Ionic radii: variation with coordination number CN and oxidation state



Summary

-f metals behave very differently from d metals

-Electrostatic bonding prevails for all f elements , some covalency in actinides

-Very similar chemical properties along the series of 4f elements

-Ionic contraction along the series

-Only one stable oxidation state (+3) for 4 f ions, +2 and +4 can be stabilized in specific conditions

-Many important applications in material science and medicine