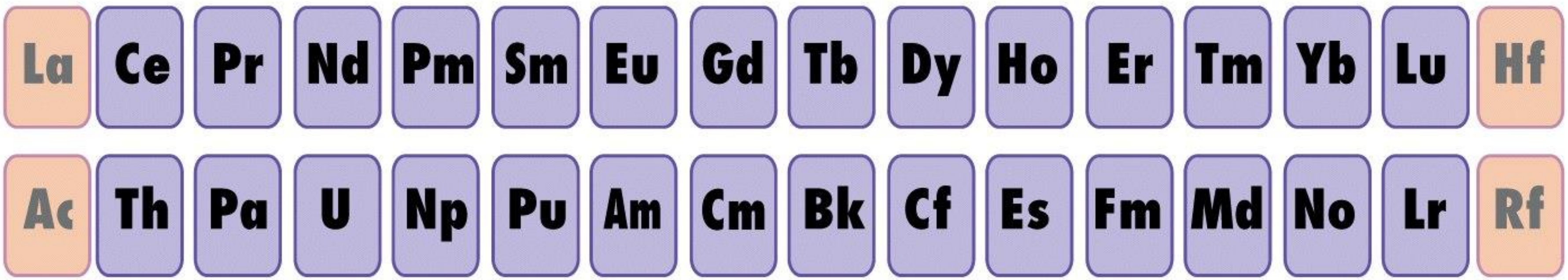
Elementi del blocco f



Lantanide generico = Ln, $4f^{n}5d^{1}6s^{2}$

Attinide generico = An, $5f^{n}6d^{1}7s^{2}$

In the last 5 years, the average American (and likely European) has relied on **80** elements for quality of life.

General Electric uses **72** of the first **82** elements in its product line.

Pharmaceuticals

Pd, Rh, Os, Ir

Household Items

Rh, Pt

Refining

La, Pt

Hybrid/Electric Cars

Nd, Tb, Dy, Pr

Alternative Energy

Ru, Nd, Tb, Dy, Pr

McGroarty, D. *Wall Street Journal* 1/31/13
Jaffe, R. *2011 APS-MRS Report*

…ogni auto Toyota Prius contiene 4 kg di neodimio (Nd) in supermagneti di una lega neodimio-ferro-boro ($Nd_2Fe_{14}B$). Ogni turbina eolica contiene 400 kg di neodimio.

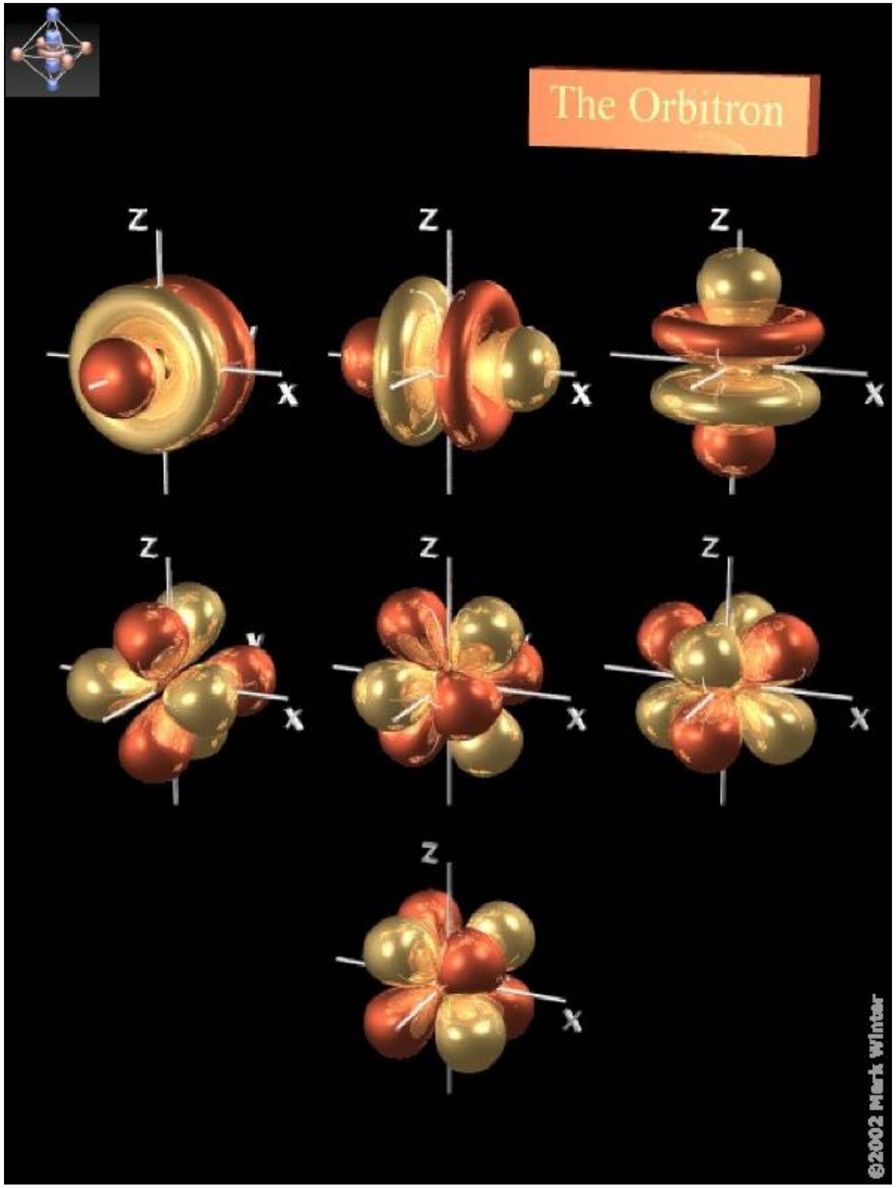
Il 97% della richiesta mondiale di neodimio viene prodotto in una miniera a Bayan Obo, nella Cina interna al confine con la Mongolia…

Il set cubico di orbitali *f*

3 piani nodali

4f = 0 nodi radiali

5f = 1 nodo radiale



f_{x^3} f_{y^3} f_{z^3}

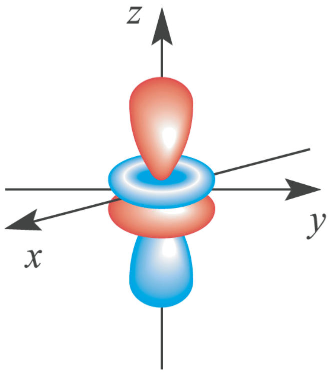
$f_{x(z^2-y^2)}$

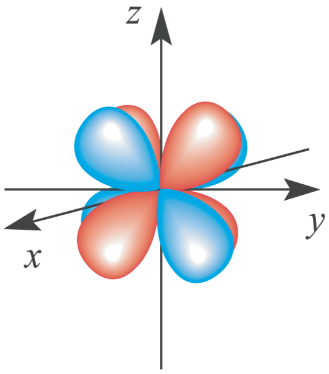
$f_{z(x^2-y^2)}$

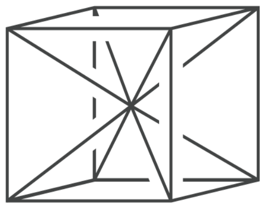
$f_{y(z^2-x^2)}$

f_{xyz}

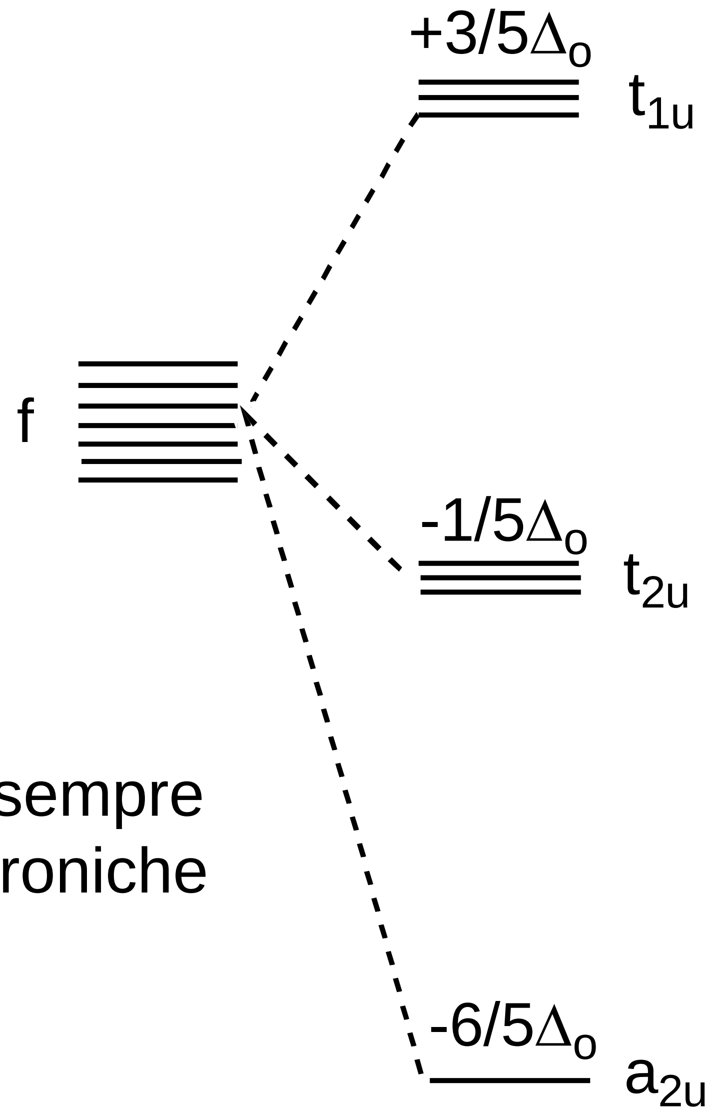
Il set cubico di orbitali *f*







Splitting in campo ottaedrico



Splitting modesto, sempre configurazioni elettroniche ad alto spin

Table 22.2 Names, symbols, and selected properties of the lanthanoids

Z	Name	Symbol	Configuration (M^{3+})	$E^{\ominus}$/V	$r(M^{3+})$/pm*	O.N.†
57	Lanthanum	La	[Xe]	−2.38	116	2(n), **3**, 4
58	Cerium	Ce	[Xe]f^1	−2.34	114	2(n), **3**, 4
59	Praseodymium	Pr	[Xe]f^2	−2.35	113	2(n), **3**, 4
60	Neodymium	Nd	[Xe]f^3	−2.32	111	2(n), **3**
61	Promethium	Pm	[Xe]f^4	−2.29	109	**3**
62	Samarium	Sm	[Xe]f^5	−2.30	108	2(n), **3**
63	Europium	Eu	[Xe]f^6	−1.99	107	2, **3**
64	Gadolinium	Gd	[Xe]f^7	−2.28	105	**3**
65	Terbium	Tb	[Xe]f^8	−2.31	104	**3**, 4
66	Dysprosium	Dy	[Xe]f^9	−2.29	103	2(n), **3**
67	Holmium	Ho	[Xe]f^{10}	−2.33	102	**3**
68	Erbium	Er	[Xe]f^{11}	−2.32	100	**3**
69	Thulium	Tm	[Xe]f^{12}	−2.32	99	2(n), **3**
70	Ytterbium	Yb	[Xe]f^{13}	−2.22	99	2, **3**
71	Lutetium	Lu	[Xe]f^{14}	−2.30	98	**3**

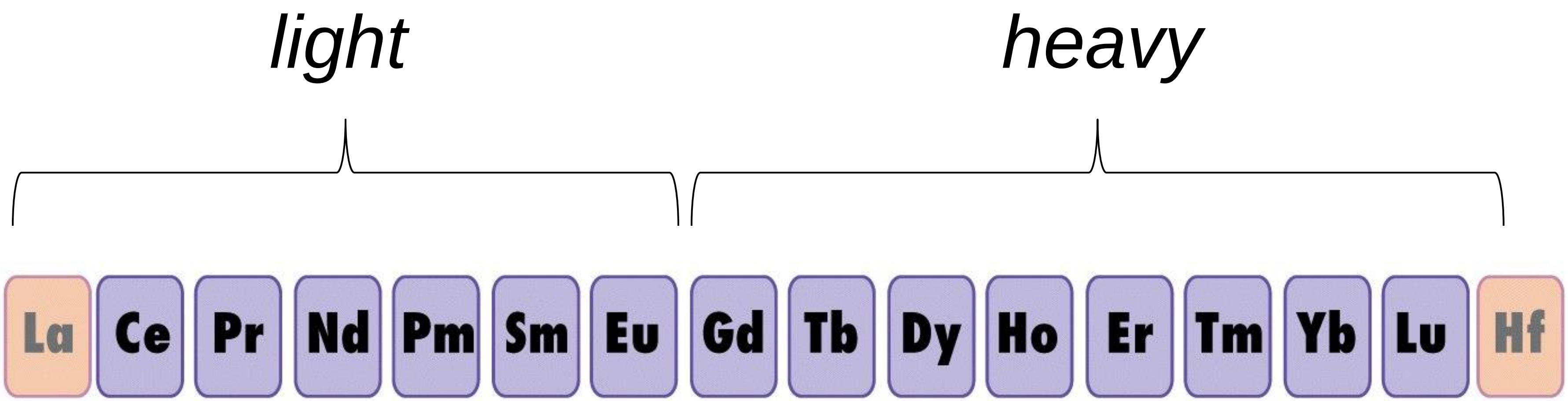
* Ionic radii for coordination number 8 from R.D. Shannon, *Acta Cryst.*, 1976, **A32**, 751.
† Oxidation numbers in bold type indicate the most stable states; (n) indicates that the state is stable only in nonaqueous conditions.

Ce^{4+}, f^0

Eu^{2+}, f^7

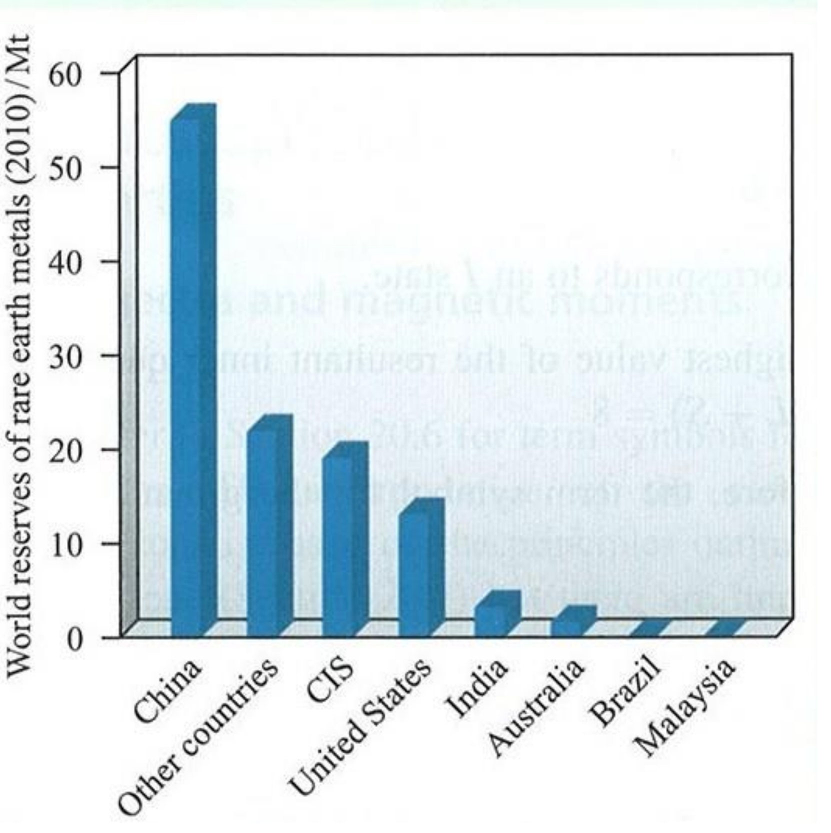
Metal	$\Delta_a H^o(Ln)$ / kJ mol^{-1}	$IE_1 + IE_2 + IE_3$ / kJ mol^{-1}	$\Delta_{hyd} H^o(Ln^{3+}$, g)/ kJ mol^{-1}	$E^o_{Ln^{3+}/Ln}$ / V	$E^o_{Ln^{2+}/Ln}$ / V
La	431	3455	−3278	−2.38	
Ce	423	3530	−3326	−2.34	
Pr	356	3631	−3373	−2.35	−2.0
Nd	328	3698	−3403	−2.32	−2.1
Pm	348	3741	−3427	−2.30	−2.2
Sm	207	3873	−3449	−2.30	−2.68
Eu	177	4036	−3501	−1.99	−2.81
Gd	398	3750	−3517	−2.28	
Tb	389	3792	−3559	−2.28	
Dy	290	3899	−3567	−2.30	−2.2
Ho	301	3924	−3613	−2.33	−2.1
Er	317	3934	−3637	−2.33	−2.0
Tm	232	4045	−3664	−2.32	−2.4
Yb	152	4195	−3724	−2.19	−2.76
Lu	428	3886	−3722	−2.28	

† Values of $\Delta_{hyd} H^\circ(M^{3+}$, g) are taken from: L.R. Morss (1976) *Chem. Rev.*, vol. 76, p. 827.



Terre Rare (*rare earth metals*, REM o RE) = 15 elementi La – Lu (Z = 57–71) + Sc (Z = 21) + Y (Z = 39)

Risorse mondiali e produzione



Nel 2010: 114.000 tonnellate di REM

Ce, La, Nd, Y > 10.000 t/anno

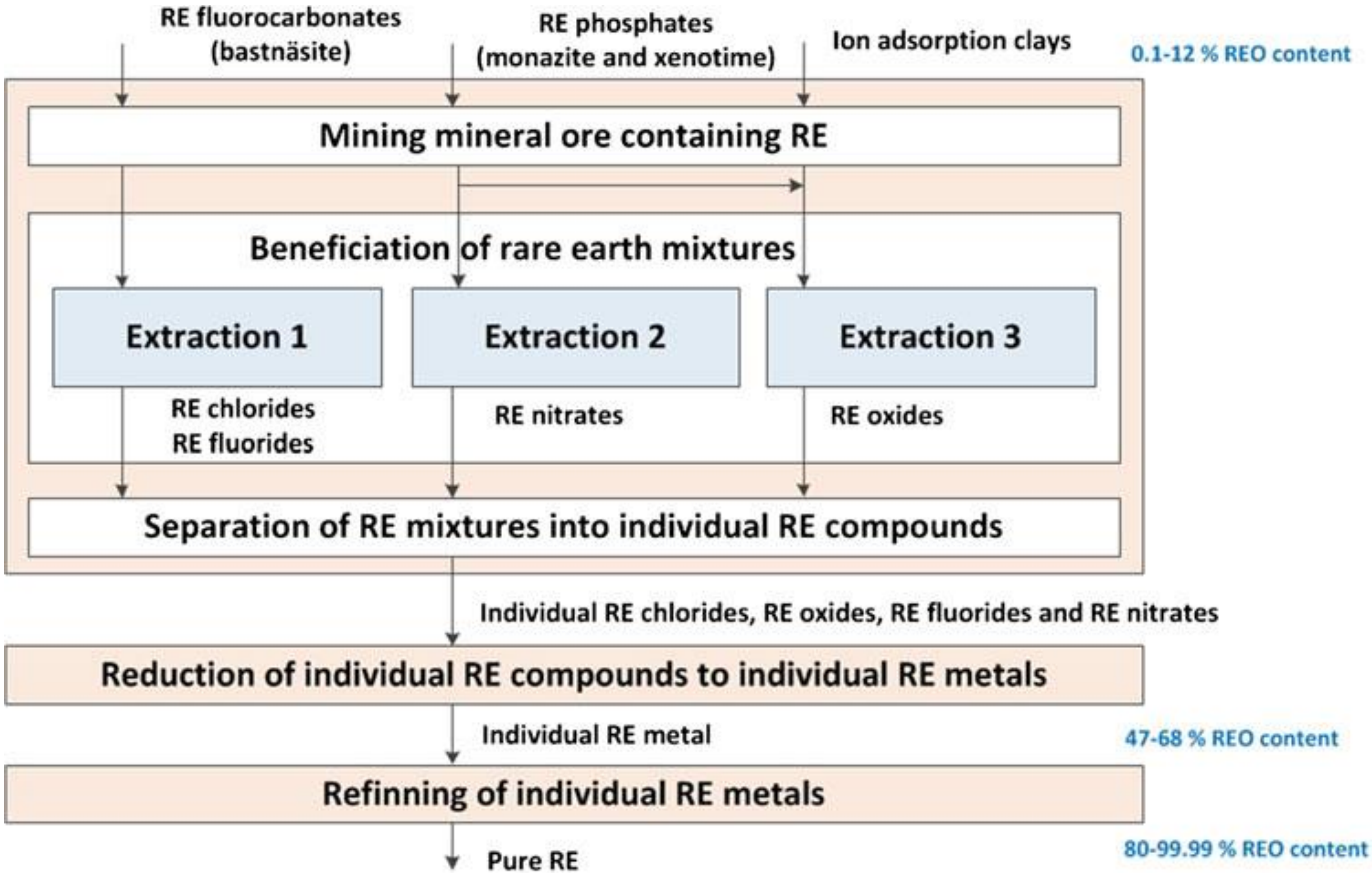
Pr, Dy > 1000 t/anno

Gd, Sm, Eu, Tb > 100 t/anno

- **bastnäsite** $[Ce,La,Nd](CO_3)F$
- **monazite** $[Ce,La,Nd,Th](PO_4)$
- **xenotime** $[Y, Ln,Th](PO_4)$

Ln leggeri (bastnäsite, monazite)

Ln pesanti (xenotime)



Miniera di Bayan Obo
(4.1% di REO)

Miniera di Mountain Pass (7.7% di REO)

Arricchimento chimico della bastnasite

$$2RECO_3F + 3H_2SO_4 \rightarrow RE_2(SO_4)_3 + 2HF + 2H_2CO_3$$

H_2SO_4 al 98%, 500 ºC, arrostimento acido

$$4/3RE_2(SO_4)_3 + 12H_2O + 2NaCl \rightarrow RE_2(SO_4)_3 \cdot Na_2SO_4 \cdot 12H_2O\downarrow + 2/3RECl_3$$

$$RE_2(SO_4)_3 \cdot Na_2SO_4 \cdot 12H_2O + 6NaOH \rightarrow 2RE(OH)_3\downarrow + 4Na_2SO_4 + 12H_2O$$

$$RE(OH)_3 + 3HCl \rightarrow RECl_3 + 3H_2O$$

1200 ºC

$$3RECO_3F + 3Cl_2 \rightarrow REF_3 + 2RECl_3 + 3/2O_2 + 3CO_2$$

$$\nearrow$$

$$REF_3 + 3NaOH \rightarrow RE(OH)_3 + 3NaF$$

Arricchimento chimico di monazite e xenotime

(processo Rhône-Poulenc)

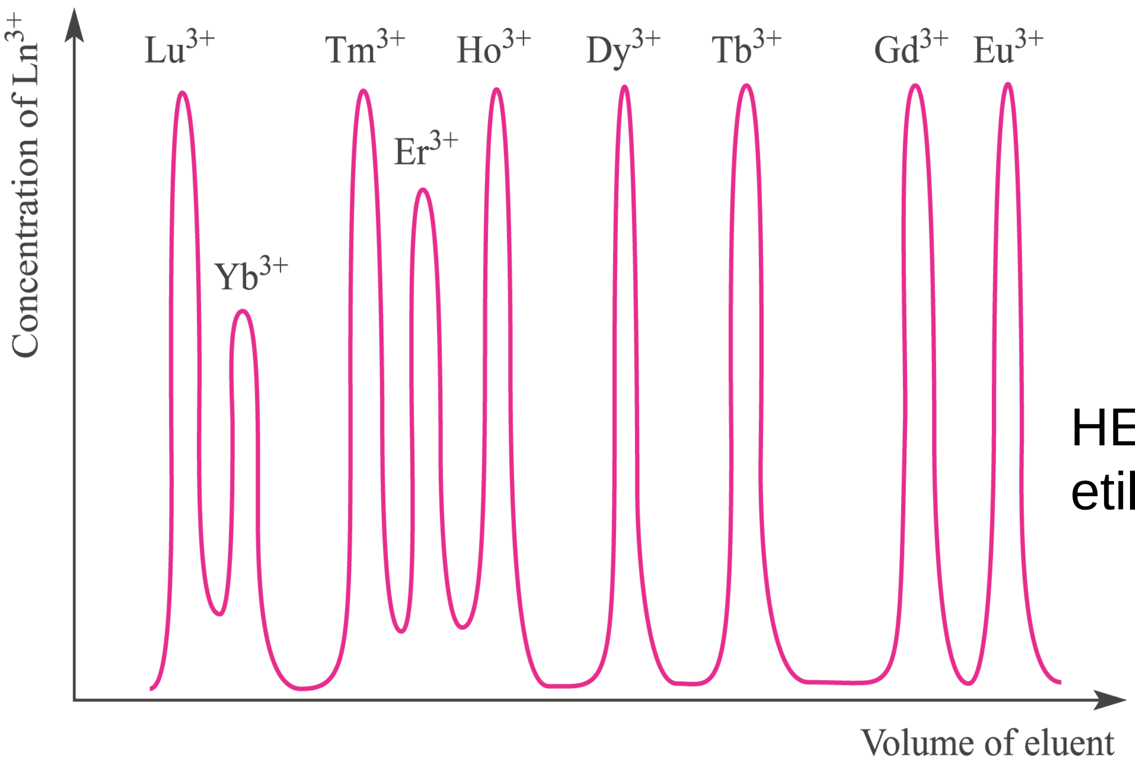
$$REPO_4 + 3NaOH \rightarrow RE(OH)_3\downarrow + Na_3PO_4$$

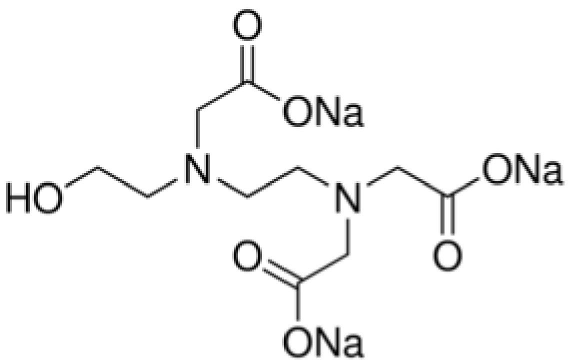
NaOH 60-70%, 140-150 ºC

$$RE(OH)_3 + 3HNO_3 \rightarrow RE(NO_3)_3 \cdot 3H_2O$$

Torio rimosso come ThO_2, insolubile

Sequenza di eluizione da una colonna a scambio cationico (fase stazionaria non selettiva, e.g. Dowex) dei complessi dei lantanidi più pesanti eluendo con una soluzione di $EDTA^{4-}$

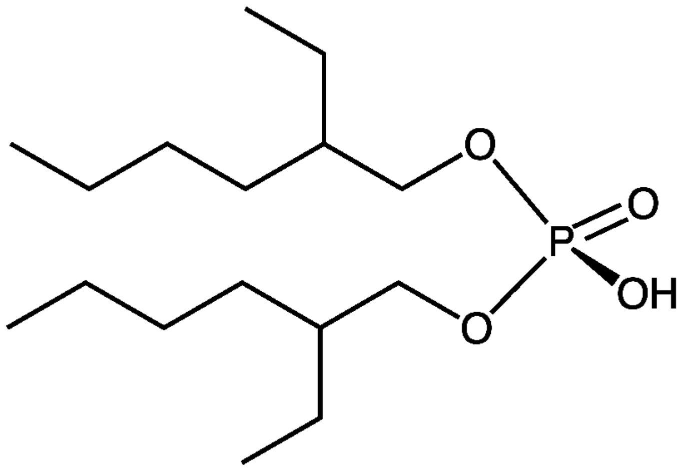




HEDTA = acido N-idrossietil-etilendiaminotriacetico

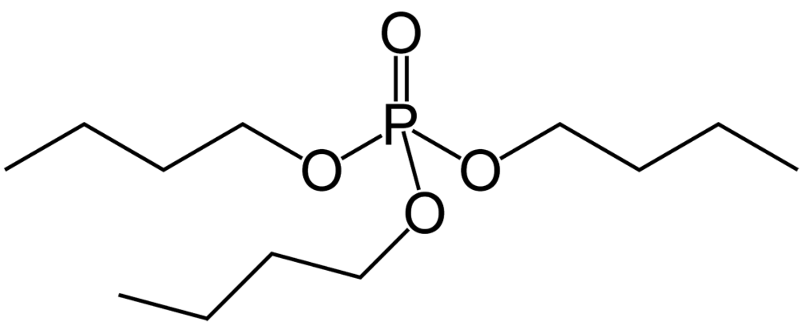
SX, *Solvent eXtraction*

fattore di separazione $\alpha_B^A = \frac{D_A}{D_B}$



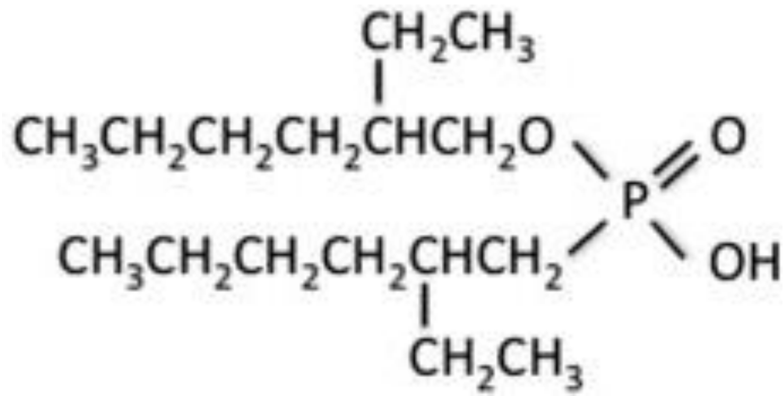
acido di-2-etil-esilfosforico (**HDEHP** o DEHPA) per RE come cloruri o solfati

$[RE^{3+}]aq + [6(HA)]org \rightarrow [RE(A)_3(HA)_3]org + 3[H^+]aq$



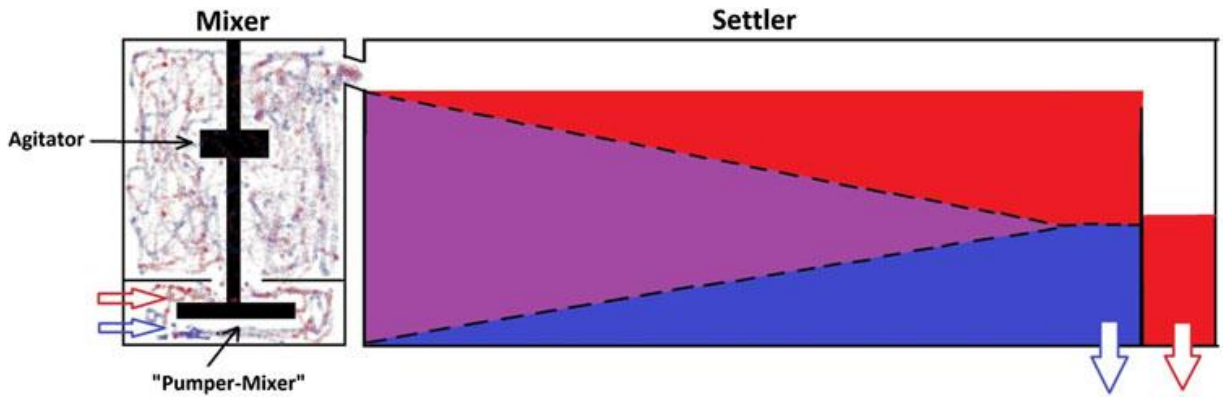
tri-*n*-butil fosfato (**TBP**) per RE come nitrati

$[RE(NO_3)_3 \cdot 3H_2O]aq + 3[TBP]org \rightarrow [RE(NO_3)_3 \cdot TBP_3]org + 3H_2O$

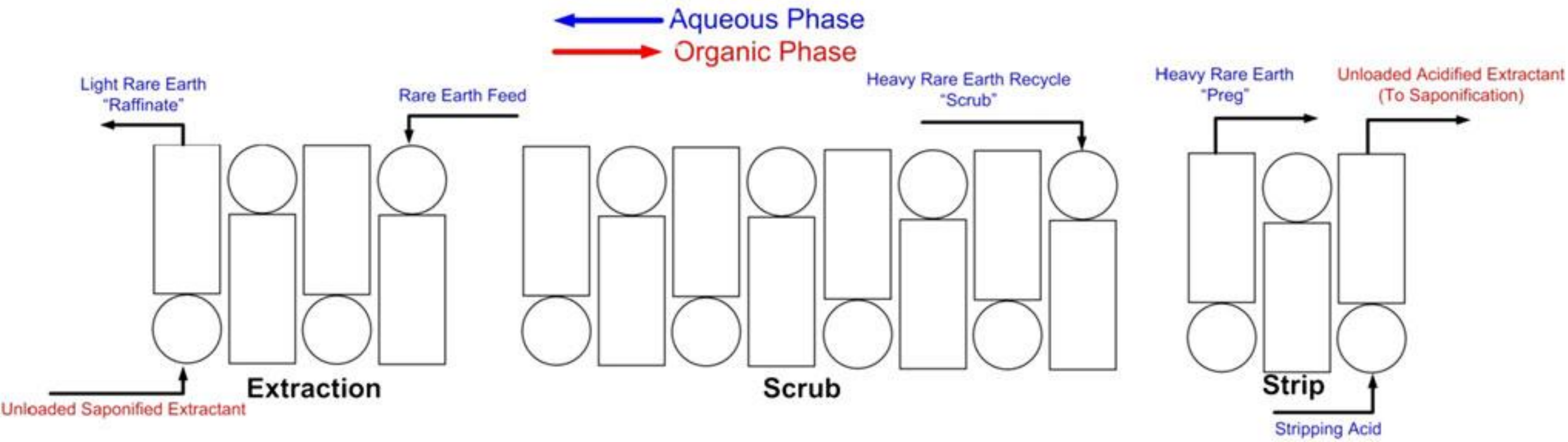


acido 2-etilesilfosfonico mono-2-etilesil estere (**EHEHPA** o PC88A)

Unità *mixer-settler*



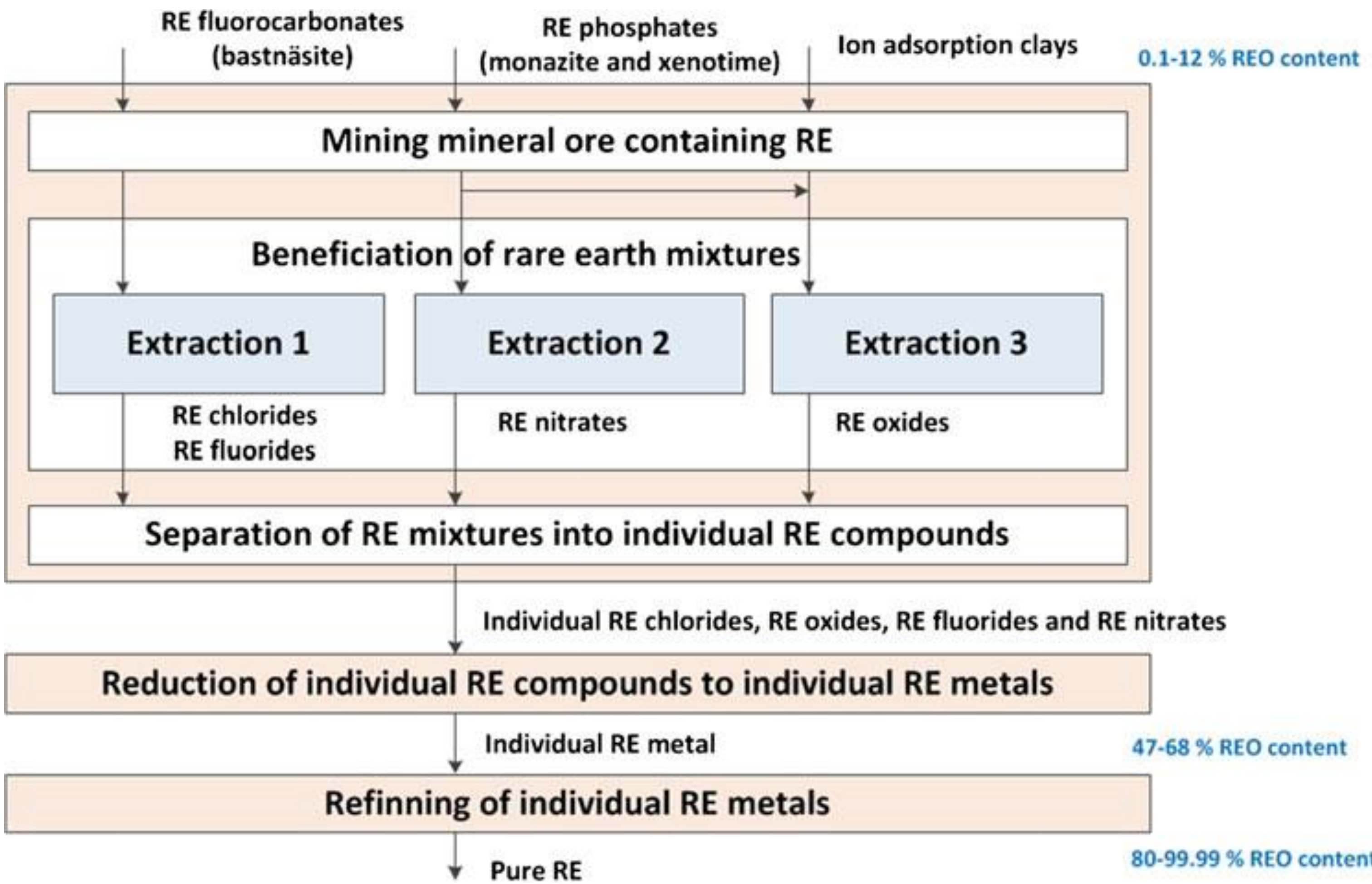
Schema di impianto SX



- **bastnäsite** $[Ce,La,Nd](CO_3)F$
- **monazite** $[Ce,La,Nd,Th](PO_4)$
- **xenotime** $[Y, ln,Th](PO_4)$

} Ln leggeri

Ln pesanti

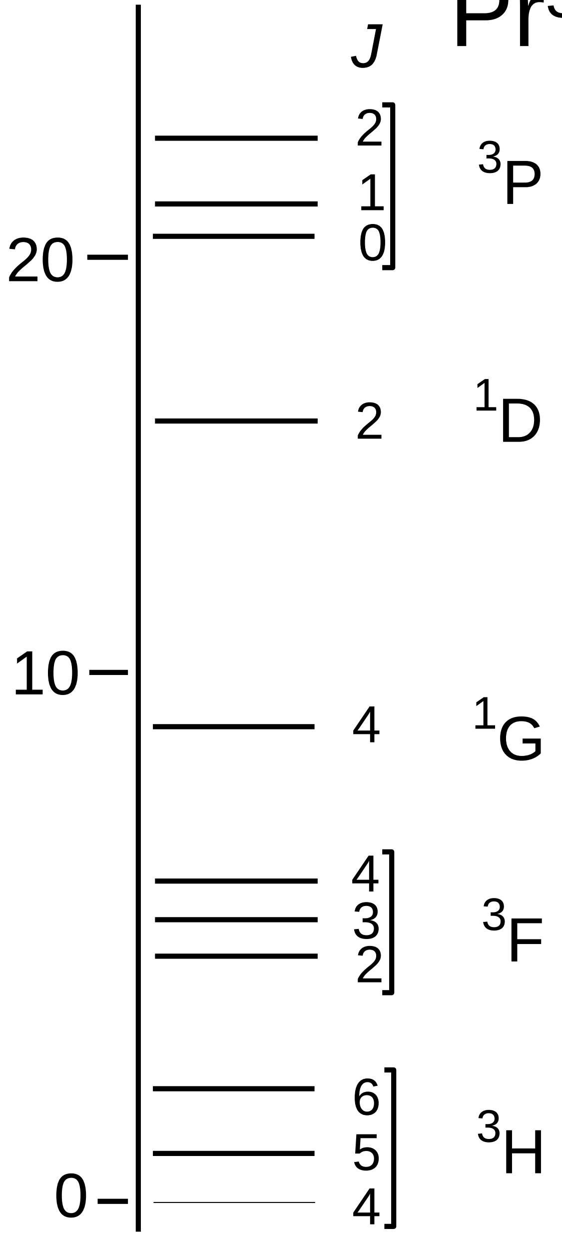


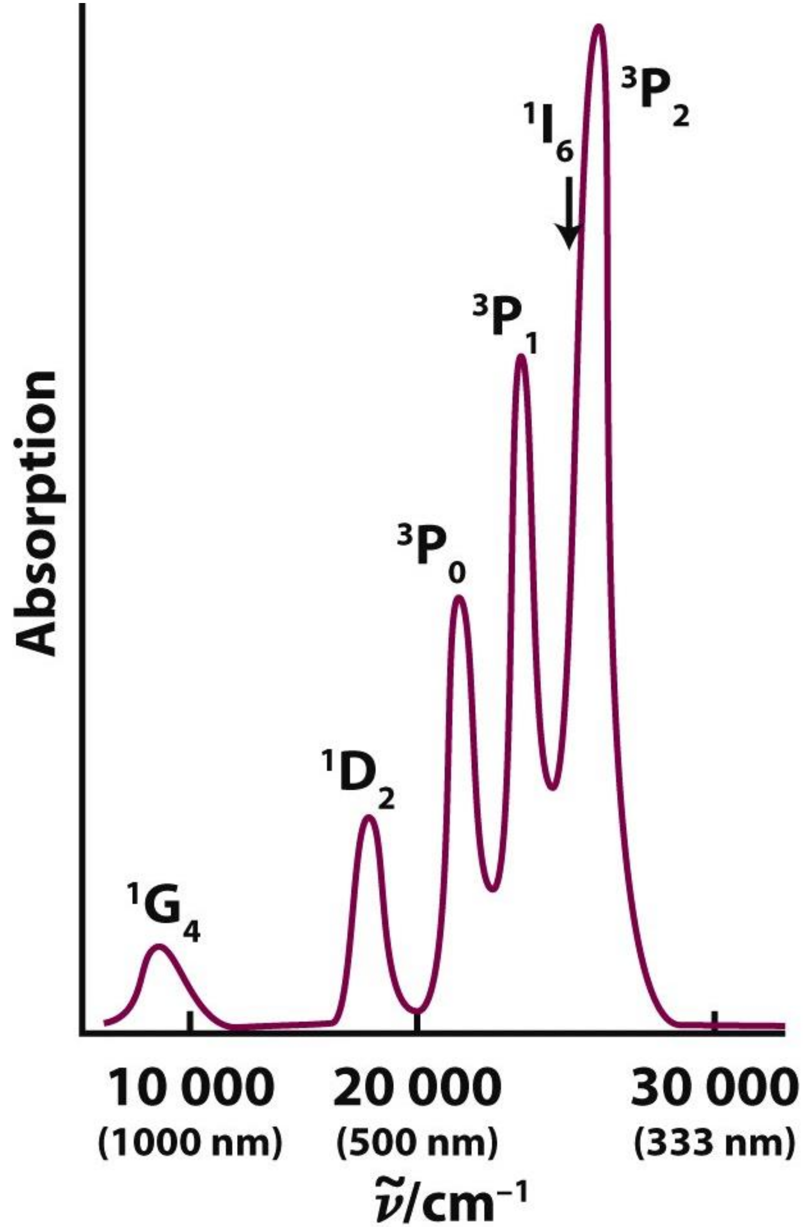
Metal ion	Colour	Ground state electronic configuration	Ground state term symbol	Magnetic moment, μ (298 K) / μ_B	
				Calculated from equation 25.1	Observed
La^{3+}	Colourless	$[Xe]4f^0$	$^1S_0$	0	0
Ce^{3+}	Colourless	$[Xe]4f^1$	$^2F_{5/2}$	2.54	2.3–2.5
Pr^{3+}	Green	$[Xe]4f^2$	$^3H_4$	3.58	3.4–3.6
Nd^{3+}	Lilac	$[Xe]4f^3$	$^4I_{9/2}$	3.62	3.5–3.6
Pm^{3+}	Pink	$[Xe]4f^4$	$^5I_4$	2.68	2.7
Sm^{3+}	Yellow	$[Xe]4f^5$	$^6H_{5/2}$	0.84	1.5–1.6
Eu^{3+}	Pale pink	$[Xe]4f^6$	$^7F_0$	0	3.4–3.6
Gd^{3+}	Colourless	$[Xe]4f^7$	$^8S_{7/2}$	7.94	7.8–8.0
Tb^{3+}	Pale pink	$[Xe]4f^8$	$^7F_6$	9.72	9.4–9.6
Dy^{3+}	Yellow	$[Xe]4f^9$	$^6H_{15/2}$	10.63	10.4–10.5
Ho^{3+}	Yellow	$[Xe]4f^{10}$	$^5I_8$	10.60	10.3–10.5
Er^{3+}	Rose pink	$[Xe]4f^{11}$	$^4I_{15/2}$	9.58	9.4–9.6
Tm^{3+}	Pale green	$[Xe]4f^{12}$	$^3H_6$	7.56	7.1–7.4
Yb^{3+}	Colourless	$[Xe]4f^{13}$	$^2F_{7/2}$	4.54	4.4–4.9
Lu^{3+}	Colourless	$[Xe]4f^{14}$	$^1S_0$	0	0

91 microstati

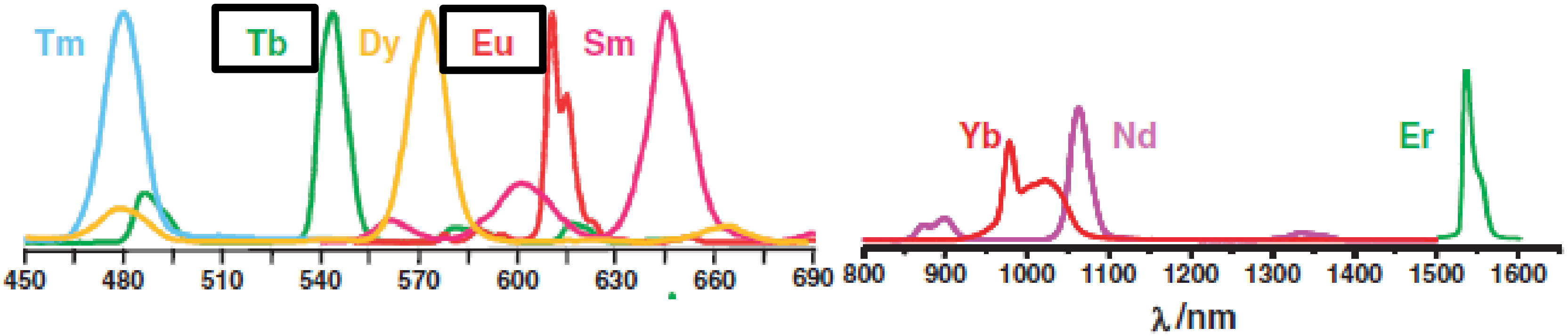
Pr^{3+}, f^2

$$\frac{[2(2l+1)]!}{x! \times [2(2l+1)-x]!}$$

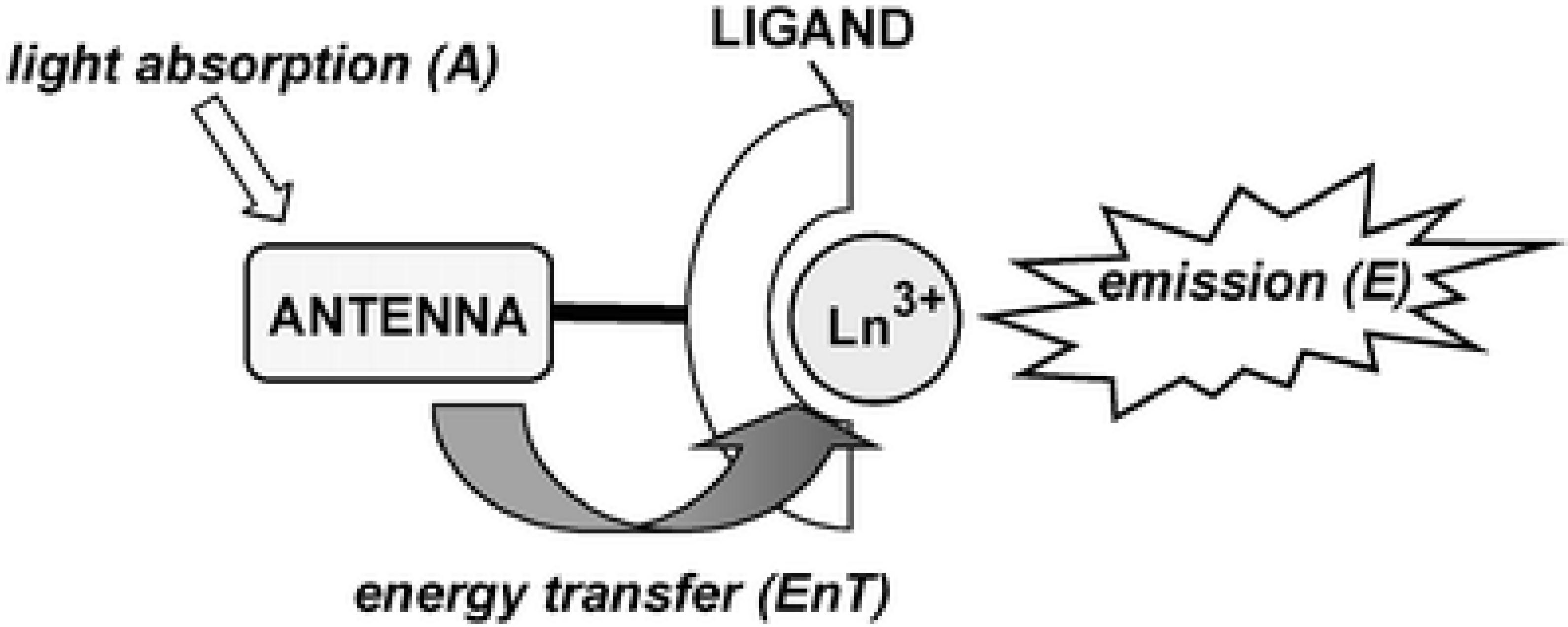




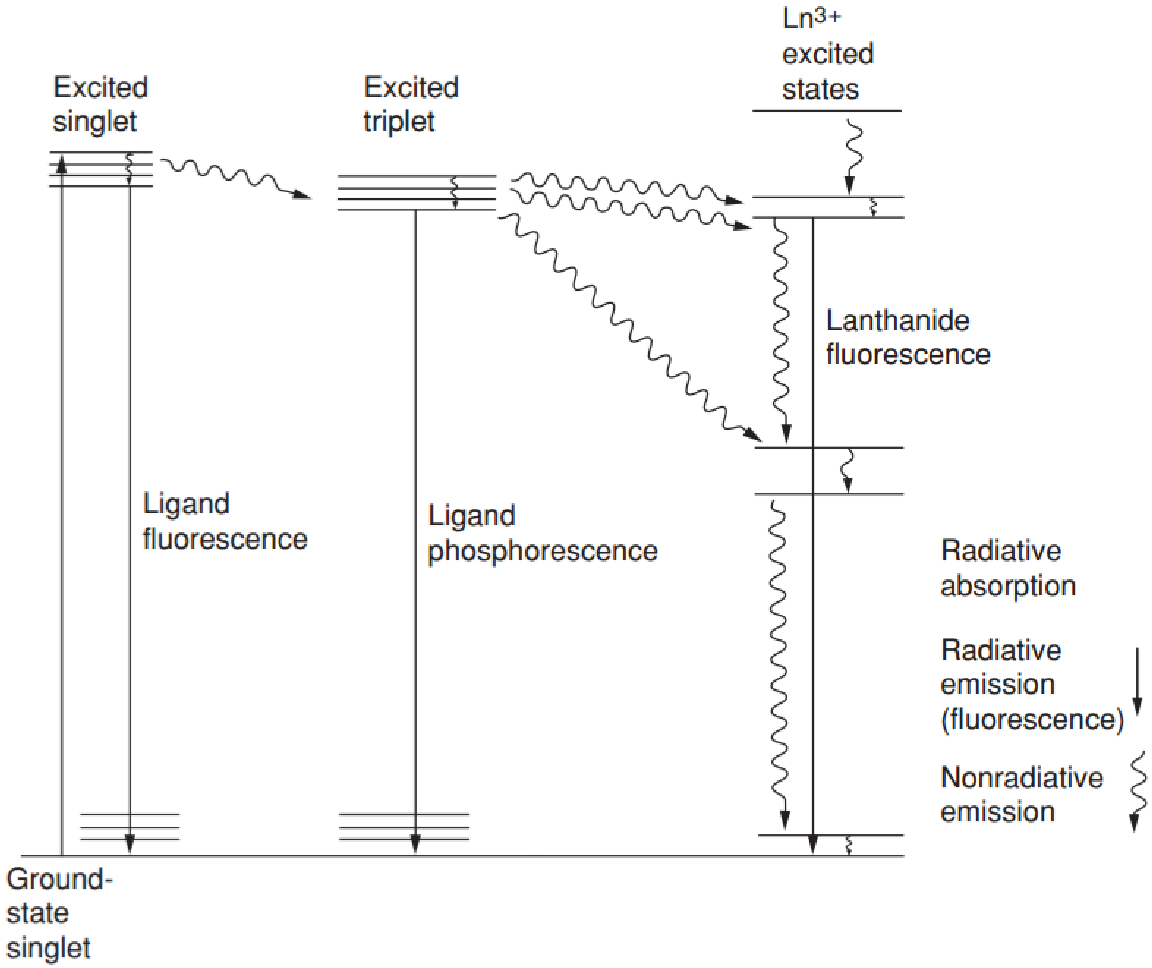
Spettri di emissione di alcuni cationi dei lantanidi



Sensibilizzazione (*antenna excitation*)

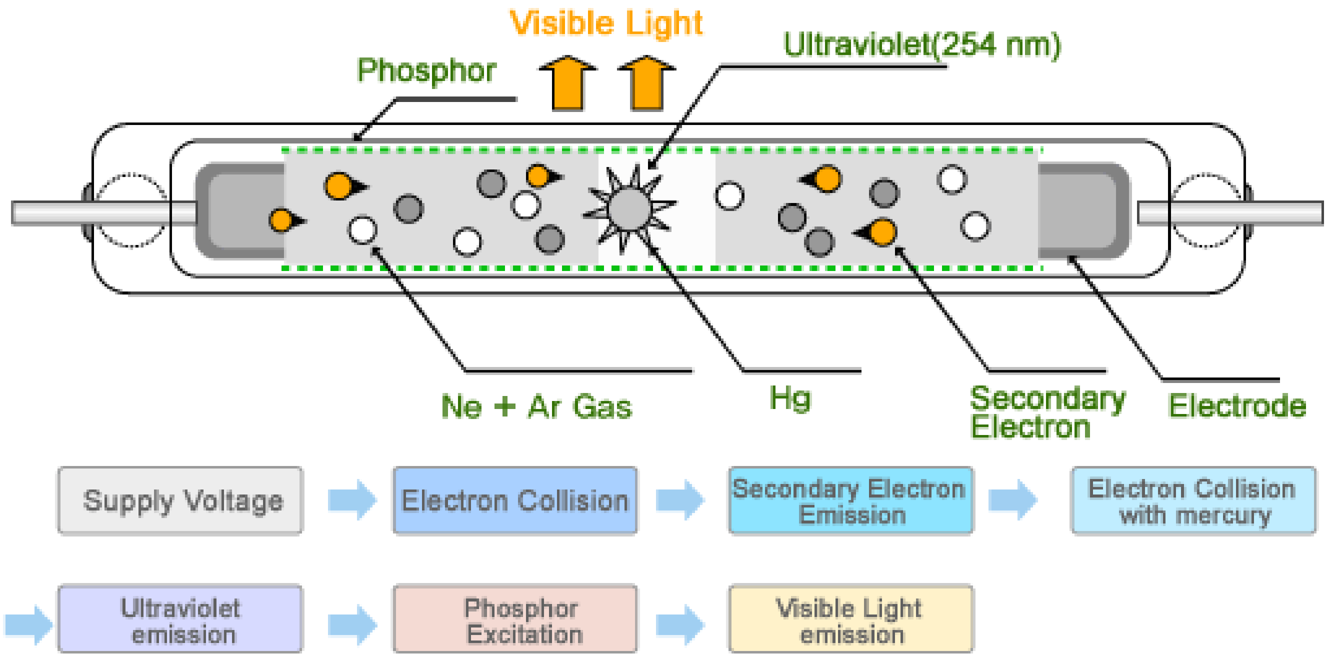


Sensibilizzazione (*antenna excitation*)



Phosphors a base di lantanidi per lampade fluorescenti (*Cold Cathode Fluorescent Lamp*, CCFL)

Cold Cathode Fluorescent Lamp (CCFL)



phosphors a base di Y, La, Ce, Eu, Gd, Tb

Lanthanide-doped LED

White-emitting LED = core LED blu (GaN, λ_{em} = 450 – 470 nm) ricoperto da uno strato di resina contenente un Ln *phospor* che emette nel giallo (e.g. *yttrium aluminium garnet, YAG,* drogato con cerio (YAG:Ce)).

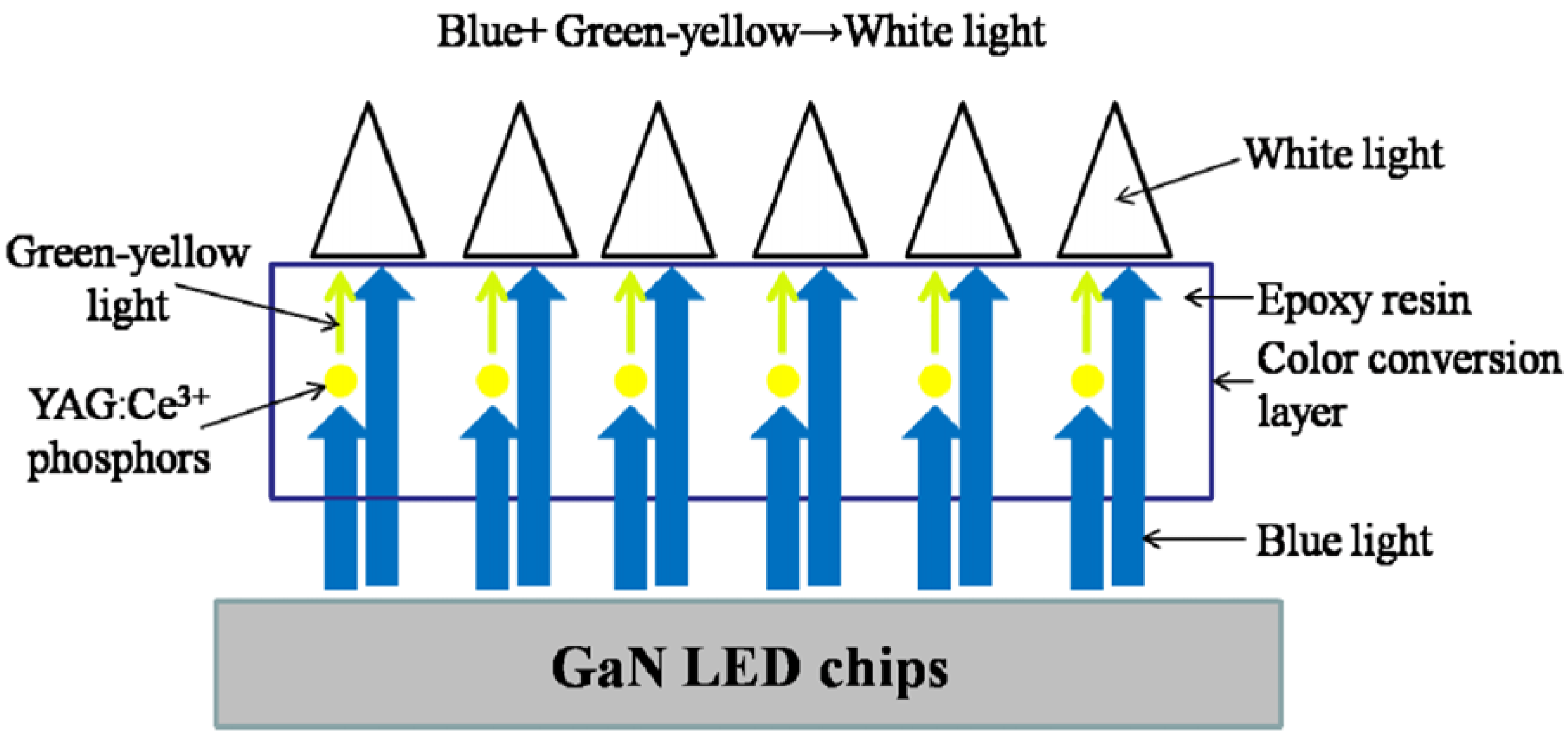
Blu + giallo = bianco

Granato (*garnet*) = $M_3M'_2(XO_4)_3$, (M/M' = $2^+/3^+$, X = Si, Al, Ga, Ge)

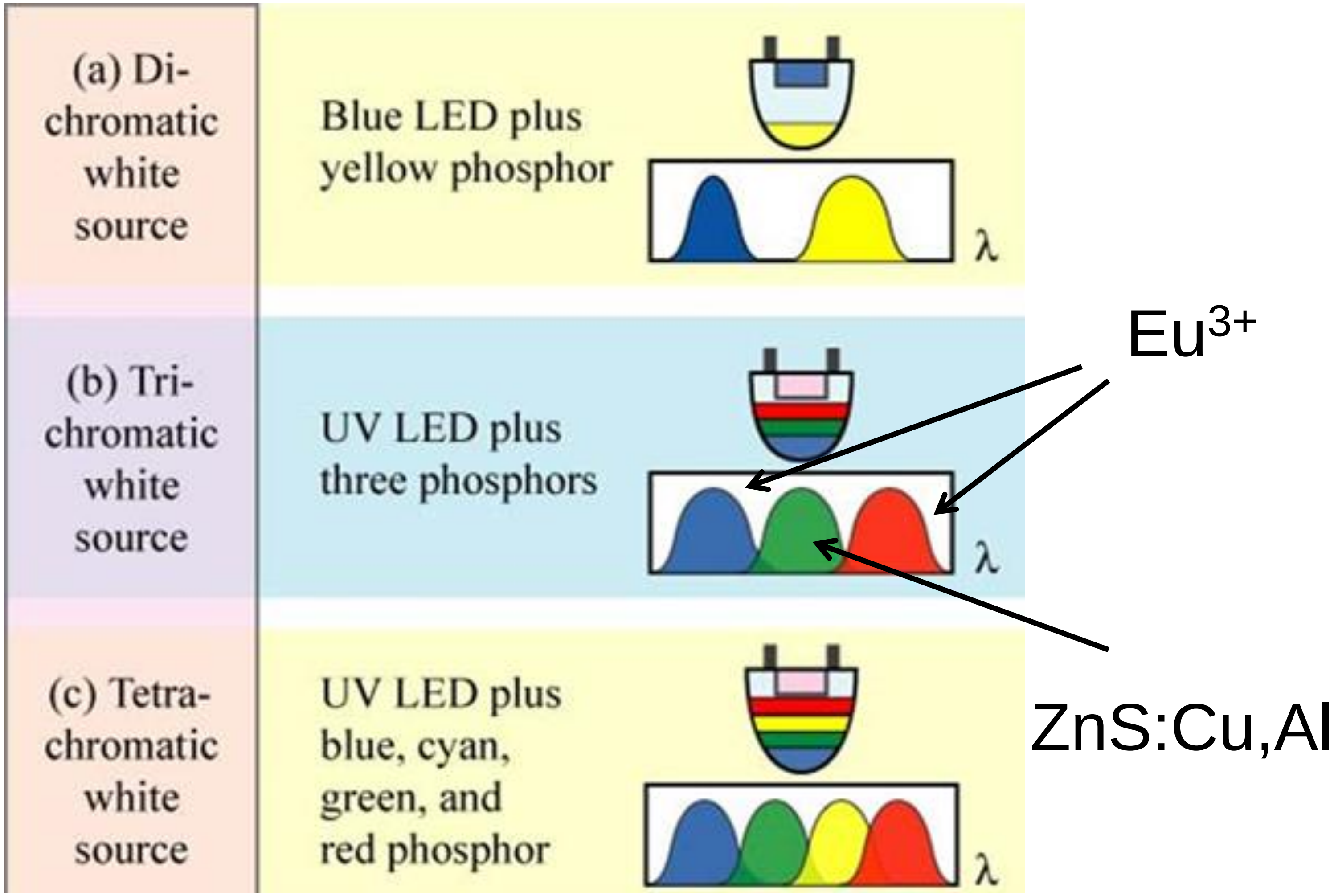
Granato di ittrio e alluminio (YAG) = $Y_3Al_5O_{12}$

La struttura del granato definisce dei siti ottacoordinati che possono venire occupati da ioni dei lantanidi (e.g. al posto di Y^{3+})

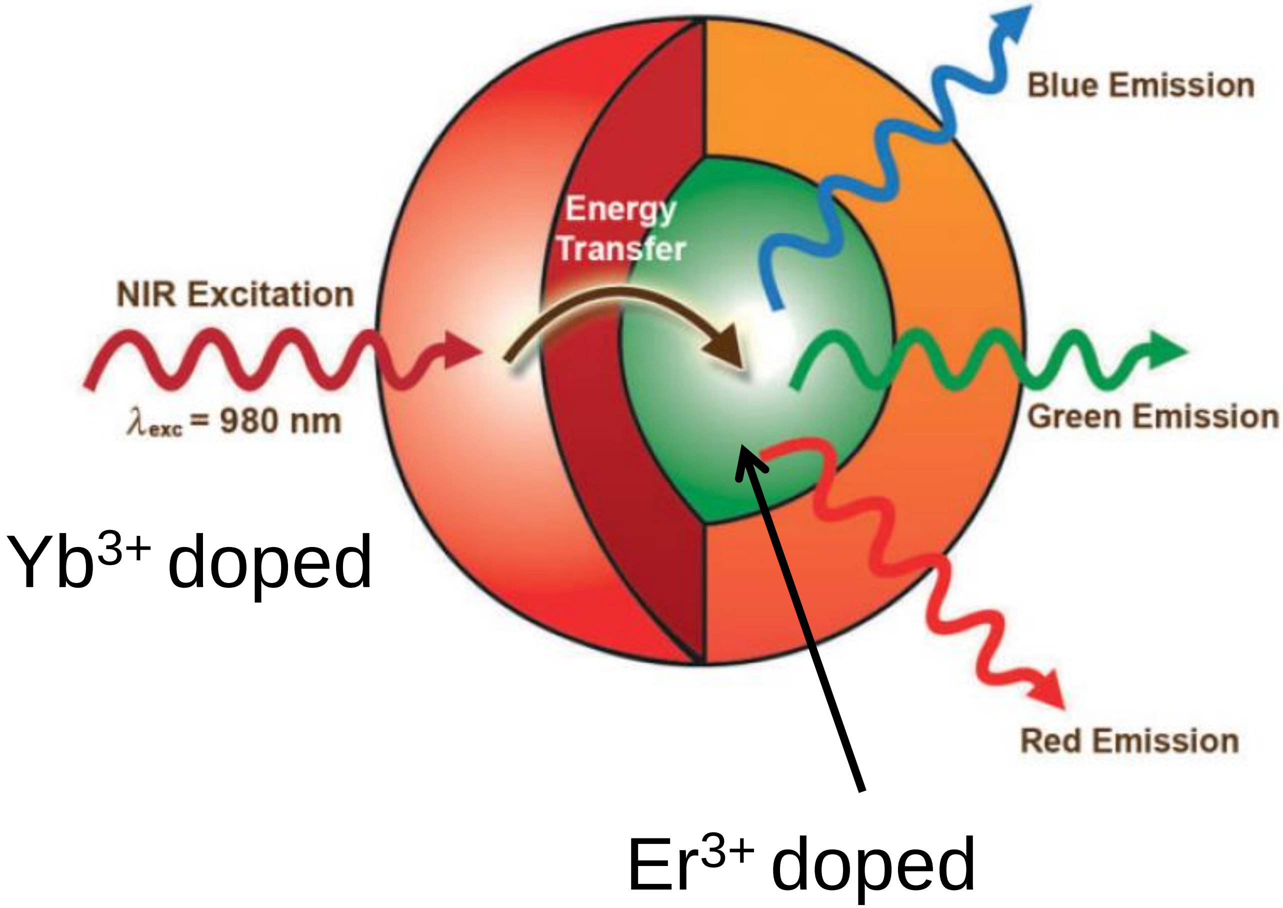
Lanthanide-doped LED



Lanthanide-doped LED

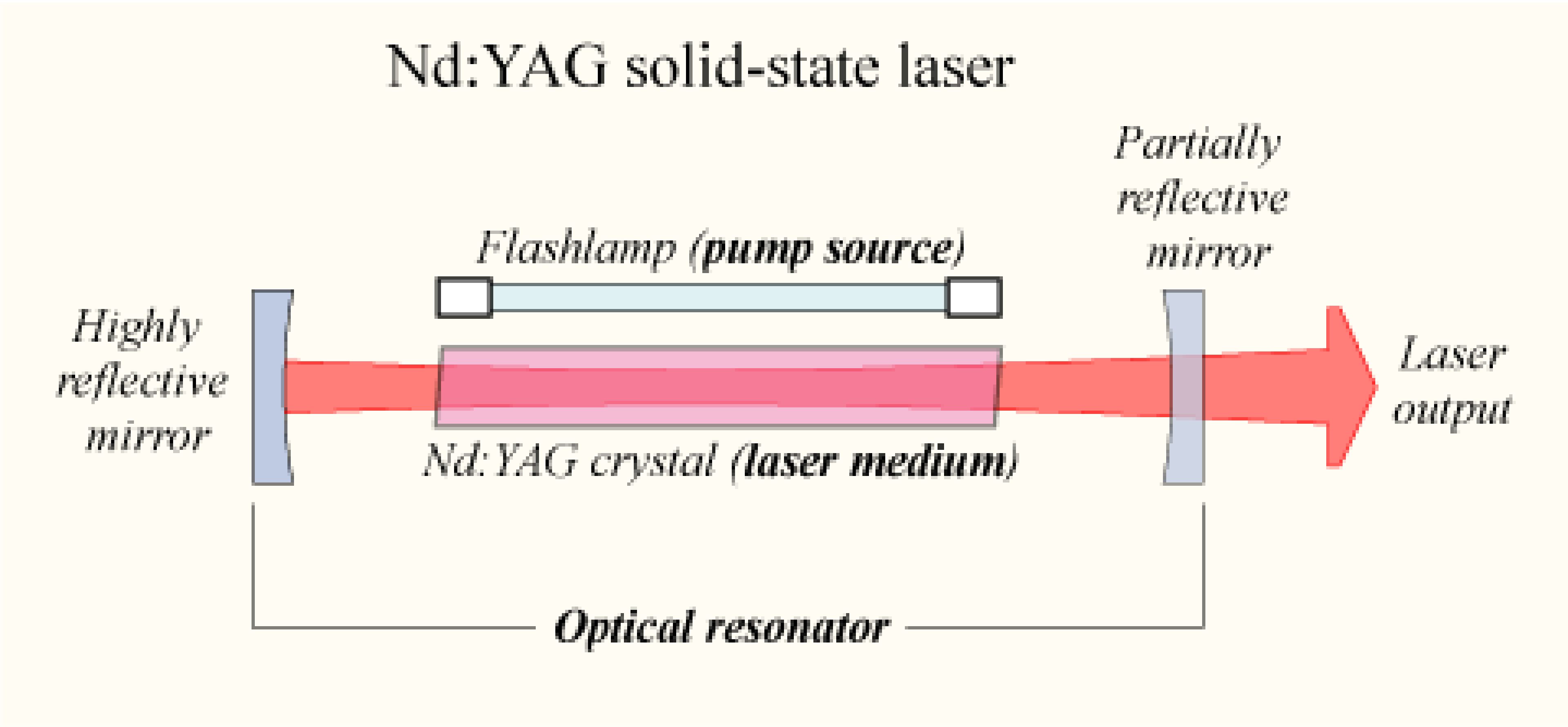


Lanthanide-doped, NIR-excited upconverting nanoparticles



Laser Nd:YAG (*yttrium aluminum garnet,* $Y_3Al_5O_{12}$)

LASER = *Light Amplification by Stimulated Emission of Radiation*

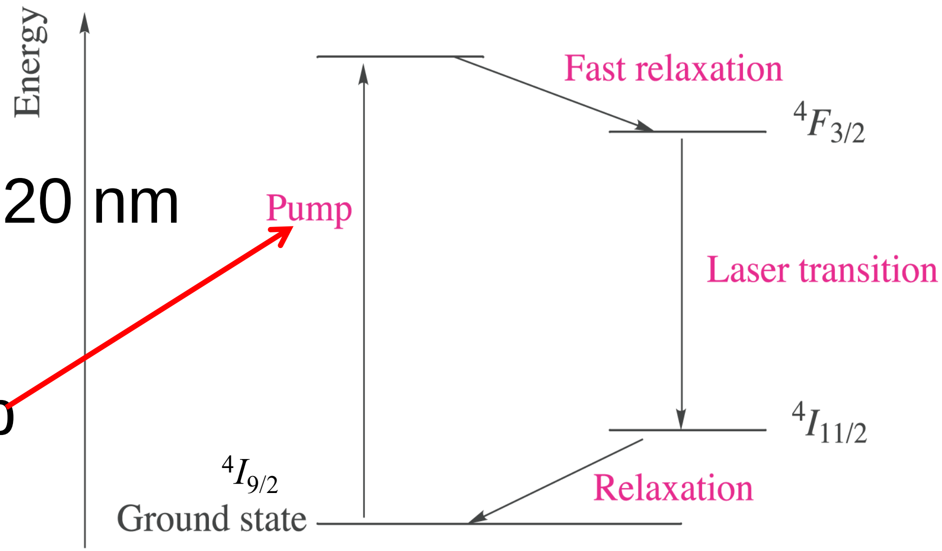


Laser Nd:YAG (*yttrium aluminum garnet,* $Y_3Al_5O_{12}$)

granati: $M_3M'_2(XO_4)_3$ X = Si, Al, Ga, Ge

730–760 e 790–820 nm

Kripton flash lamp



1064 nm

532 nm

355 nm

266 nm

LASER a 4 livelli

$$\mu = g_J\{J(J+1)\}^{1/2}\ \mu_B$$

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

Metal ion	Colour	Ground state electronic configuration	Ground state term symbol	Magnetic moment, μ (298 K) / μ_B	
				Calculated from equation 25.1	Observed
La^{3+}	Colourless	$[Xe]4f^0$	$^1S_0$	0	0
Ce^{3+}	Colourless	$[Xe]4f^1$	$^2F_{5/2}$	2.54	2.3–2.5
Pr^{3+}	Green	$[Xe]4f^2$	$^3H_4$	3.58	3.4–3.6
Nd^{3+}	Lilac	$[Xe]4f^3$	$^4I_{9/2}$	3.62	3.5–3.6
Pm^{3+}	Pink	$[Xe]4f^4$	$^5I_4$	2.68	2.7
Sm^{3+}	Yellow	$[Xe]4f^5$	$^6H_{5/2}$	0.84	1.5–1.6
Eu^{3+}	Pale pink	$[Xe]4f^6$	$^7F_0$	0	3.4–3.6
Gd^{3+}	Colourless	$[Xe]4f^7$	$^8S_{7/2}$	7.94	7.8–8.0
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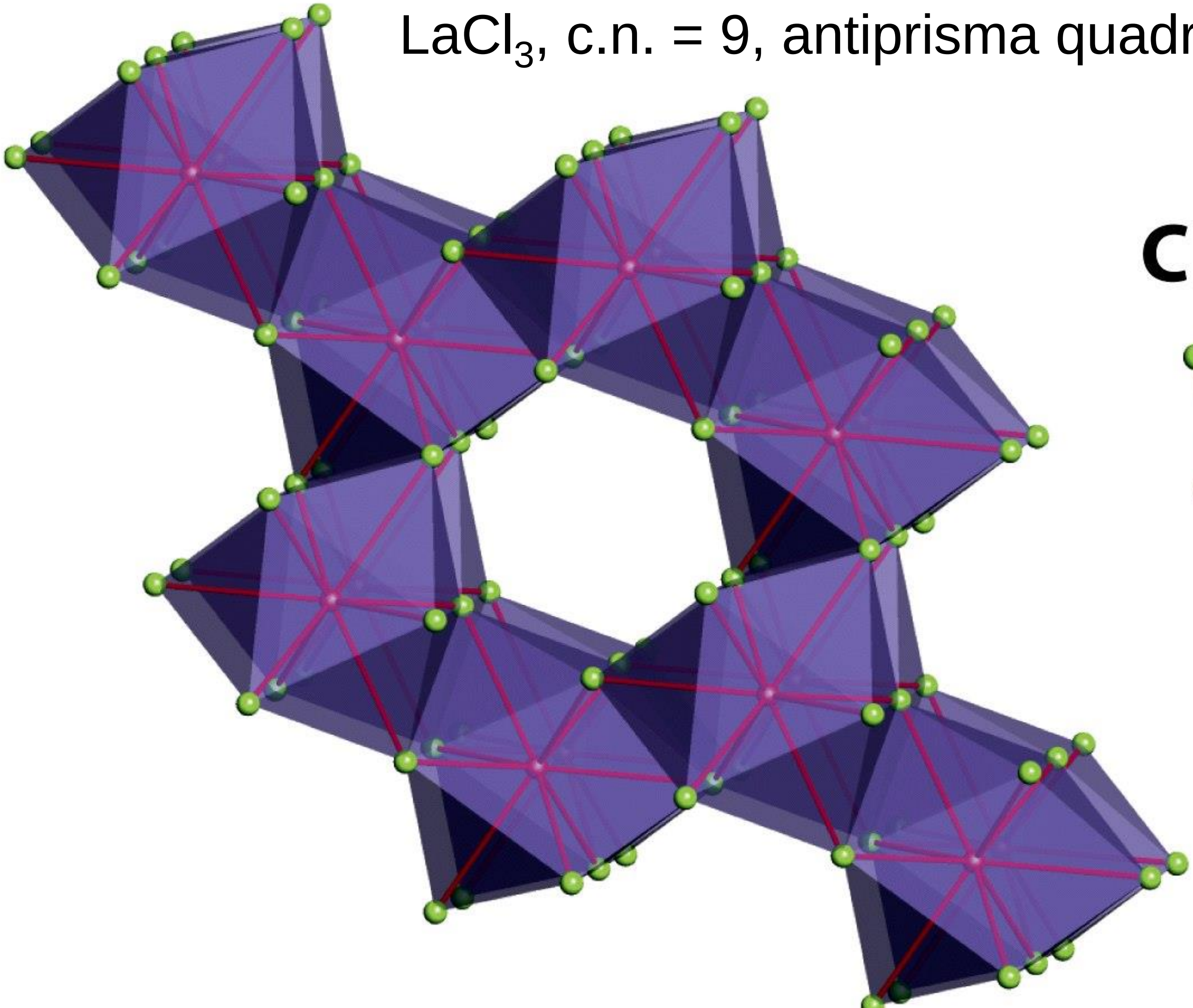
Lu^{3+}	Colourless	$[Xe]4f^{14}$	$^1S_0$	0	0

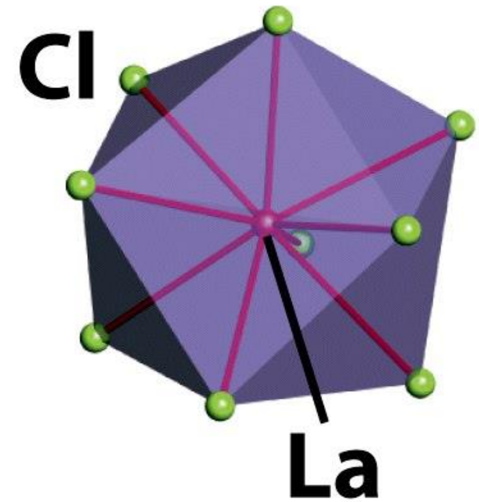
Supermagneti

$SmCo_5$ o Sm_2Co_{17}

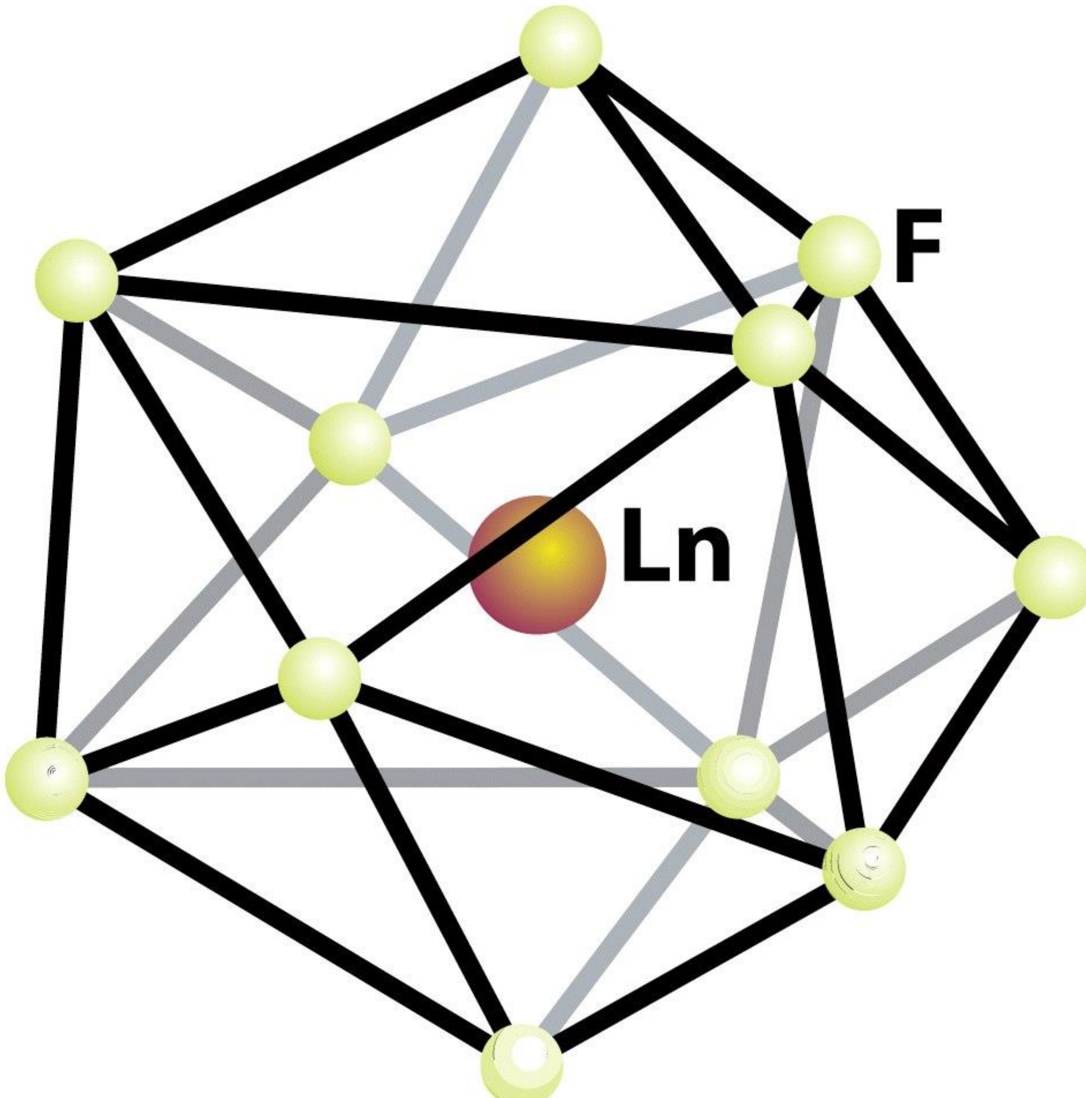
$Nd_2Fe_{14}B$

$LaCl_3$, c.n. = 9, antiprisma quadrato cappato



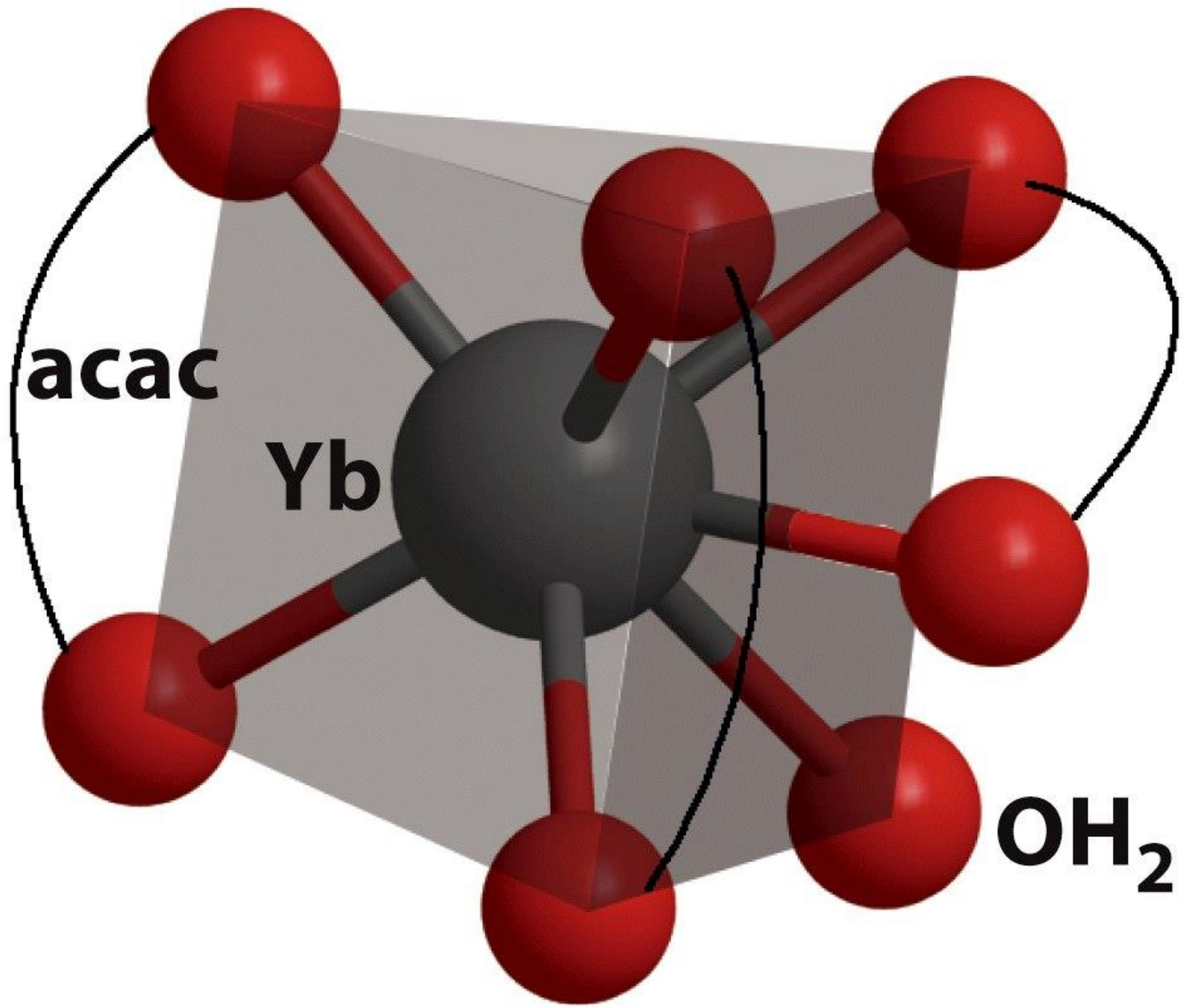


LaF$_3$, c.n. = 11, coordinazione irregolare



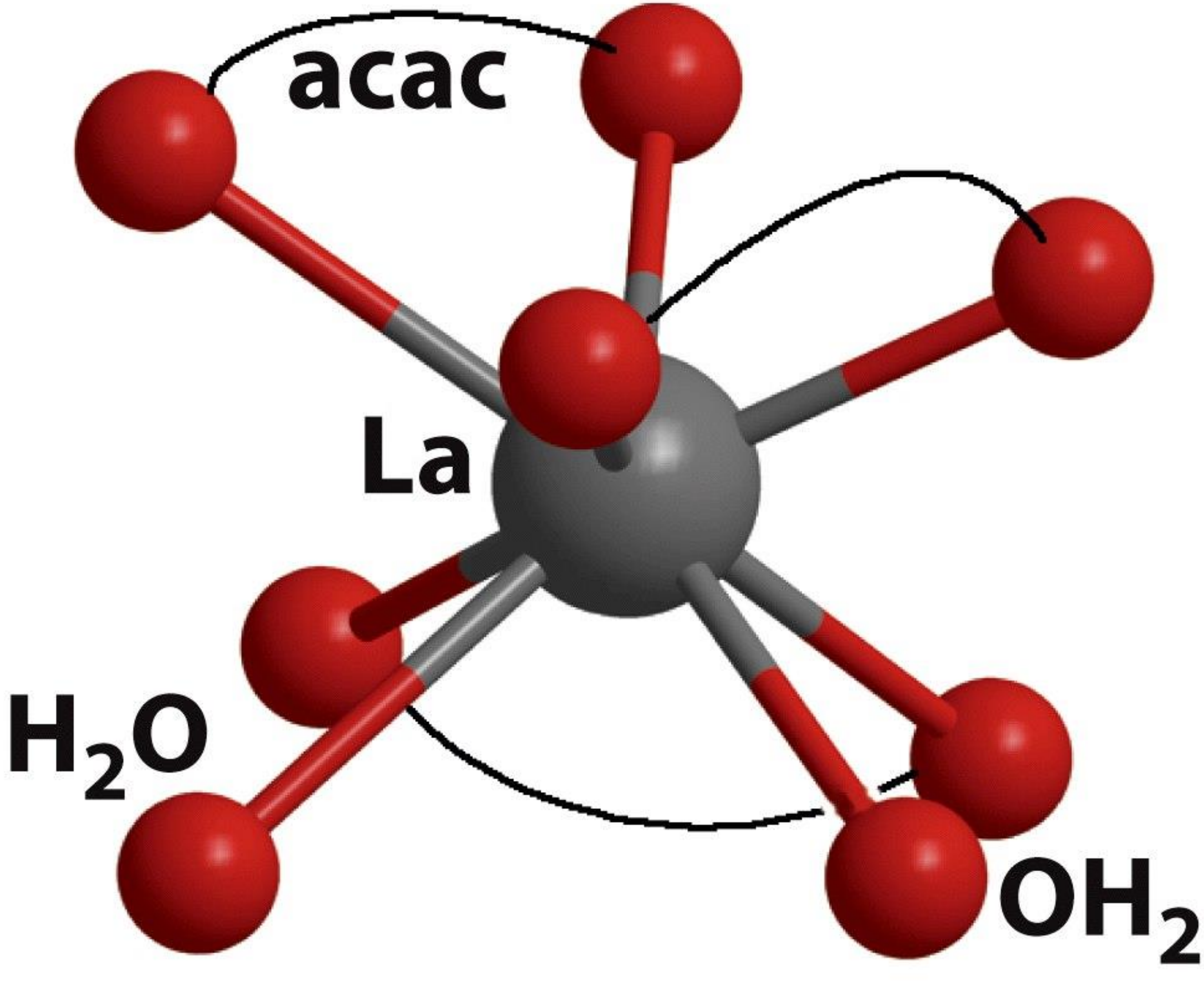
Temperatura di transizione fra isolante e conduttore (T_{IM}) in Perovskiti dei lantanidi $LnNiO_3$

	$PrNiO_3$	$NdNiO_3$	$EuNiO_3$
$r(Ln^{3+})$/pm	113	111	107
T_{IM}/K	135	200	480



[Yb(acac)$_3$(OH$_2$)]

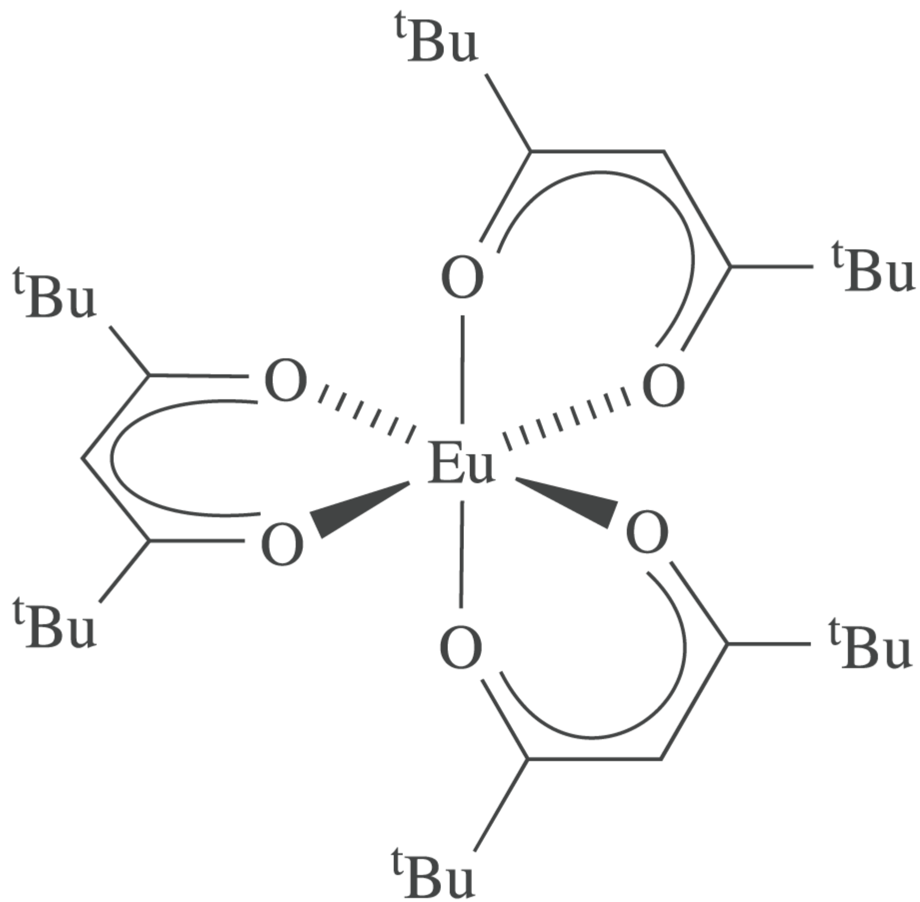
Prisma trigonale cappato



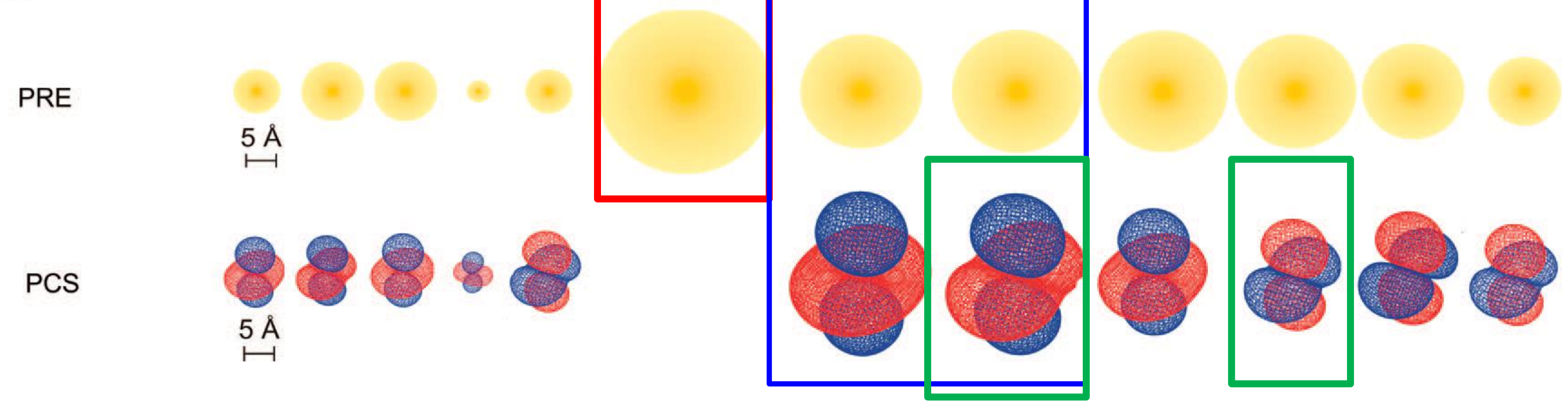
$[La(acac)_3(OH_2)_2]$

Antiprisma quadrato

NMR *shift reagents*

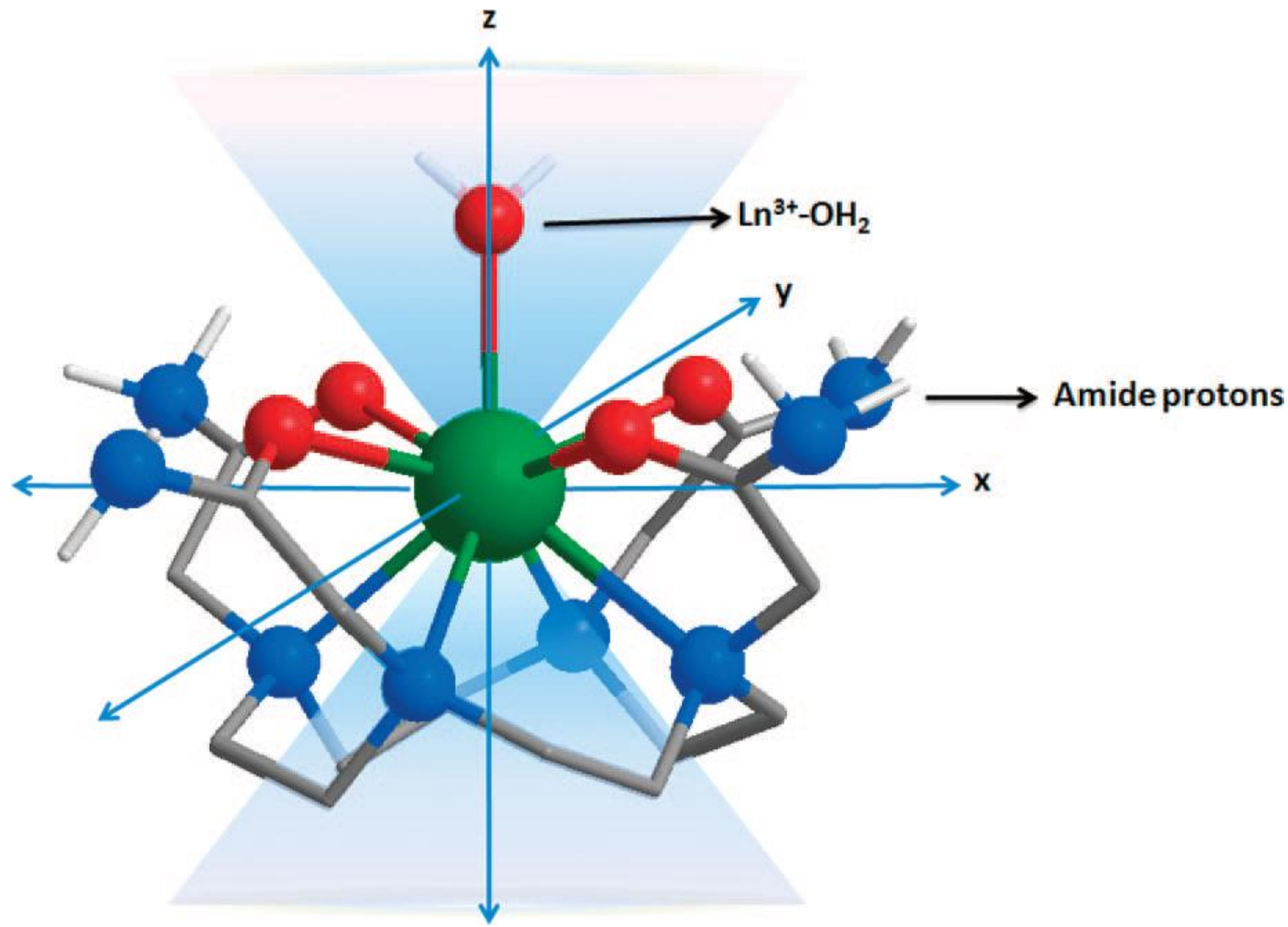


Ln	La^{3+}	Ce^{3+}	Pr^{3+}	Nd^{3+}	Sm^{3+}	Eu^{3+}	Gd^{3+}	Tb^{3+}	Dy^{3+}	Ho^{3+}	Er^{3+}	Tm^{3+}	Yb^{3+}	Lu^{3+}
$\mu_{eff}/\mu B$ cald.	0.00	2.54	3.58	3.68	0.85	0.00	7.94	9.72	10.63	10.60	9.59	7.57	4.53	0.00
$\chi/10^{-32}m^3$	0.0	5.6	11.2	11.4	0.6	6.0	55.1	82.7	99.2	98.5	80.3	50.0	18.0	0
$\Delta\chi_{ax}/10^{-32}m^3$	0	2.1	3.4	1.7	0.2	-2.3	0	42.1	34.7	18.5	-11.6	-21.9	-8.3	0
$\Delta\chi_{rh}/10^{-32}m^3$	0	0.7	2.1	0.4	-0.1	-1.6	0	11.2	20.3	5.8	-8.6	-20.1	-5.8	0

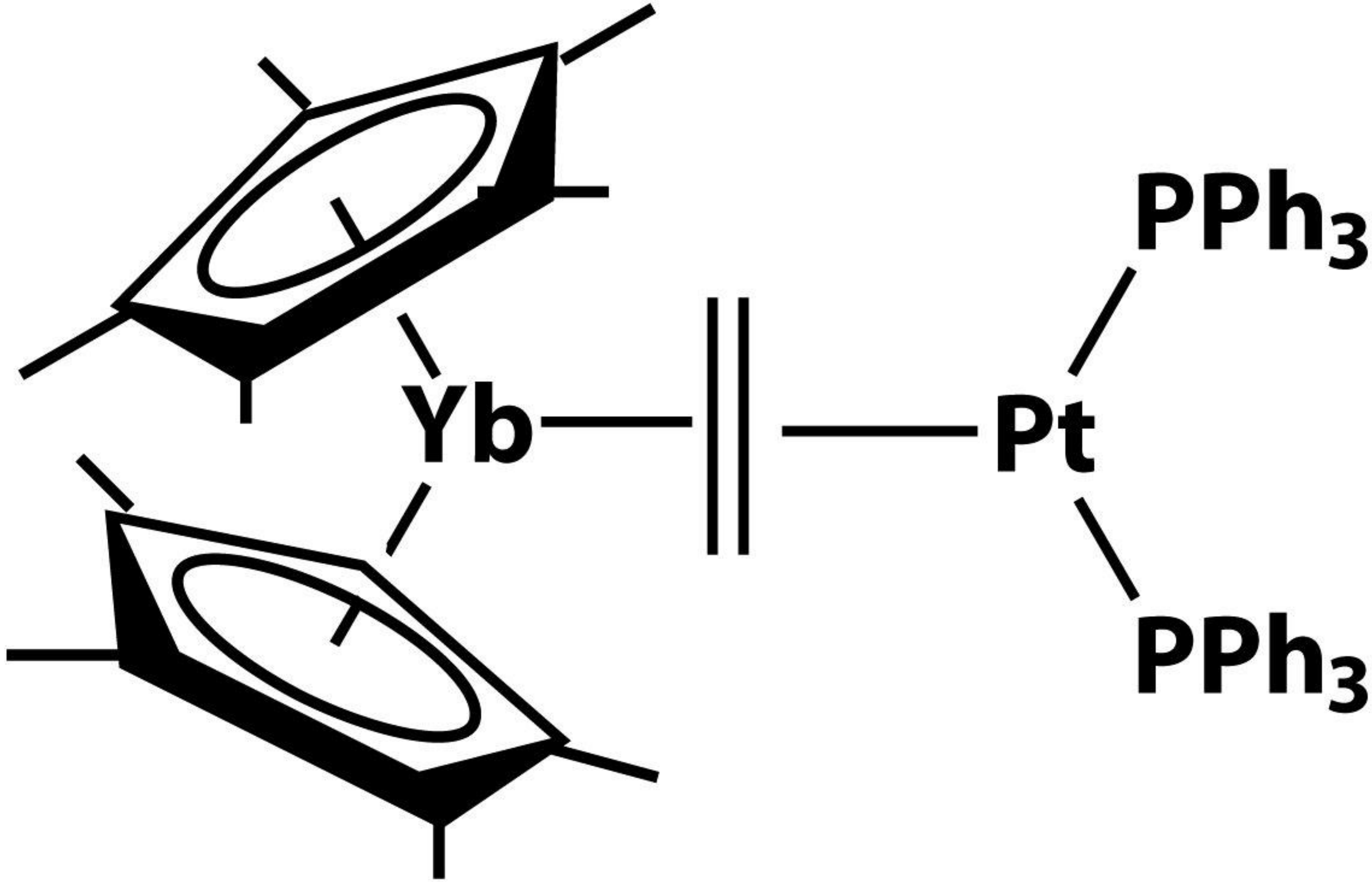


PRE = *Paramagnetic Relaxation Enhancement*

PCS = *Pseudo-Contact Shift*

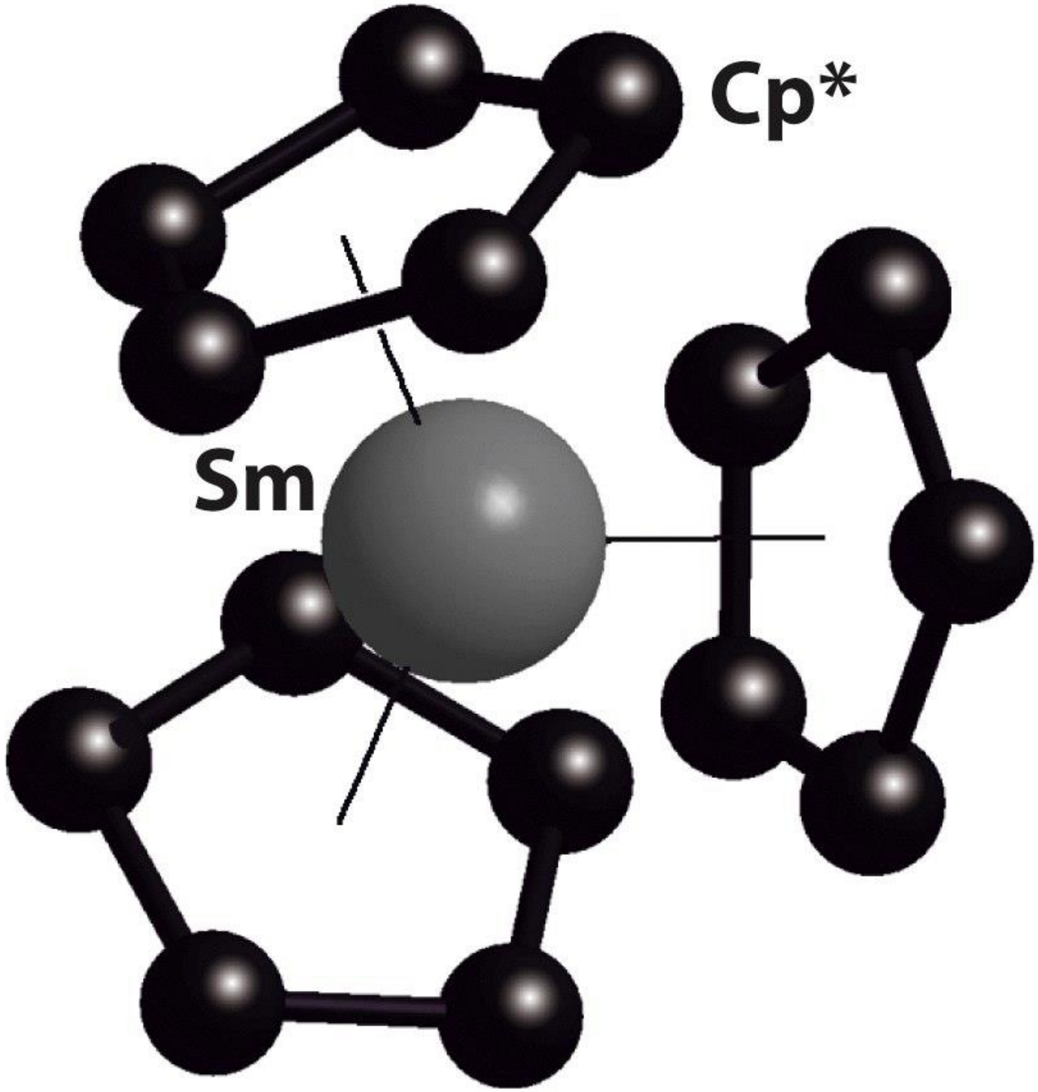


z
Ln^{3+}-OH_2
y
Amide protons
x

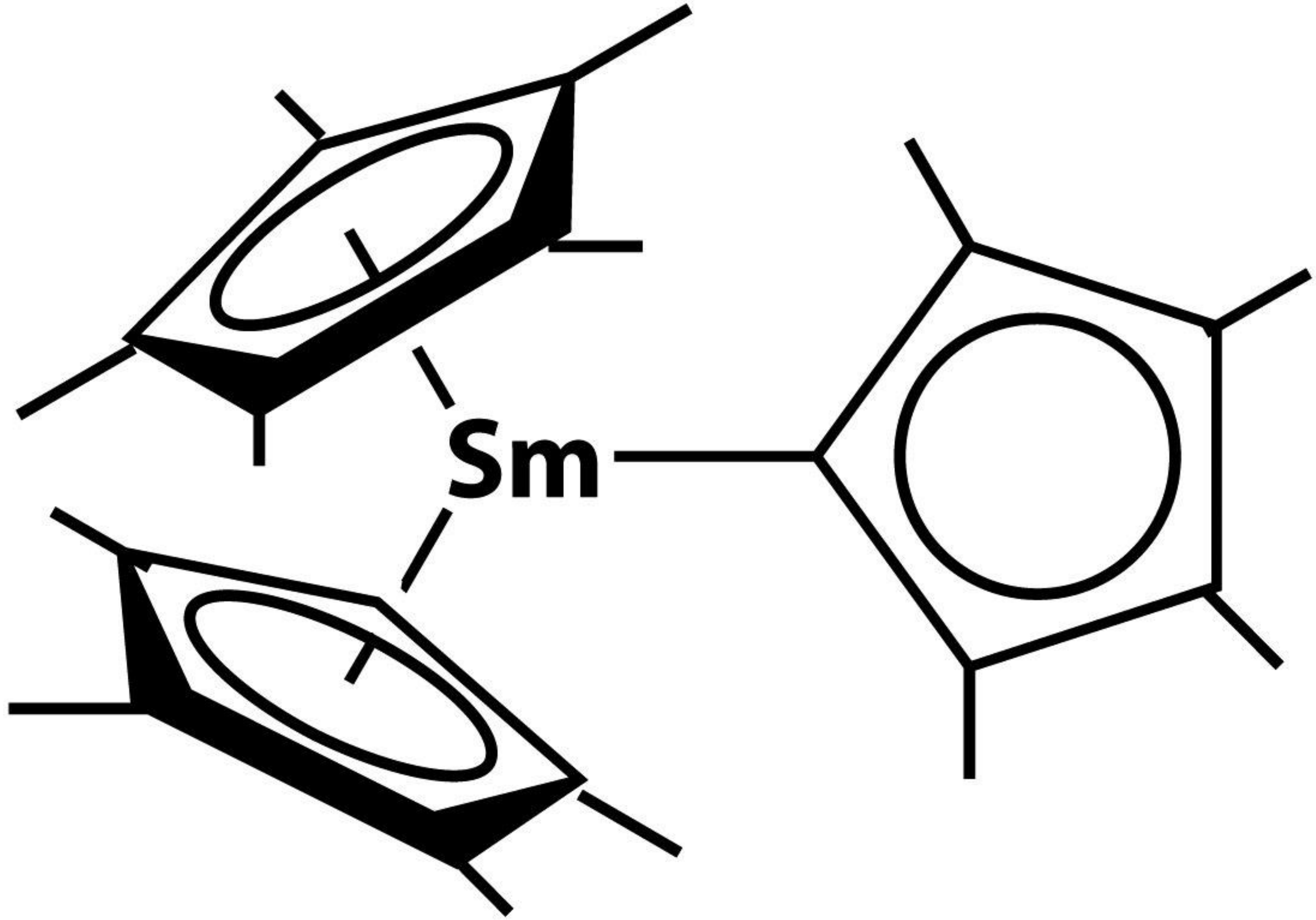


$[(Cp^{*})_2Yb(C_2H_4)Pt(PPh_3)_2]$

1987, primo complesso η^2-alchene di un lantanide



$Sm(\eta^5\text{-}Cp^*)_3$



$Sm(\eta^1\text{-}Cp^*)(\eta^5\text{-}Cp^*)_2$

$$Sm(\eta^5\text{-}Cp^*)_3 \rightleftharpoons Sm(\eta^1\text{-}Cp^*)(\eta^5\text{-}Cp^*)_2$$

Metatesi di legame σ