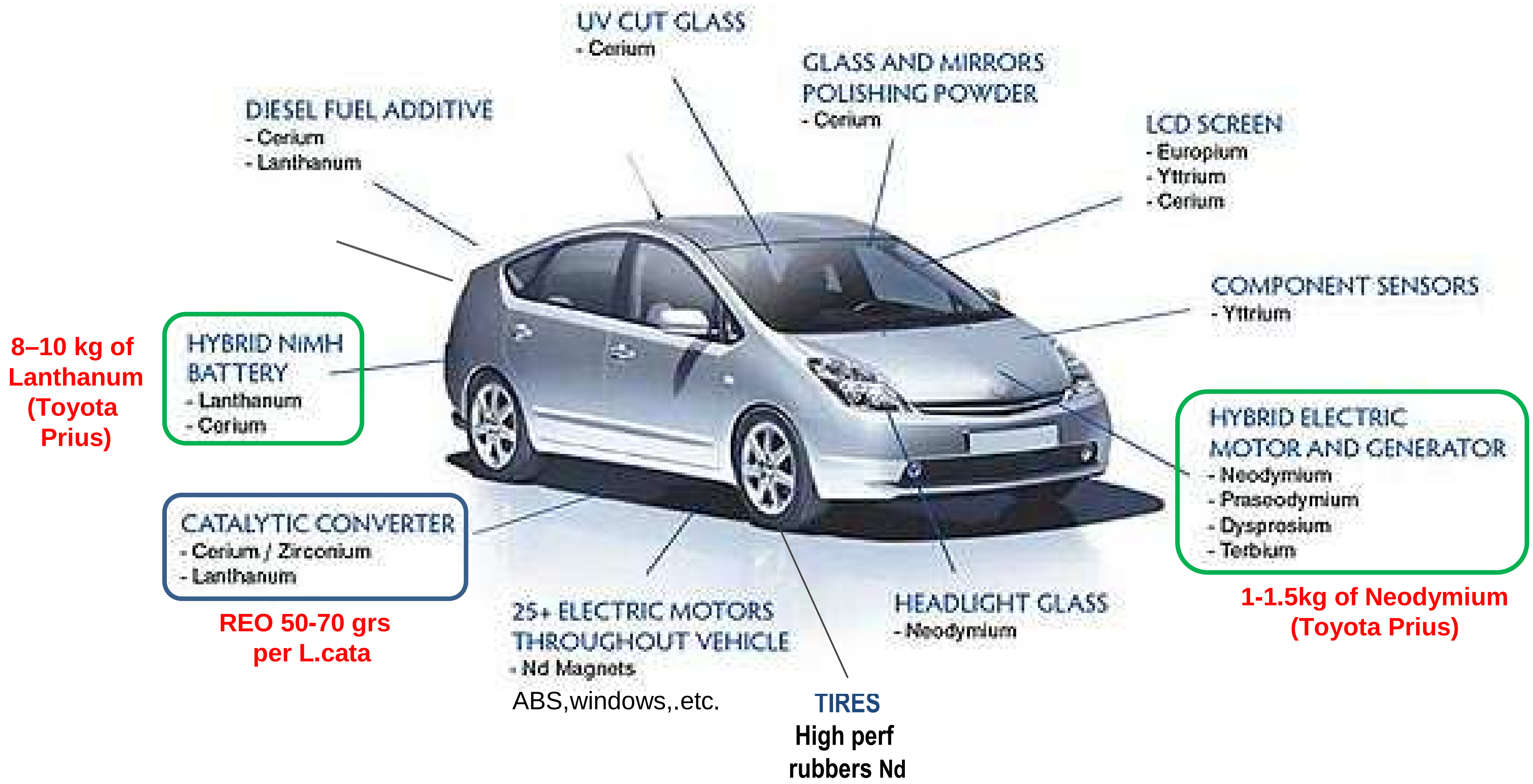
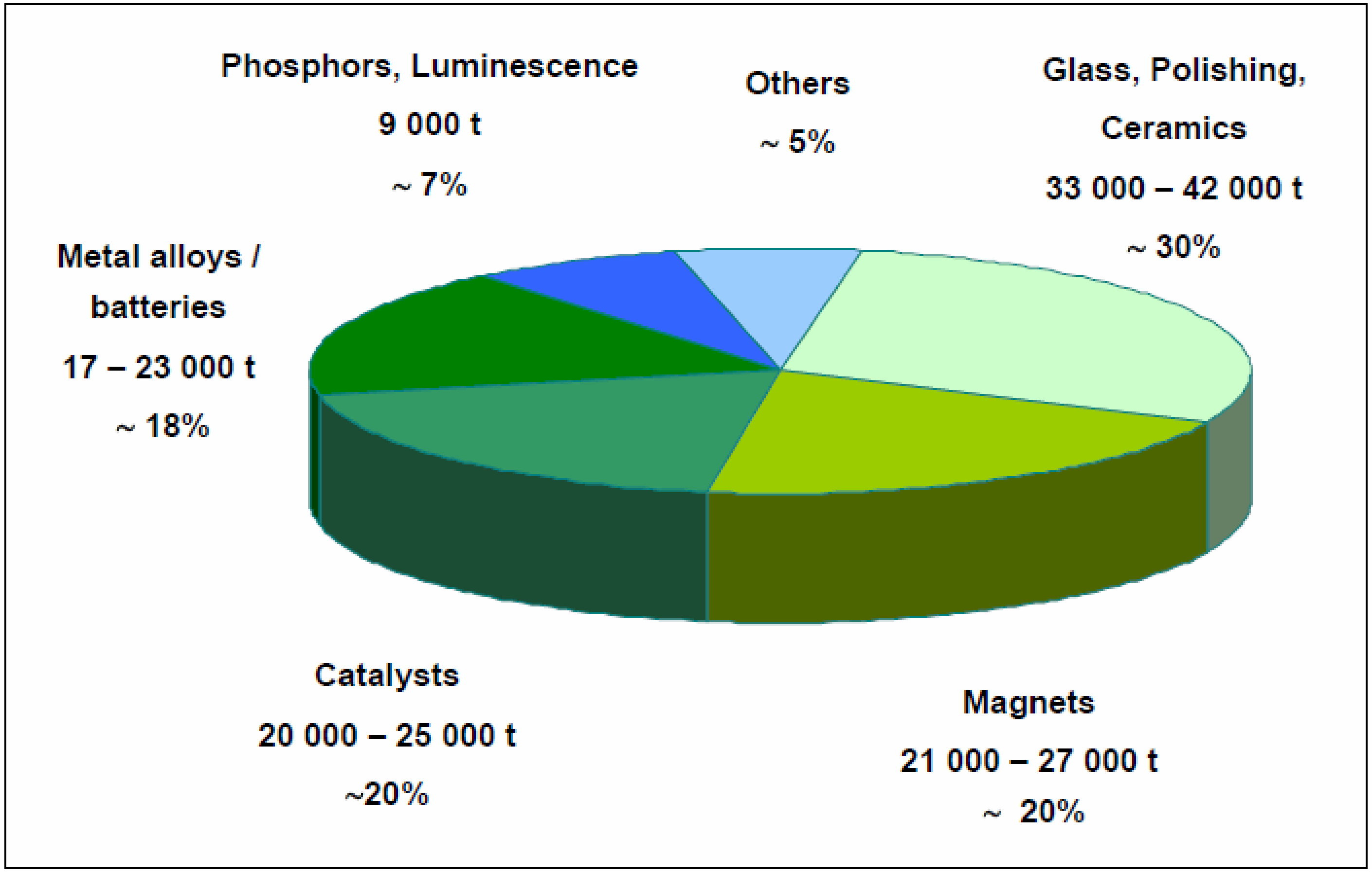
Rare Earths are everywhe

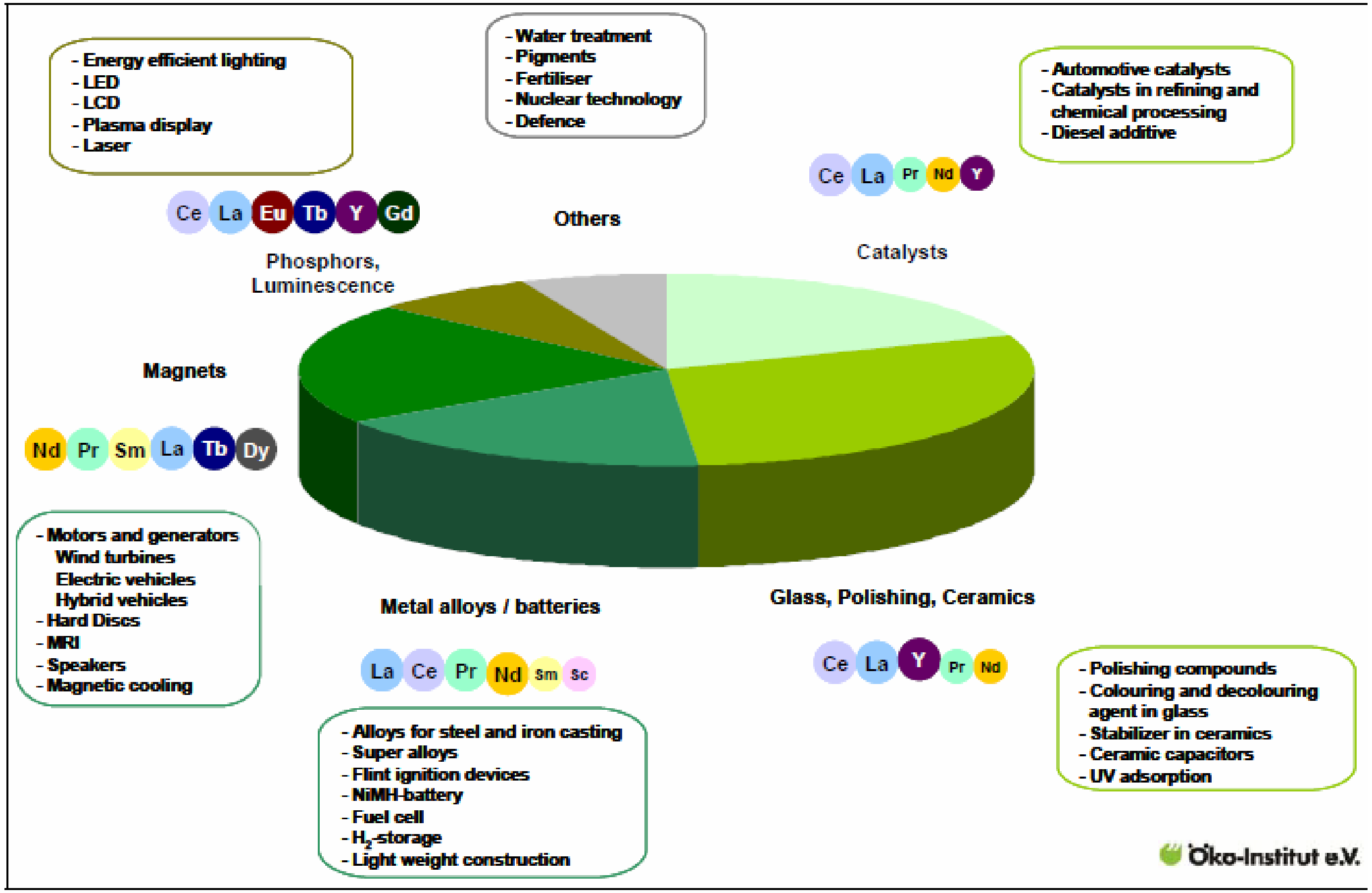
Cars industry



The Rare Earths demand



The Rare Earths demand



The Rare Earths demand

Strategic elements in several key technologies

1) Powerful permanent magnets for windmills, traction engines, holders…

2) Luminescent materials for lightning such as energy saving lamps and displays TV, LCD, laser

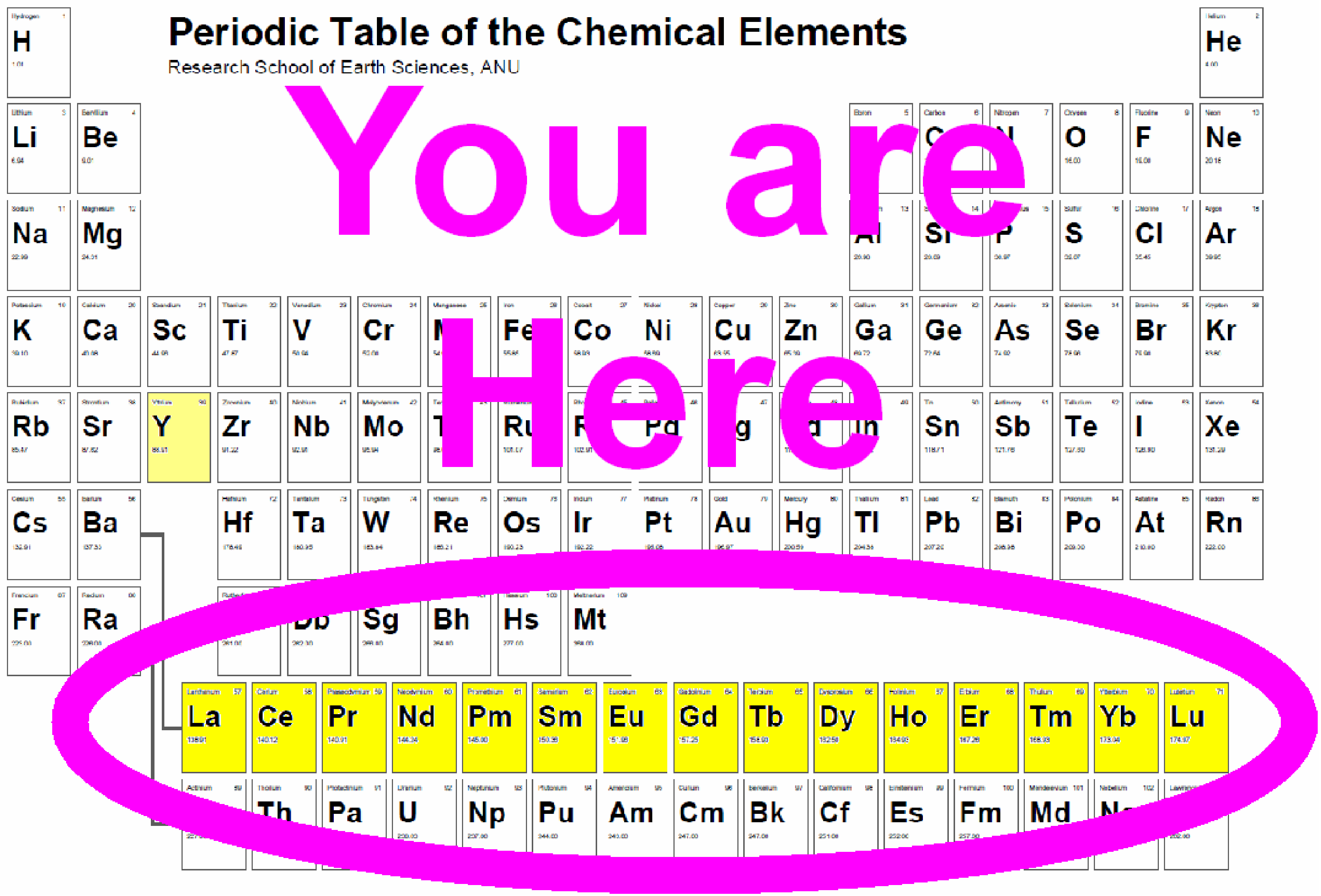
3) Catalytic converters for cars and trucks to decrease CO ,CHx and NOx in exhaust gases.

4) Rechargeable batteries for hybrid cars using RE metal hydrides for H storage

5) Polishing compounds forglasses and silicon substrates for optical glasses, glass disks, flat TV

RARE EARTHS ELEMENTS

- Not so rare but having an heterogeneous repartition on the planet
- A group of 14 elements strongly united , more than 15% of the periodic chart at the disposal of the chemist and physicist
- Form a block chemically very homogeneous
- but abundance by element varies.
- Physics change totally from one element to another

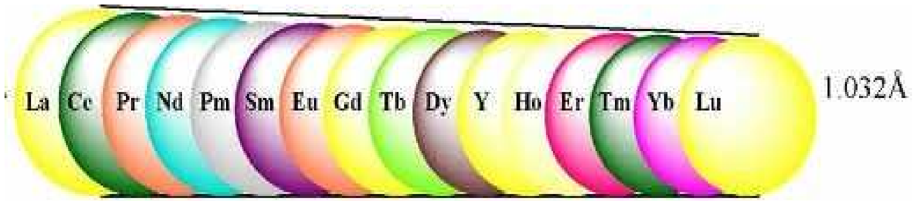

Periodic Table of the Chemical Elements
Research School of Earth Sciences, ANU
You are
Here
H He
Li Be O F Ne
Na Mg S Cl Ar
K Ca Sc Ti V Cr Fe Co Ni Cu Zn Ga Ge As Se Br Kr
Rb Sr Y Zr Nb Mo Sn Sb Te I Xe
Cs Ba Hf Ta W Re Os Ir Pt Au Hg Tl Pb Bi Po At Rn
Fr Ra Sg Bh Hs Mt
La Ce Pr Nd Pm Sm Eu Gd Tb Dy Ho Er Tm Yb Lu
Pa U Np Pu Am Cm Bk Cf Es Fm Md

- Peut être rappeler que Un atome est constitué d'un noyau concentrant plus de 99,9 % de sa masse, autour duquel se distribuent des électrons pour former un nuage 100 000 fois plus étendu que le noyau lui-même.
- Les électrons occupent des orbitales atomiques en interaction avec le noyau
- Le nuage électronique est stratifié en niveaux d'énergie quantifiés autour du noyau définissant des couches et des sous-couches électroniques
- Montrer un petit dessin pour illustrer ces couches autour du noyau

Atomic structure of the Rare Earths

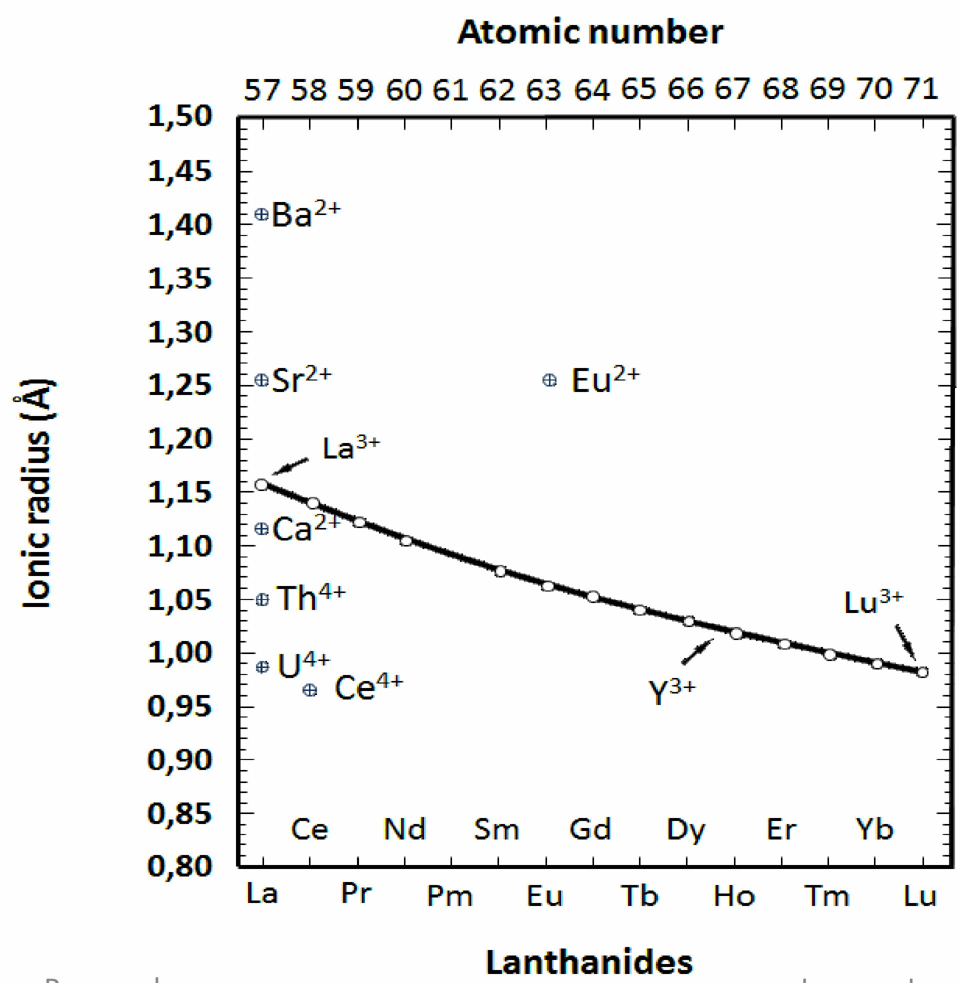
- Structure **4fn 5d1 6s2**

  Outer electrons on 3 kinds of orbital
- 3 external electrons on the 5d1 et 6s2 escape easily from the atom et are responsible of a monotone chemistry
- RE $\longrightarrow$ RE^{3+} +3 e-
- The only variable parameter is the size which varies from La^{3+} the largest one, ionic radius closed to 1.2 A to $Lu^{3+}$the smallest, ionic radius close to 0.7 A.
- Two exceptions; **Cerium** with **Ce^{3+}** but also **Ce^{4+}** and **Europium** with **Eu^{3+}** but also **Eu^{2+}**



Atomic radius

Monotonic variation from La (1.6 A) to Lu (1.03)



Ionic radius

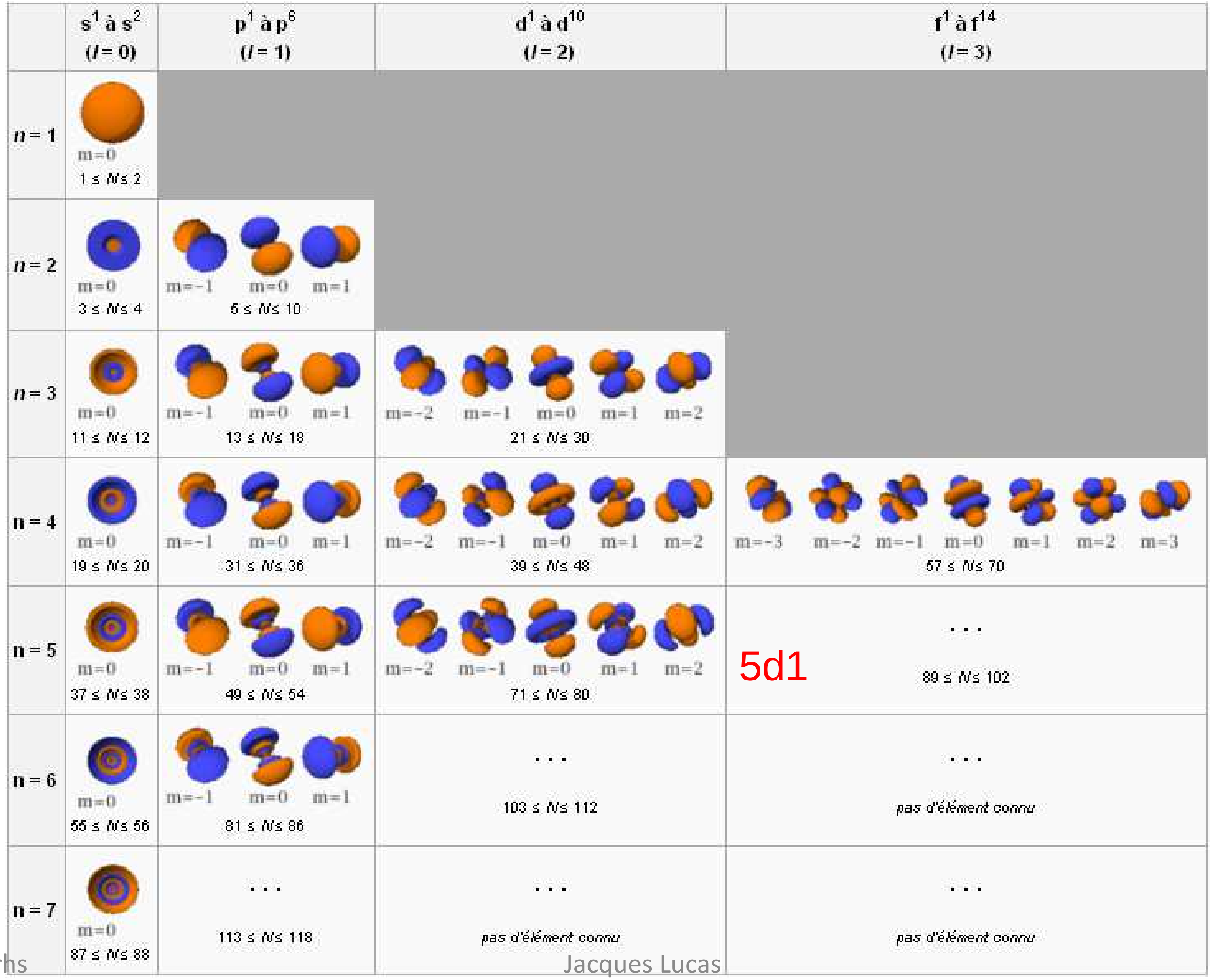
Monotonic evolution from La^{3+} to Lu^{3+}
Exception for Ce^{4+} and Eu^{2+}

Proximity with alkaline earths and uranides

The regular variation of Ln^{3+} ionic radii allows their separation by selective complexation:
rLa3+ = 1.2Ǻ → rLu3+ = 0.7Ǻ

Electric field around Lu3+ stronger than around La3+

The interesting specific electrons of the RE are on the 7 internal 4f orbital which can contains each of them 2 electrons : 14 possibilities→ 14 Rare Earth. Example: Gd^{3+}, 4f7, 7 unpaired electrons

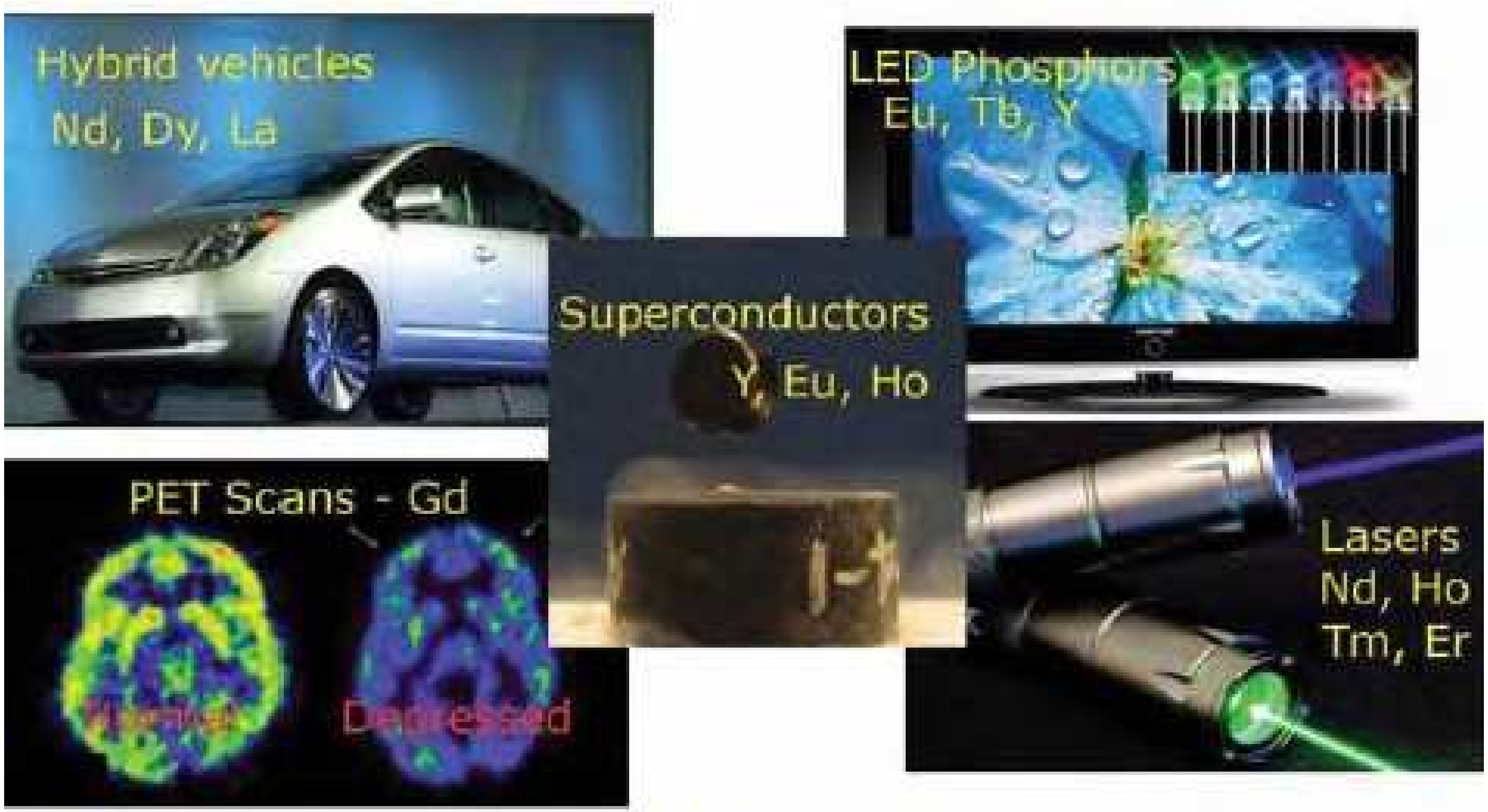


	s^1 à s^2 (l = 0)	p^1 à p^6 (l = 1)	d^1 à d^{10} (l = 2)	f^1 à f^{14} (l = 3)
n = 1	m=0 1 ≤ N ≤ 2			
n = 2	m=0 3 ≤ N ≤ 4	m=-1 m=0 m=1 5 ≤ N ≤ 10		
n = 3	m=0 11 ≤ N ≤ 12	m=-1 m=0 m=1 13 ≤ N ≤ 18	m=-2 m=-1 m=0 m=1 m=2 21 ≤ N ≤ 30	
n = 4	m=0 19 ≤ N ≤ 20	m=-1 m=0 m=1 31 ≤ N ≤ 36	m=-2 m=-1 m=0 m=1 m=2 39 ≤ N ≤ 48	m=-3 m=-2 m=-1 m=0 m=1 m=2 m=3 57 ≤ N ≤ 70
n = 5	m=0 37 ≤ N ≤ 38	m=-1 m=0 m=1 49 ≤ N ≤ 54	m=-2 m=-1 m=0 m=1 m=2 71 ≤ N ≤ 80	. . . 89 ≤ N ≤ 102
n = 6	m=0 55 ≤ N ≤ 56	m=-1 m=0 m=1 81 ≤ N ≤ 86	. . . 103 ≤ N ≤ 112	. . . *pas d'élément connu*
n = 7	m=0 87 ≤ N ≤ 88	. . . 113 ≤ N ≤ 118	. . . *pas d'élément connu*	. . . *pas d'élément connu*

Physics of the Rare Earths

- In the atomic structure of the RE : 4fn 5d16s2, the electrons of the internal electronic shell 4fn with n going from 1 to 14 decides on the physics and on the personality of each RE.
- The seven 4f internal orbital can contains 2 electrons each leading to 14 electronic structure possibilities
- From La^{3+} *structure 4f0* to Lu^{3+} *structure 4f14*
- In the middle for example Gadolinium Gd^{3+} *structure 4f7 contains 7 unpaired electrons*
- Each RE has its own physics in contrary to its chemistry.
- Consequently 14 elements very different by their physical properties

RARE EARTHS are everywhere



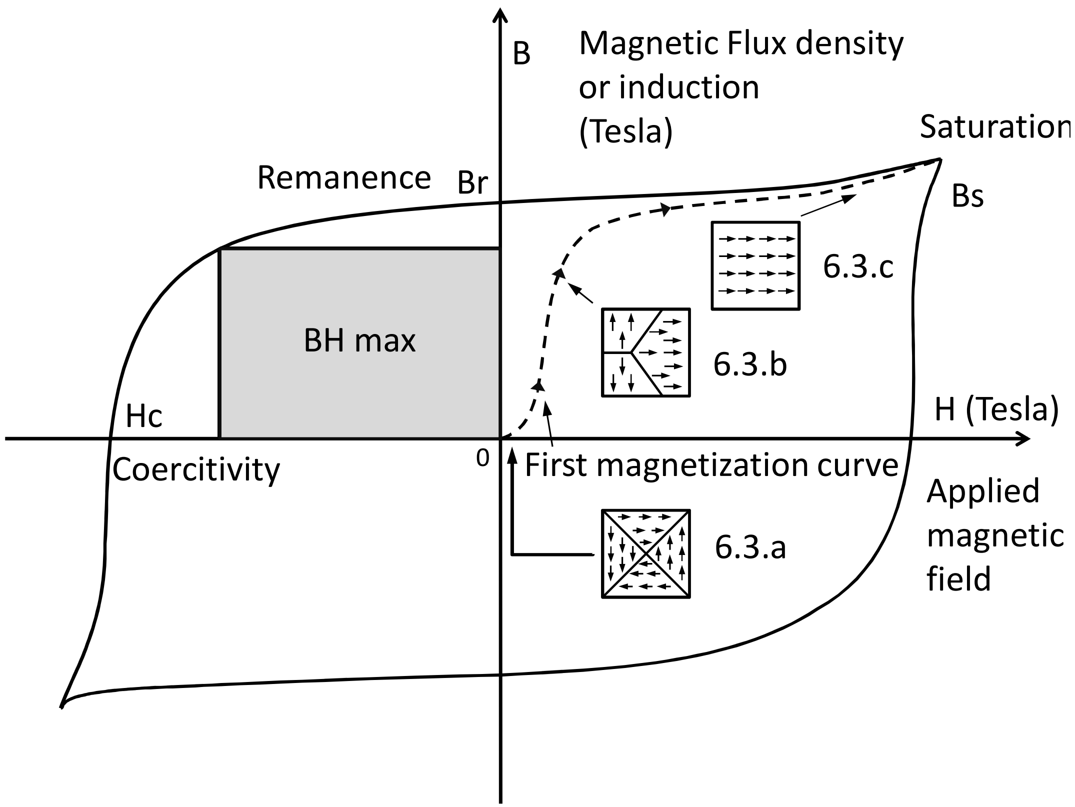
Vith the range of places that rare earth elements can be found, they seem anything by rare.

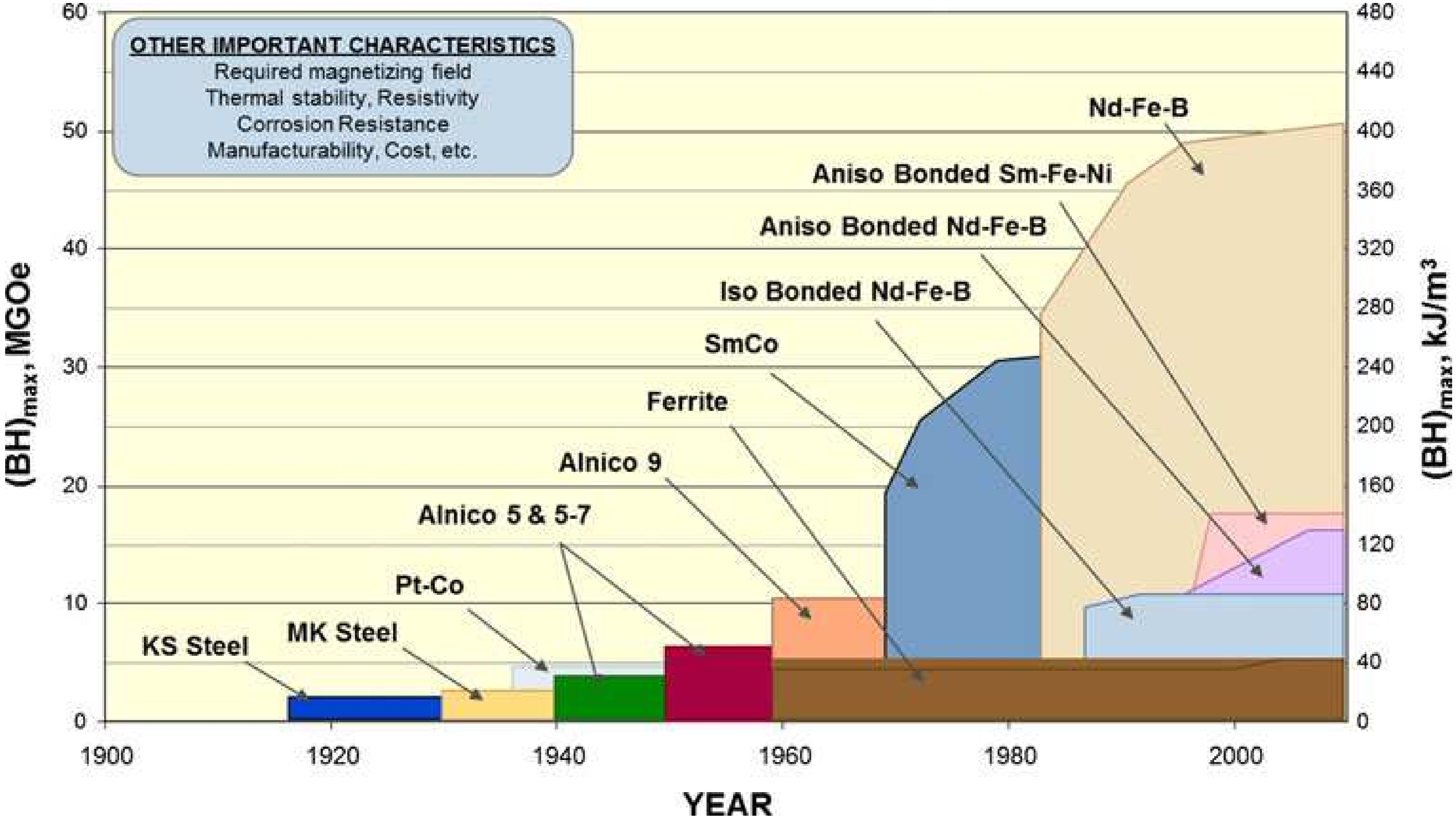
Rare Earth magnets

- Rare Earth are used to fabricate very stable and powerfull magnets.
- The **Samarium/Cobalt magnets**
- $SmCo_5$ et Sm_2Co_{17} ferromagnetic to Tc=700°C, 60% fabricated inChina
- The **Neodyme/Fer/Bore magnets** : $Nd_2Fe_{14}B$ less expensive also more powerfull but Tc= 310°C
- From 1 to 2Kg into a car
- 155Kg of **Nd** et 27 Kg de **Pr** in off-shore wind-mill per MW electricity production.

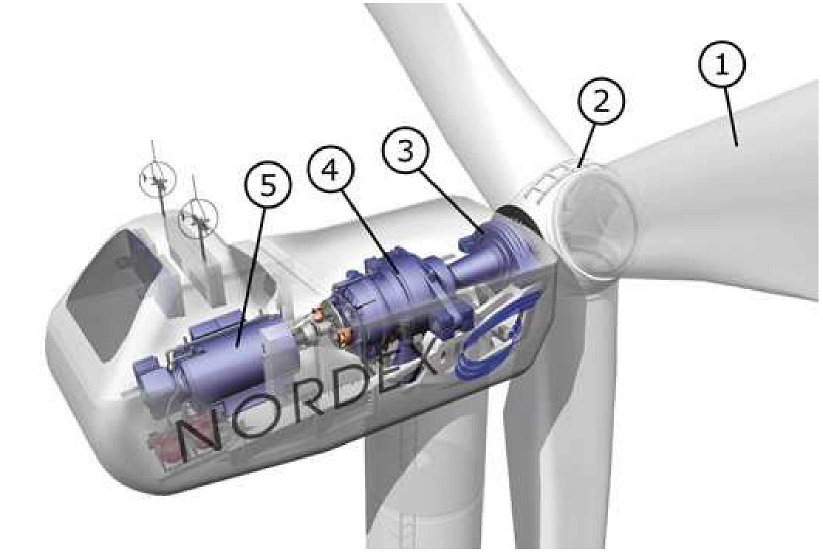
The key figures for a RE magnet illustrated in hysteresis loop

- Power →high Remanence Br
- Permanence→ high Coercitivity Hc
- Figure of merit→ BHmax energy product
- Resistant to temperature critical for electrical car engines and windmills: Curie Temperature Tc as high as possible

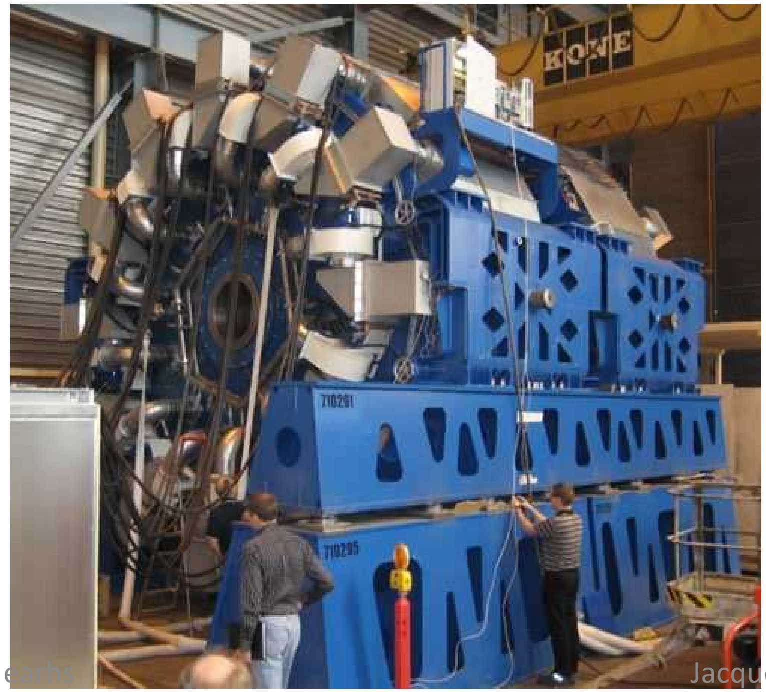




OTHER IMPORTANT CHARACTERISTICS
Required magnetizing field
Thermal stability, Resistivity
Corrosion Resistance
Manufacturability, Cost, etc.
Nd-Fe-B
Aniso Bonded Sm-Fe-Ni
Aniso Bonded Nd-Fe-B
Iso Bonded Nd-Fe-B
SmCo
Ferrite
Alnico 9
Alnico 5 & 5-7
Pt-Co
MK Steel
KS Steel
(BH)max, MGOe
(BH)max, kJ/m3
YEAR
0
10
20
30
40
50
60
0
40
80
120
160
200
240
280
320
360
400
440
480
1900
1920
1940
1960
1980
2000

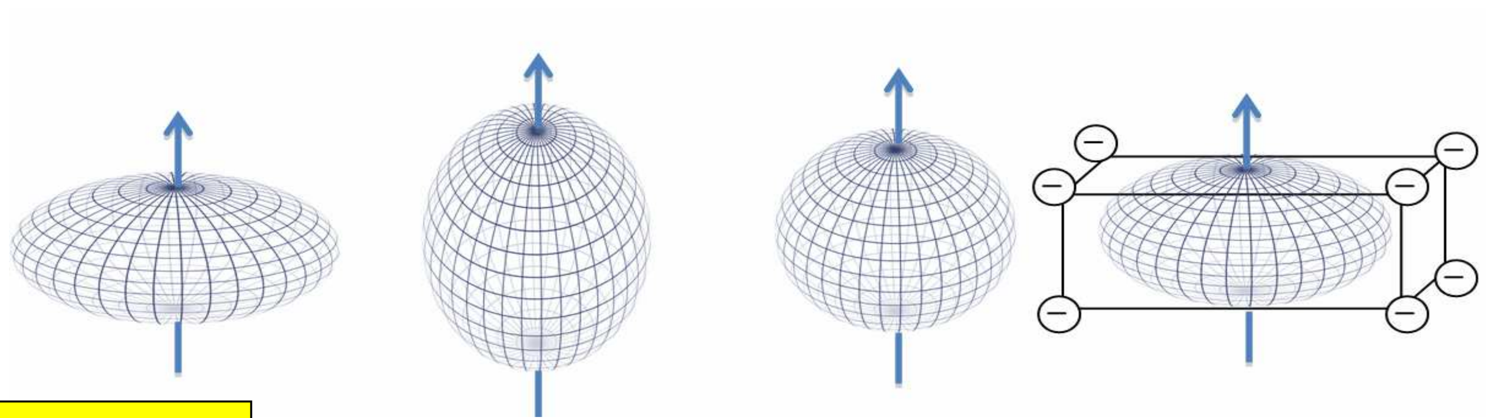


1 blades
2 hub
3 rotor bearing
4 gear box
5 generator



Two tons of NdFeB magnets are used in this wind mill Permanent Magnet Generator PMG. This turbine can produce several megawatt of electricity. Thanks to NdFe magnets gearbox is not necessary. This decrease vibration stress and improve reliability with the benefit of lower maintenance.

Magnetic anisotropy the key factor for permanent magnets with high coercitivity. Hc. Some RE bring the anisotropy facilitating magnetic dipoles alignments
Asymmetric filling of 4f orbitals required
The 4f electrons cloud must be non spherical



Ce^{3+} f1, Pr^{3+} f2
Nd^{3+} f3,

Tb^{3+}f8, Dy^{3+} f9
Yb^{3+}f13
Squeezed electrons cloud

Sm^{3+}f5, Er^{3+}f11
Tm^{3+}f12, Yb^{3+}f13
Elongated electrons cloud

Gd^{3+}f7
Spherical electrons cloud

Nd^{3+} in the Tetragonal site of $Nd_2Fe_{14}B$ magnet structure
Fe bring the magnetization
Nd bring the anisotropy

Rare-earth Photonic Materials for Green Technology

Optical Fiber Communication

Solid-state Lighting

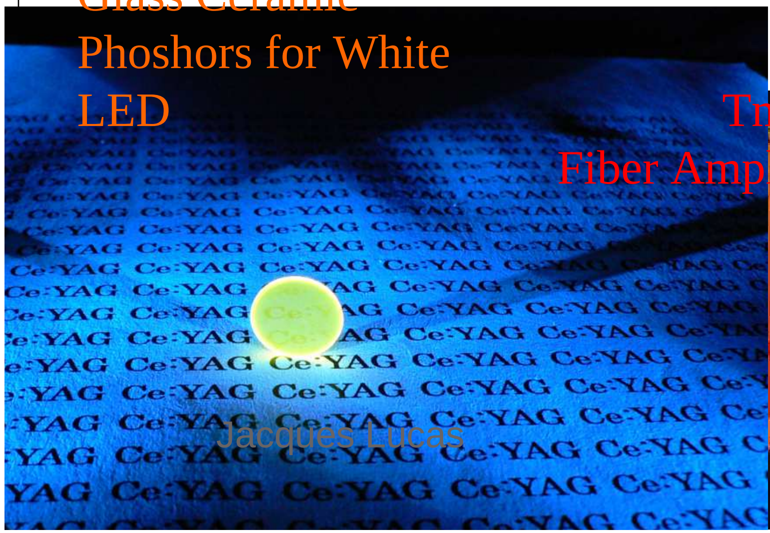
Photovoltaic Generation

LCD-backlight

Er-Doped Fiber Amplifier

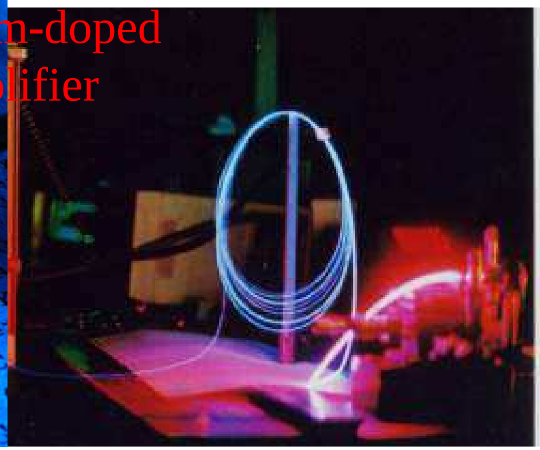
QC Phosphors for PV

Glass Ceramic Phoshors for White LED



Jacques Lucas

Tm-doped Fiber Amplifier



Rare earhs

Application domains

Cathodoluminescence: TV or plasma screens

Red color due to Eu^{3+} excitation
Blue color due to Eu^{2+} excitation
Green color due to Tb^{3+} excitation

Radioluminescence due to high energy radiation such as X rays

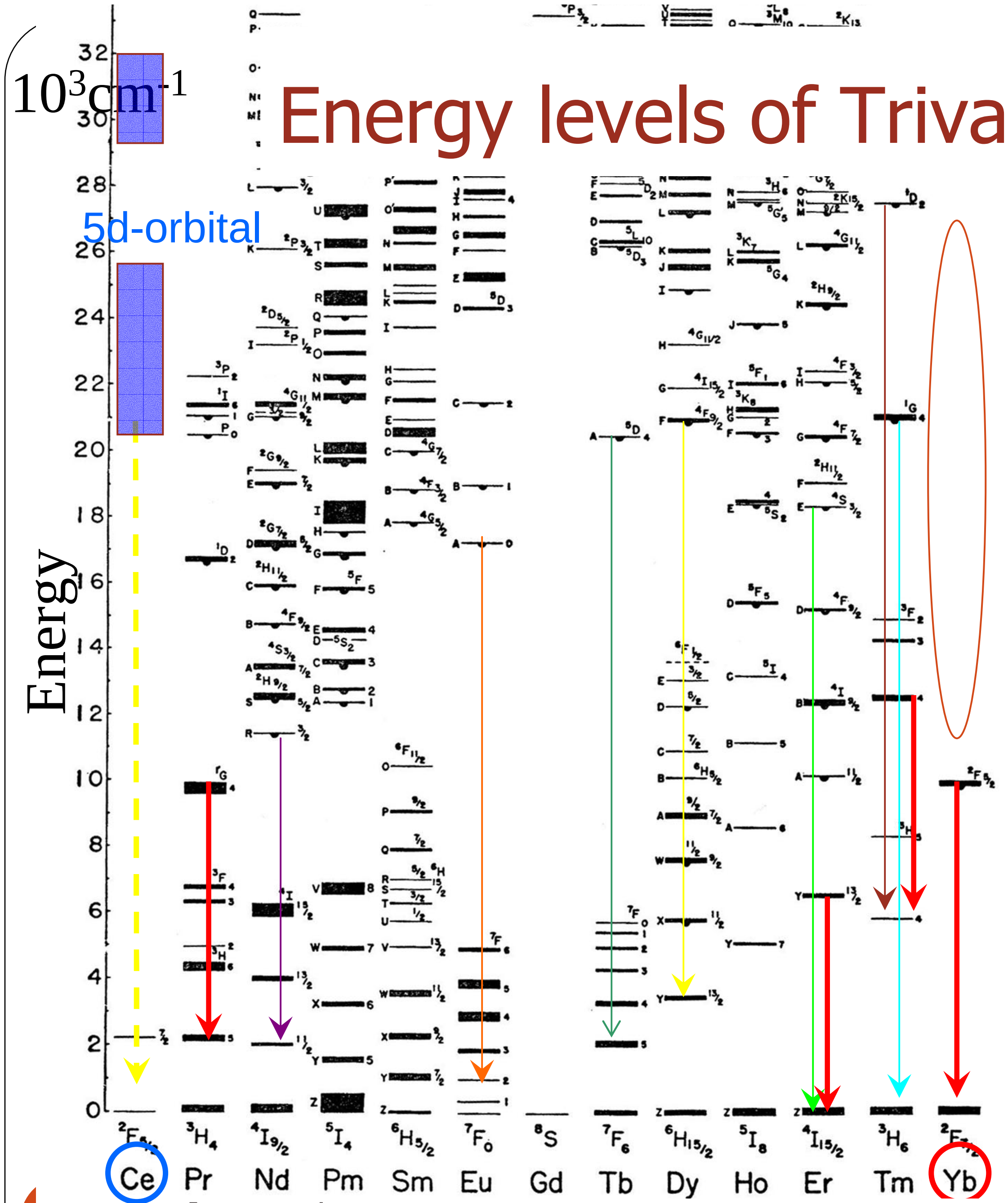
X,γ rays detection
Tb^{3+}, Tm^{3+} strong green emission under X rays (decrease XR examination time by factor of ten) An X-ray intensifying screen

Photo storage or retarded emission (afterglow)
Eu^{2+} in strontium aluminates emit green light, hours after UV exposition

Fluorescence : fluocompact discharge lamps (excited Hg vapor and glass bulb containing phosphors (substitute of incandescent filament).
Glass doped by Eu^{2+}(blue), Ce^{3+}/Tb^{3+} (yellow, green) Eu^{3+} (red) →**white light**

ED : new light source sine the invention of blue UV diodes

Energy levels of Trivalent Ln^{3+} ions



Visible transition

Key element for phosphors;

Tm^{3+}, Er^{3+}, Tb^{3+}, Eu^{3+}

Near-infrared:

Nd^{3+}:1.06μm for YAG laser

Telecom wavelengths

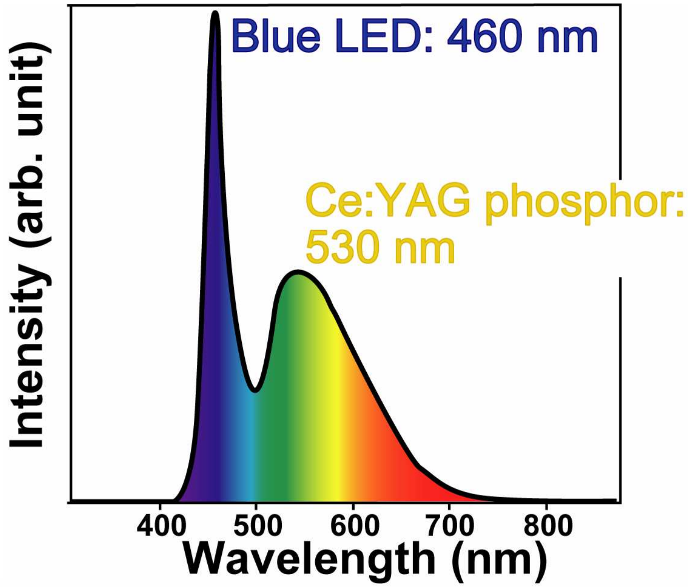
Pr^{3+}: 1.3μm

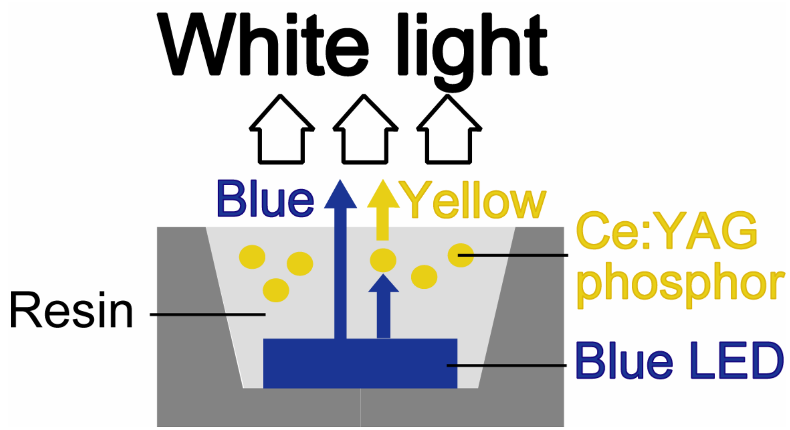
Tm^{3+}: 1.46μm

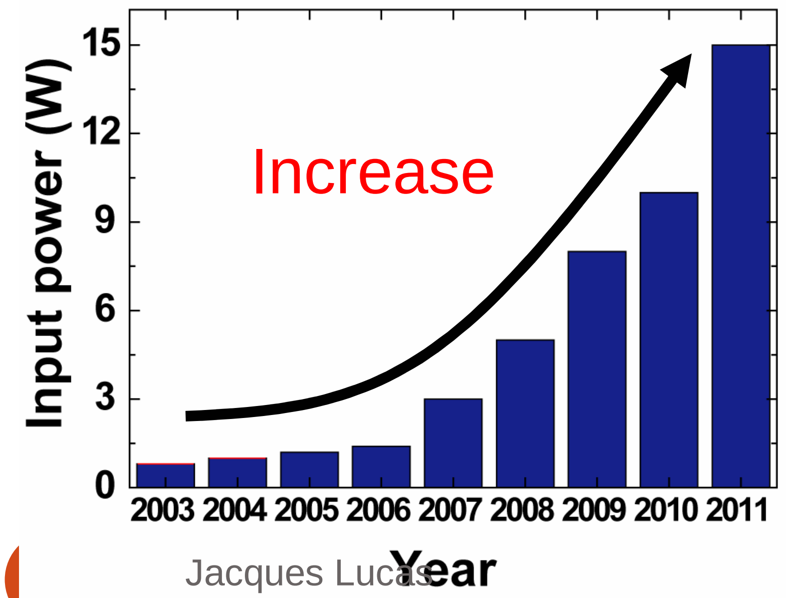
Er^{3+}: 1.55μm

$4f^1$ Number of Ce:4f electron Yb:4f-hole $4f^{13}$ Only two 4f-levels +5d-levels

Present status of wLED







Problem of organic resin

Heat generation of LED chip is becoming more and more serious.

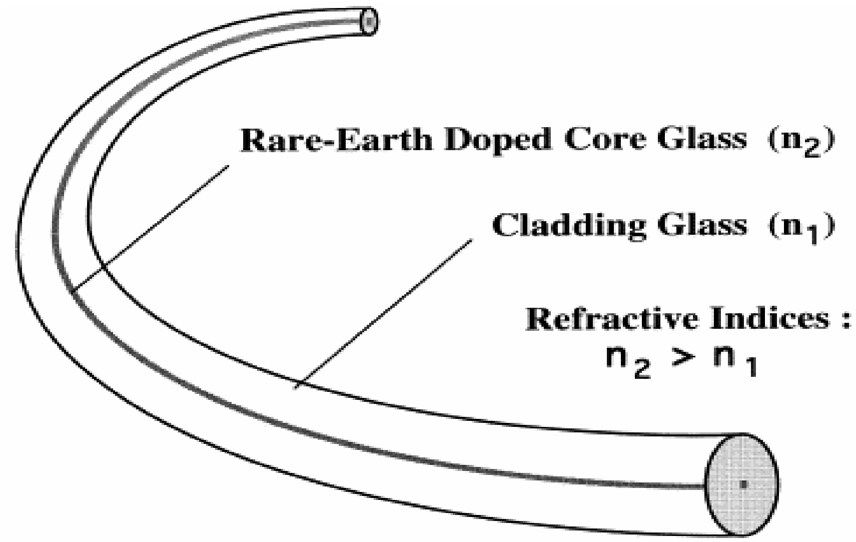
↓

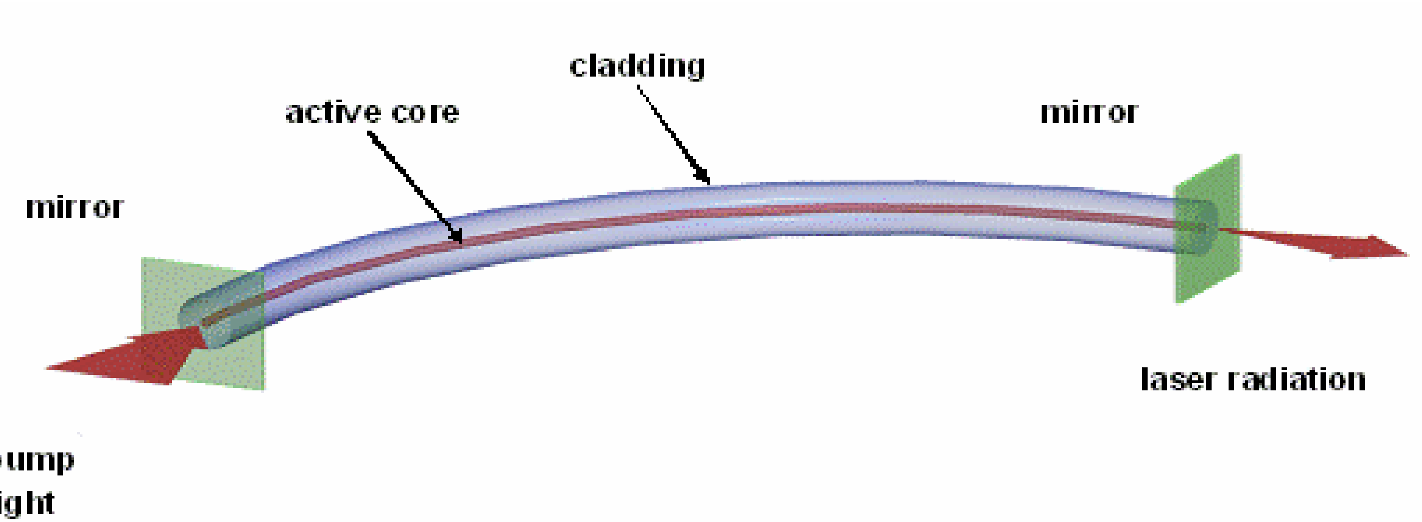
- Thermal degradation
- Degradation of luminous intensity

Optical amplifier
or
Fiber laser
RE core doped
optical fiber

Erbium doped optical fiber used for telecom signal regeneration

Ytterbium doped fiber laser
emits kW output power used for cutting, welding holes drilling





Rare Earth in automobile catalysis using Ce oxyde

Catalytic exhaust pipes

The key reaction $Ce_2O_3 + ½ O_2 \leftrightarrow CeO_2$

Ce oxide is either oxygen donor or acceptor; regulate O_2%

Challenge: exhaust pipe with Zero emission of CO, black C particles and unburned fuel.

Catalytic substrates in Alumina doped with 20% Ce oxide impregnated by 100 à 3000 ppm Pd, Pt, Rh

The catalytic operation insured at 90% the conversion of

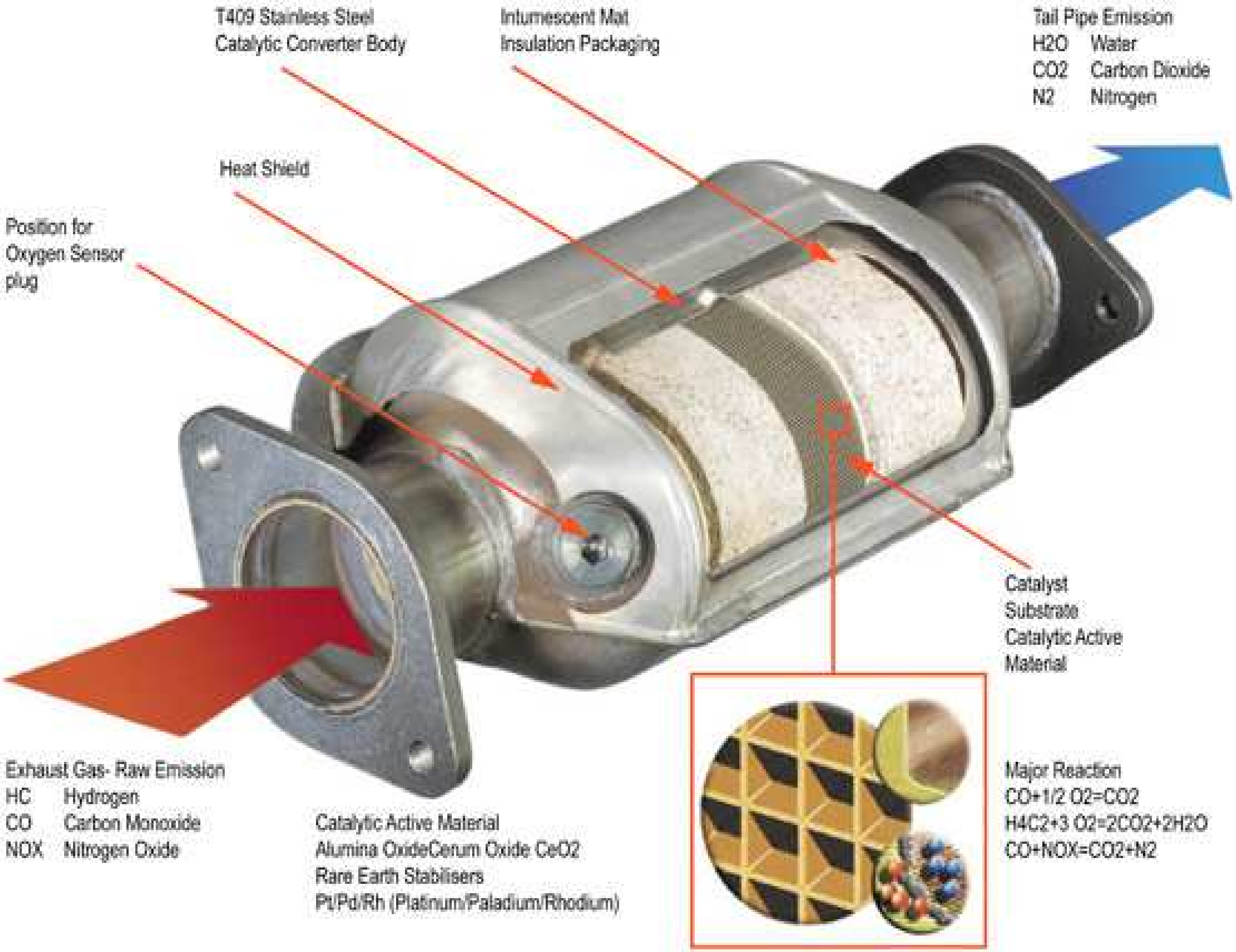
$CO \rightarrow CO_2$ et non-burned CxHy into CO_2 et H_2O

Additive to diesel fuel

Cerium under the form of organo-metallic solution improves combustion (suppressed black smokes). Ce addition lower from 600°to 200°C the combustion T on the catalysis

Also catalyze the transformation of NOx , nitrogen oxides

$NOx \rightarrow N_2 + O_2$


T409 Stainless Steel
Catalytic Converter Body
Intumescent Mat
Insulation Packaging
Tail Pipe Emission
H2O Water
CO2 Carbon Dioxide
N2 Nitrogen
Heat Shield
Position for
Oxygen Sensor
plug
Catalyst
Substrate
Catalytic Active
Material
Exhaust Gas- Raw Emission
HC Hydrogen
CO Carbon Monoxide
NOX Nitrogen Oxide
Catalytic Active Material
Alumina OxideCerum Oxide CeO2
Rare Earth Stabilisers
Pt/Pd/Rh (Platinum/Paladium/Rhodium)
Major Reaction
CO+1/2 O2=CO2
H4C2+3 O2=2CO2+2H2O
CO+NOX=CO2+N2

RE and metal/hydrides batteries for rechargeable hybrid cars such as Toyota Prius

Negative electrode MH → capacity of the alloy LaNi5 for Hydrogen storage M= Ni/TR(La,Ce…)

$MH \rightarrow H^+ + e^- + M + OH^-$ (H_2O) couple H/H^+ (E=0.5V)

Electrolyte solution KOH V = 1.3 volt

Positive electrode couple Ni^{3+} / Ni^{2+} (E= - 0.8V)

$Ni(OH)_3 + e^- \rightarrow Ni(OH)_2$

15 kilos of RE into a Prius battery

60 grammes in a tool battery

High power NiMH battery for Toyota Prius
About 10 to 15 Kg of RE (La, Ce, Pr, Nd)
RE improve the H capacity storage as well as
Oxidation/corrosion resistance

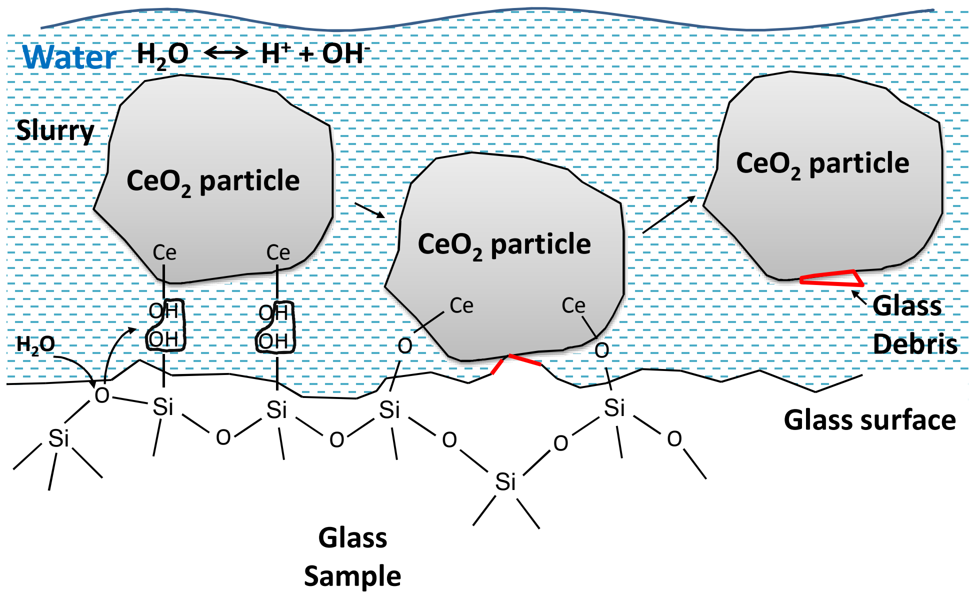
• NiMH and Lithium-based technologies will coexist in the future
• La Mischmetal sourcing accessible but requires anticipation

Rare Earths oxides for POLISHING

Target → material (glass) removal→thinning
→high quality finished surface

Objectives → polishing glass substrates such as optical
glasses (lenses etc) displays, flat TV LCD interior parts, wired glass, glass disks
→ polishing silicon substrates for electronics
The key technology: CMP Chemical Mechanical Polishing
Critical role of nano-size particles **Cerium oxide CeO_2**

Chemical Mechanical Polishing



Glass removal CeO_2 hardness similar to glass →soft scratching
MECHANICAL ROUTE

Planarization by bonding CeO_2 and SiO_2

--Si-OH---OH-Ce—
Layer by layer peeling

The **CHEMICAL ROUTE**
Key surface reactions
OH- ↔ O^{2-}
$Ce^{4+} \leftrightarrow Ce^{3+}$

Chemical Mechanical Polishing