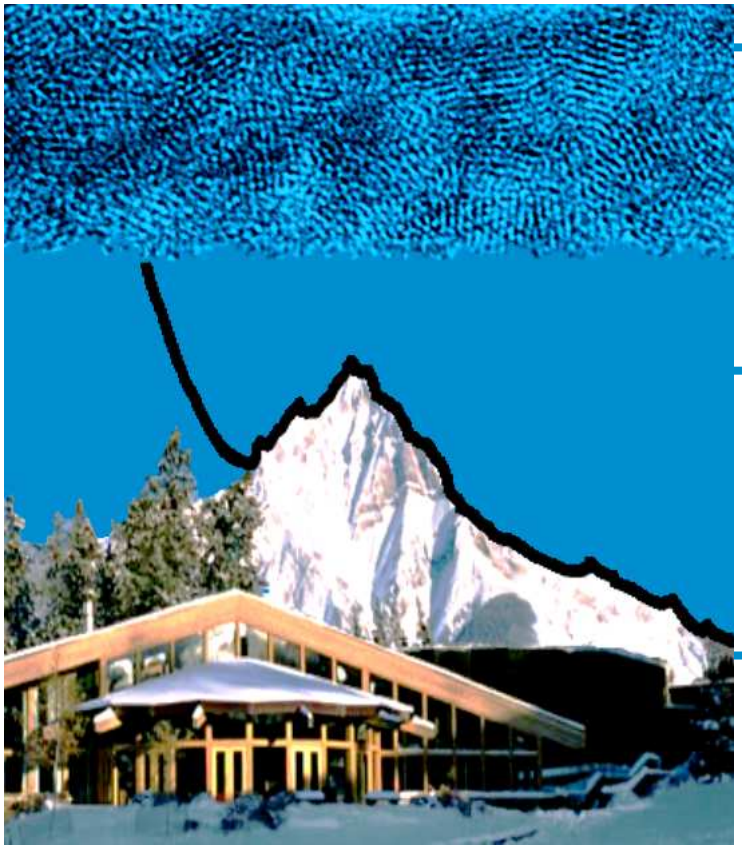
EELS STUDY of Gd_2O_3 NANO-PARTICLES

EVIDENCE of 4f ELECTRONS DELOCALIZATION in NANO-SIZED GADOLINIUM OXIDE



M. OU, J.C. LE BOSSÉ, *V. MAUCHAMP, B. MUTELET, P. PERRIAT, T. EPICIER**

Mateis umr CNRS 5510 INSA LYON **LYON, F**

LYON CITÉ CAMPUS

S. ROUX, O. TILLEMENT

LPCML umr CNRS 5620 UCBL **LYON, F**

**now at* PHYMAT umr CNRS 6630 UNIVERSITÉ Poitiers

OUTLINE

I. Problematic: ELNES of Nano-Particles *(e.g. Gd_2O_3)*

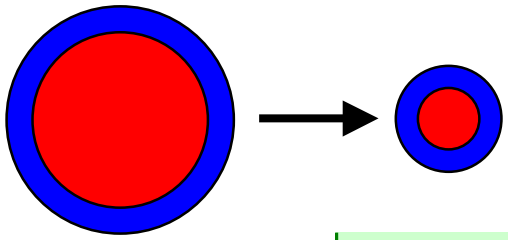
II. *FEFF* calculations of the O-K edge in Gd_2O_3 clusters

III. Conclusion: interest of Gd_2O_3 nano-hybrid based-systems for medical applications

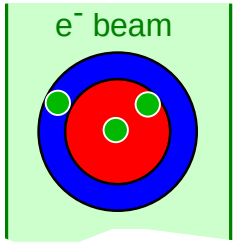
Problematic: ELNES of Nano-Particles

- **NPs properties CHANGE when DECREASING SIZE**

  owing to the $\frac{\text{'surface' atoms}}{\text{'volume' atoms}}$ ratio



- **is ELNES sensitive to the various environments of a probed chemical specie distributed on 'volume' and 'surface' sites?**



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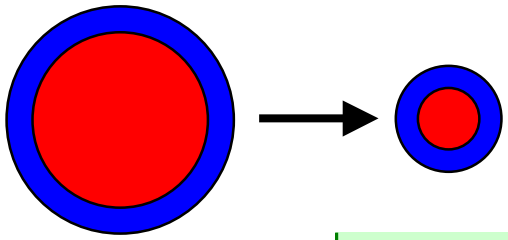

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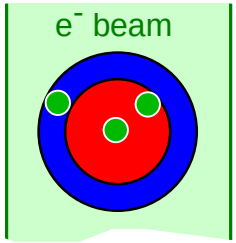


- **Application to Gd_2O_3 clusters**

Gd_2O_3 NPs in an ethylen glycol ($C_2H_6O_2$) solution

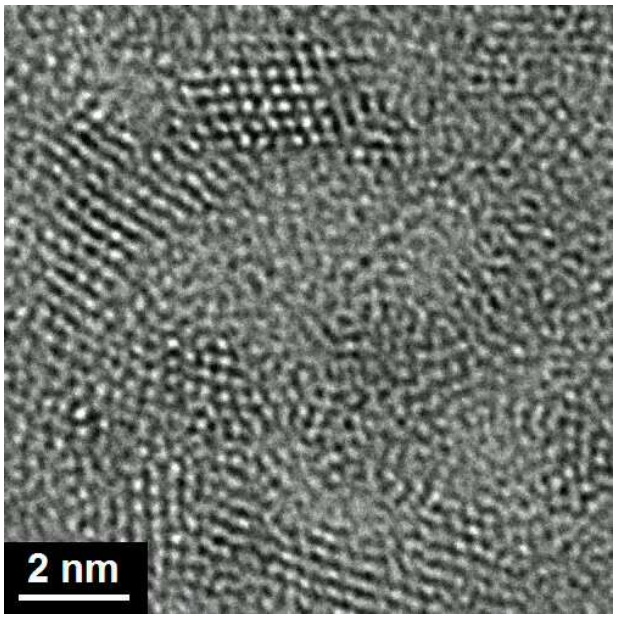
JEOL 2010F, *no corrector*

gatan DigiPEELS

incident beam focused at ≈ 10 nm (TEM mode)

probe convergence ½ angle **α = 10 mRad**
EELS collection ½ angle **β = 7 mRad**
acquisition time 15-20 sec., 0.3-0.5 eV/ch.

"2.7 nm" *sample*

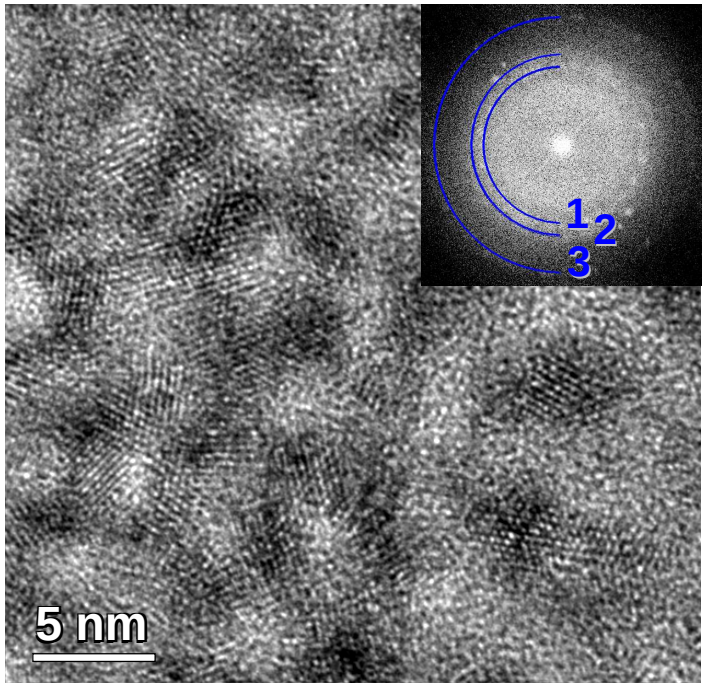


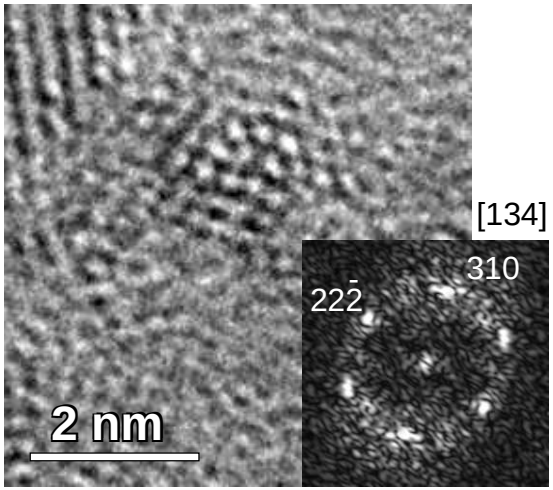
M. Ou, J.C. Le Bossé, *V. Mauchamp,* B. Mutelet, *S. Roux, O. Tillement,* P. Perriat, T. Epicier

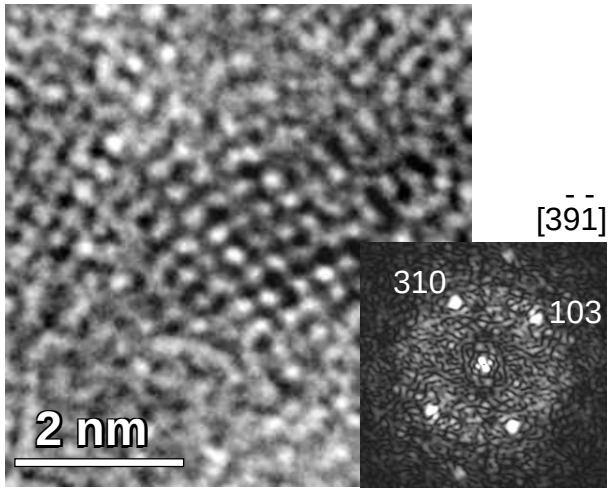
Mateis INSA LYON Microscopie Electronique et Sonde Atomique [METSA]

Crystal structure of Gd_2O_3

1 **{222}** 0.312 nm *(100)*
2 **{400}** 0.270 nm *(35)*
3 **{440}** 0.191 nm *(40)*





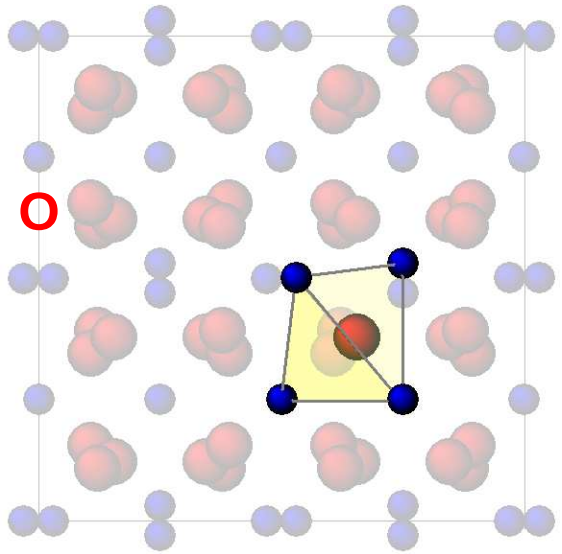


space group 206 **Ia-3, a = 1.082_5 nm**

(JCPDS 12-797)

$Gd_{(1)}$ in **8(a):** 1/4 1/4 1/4
$Gd_{(2)}$ in **24(d):** 0.96979 0 ¼
O in **48(e):** 0.39311 0.15484 0.37840

[V. GROVER et al., *J. Appl. Cryst.* **36**, (2003), 1082]



pseudo-tetraedric configuration

O-$Gd_{(2)}$	2.258_5 Å
O-$Gd_{(1)}$	2.322_3 Å
O-$Gd_{(2)}$	2.330_4 Å
O-$Gd_{(2)}$	2.439_9 Å

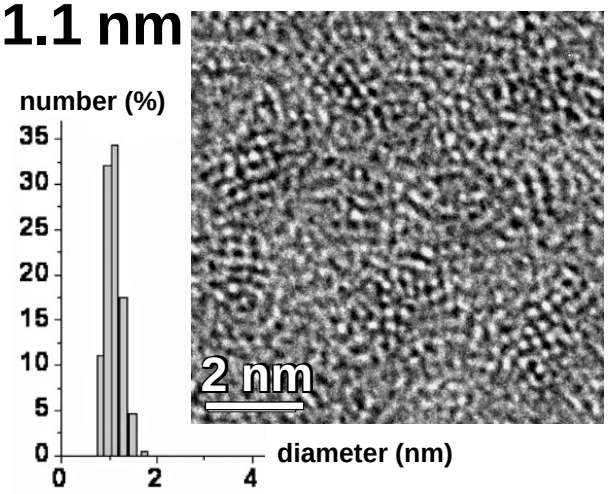
no symmetry
point group $C_1(1)$

❑ Synthesis of Gd_2O_3 clusters with DIFFERENT *controled* SIZES

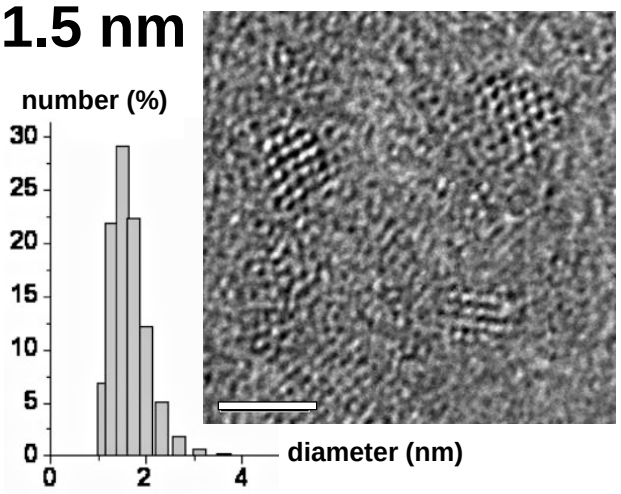
[M. OU et al., *J. Phys. Chem. C*, **113**, 10 (2009), 4038]

1.1 nm, 1.5 nm, 2.7 nm, 4.0 nm

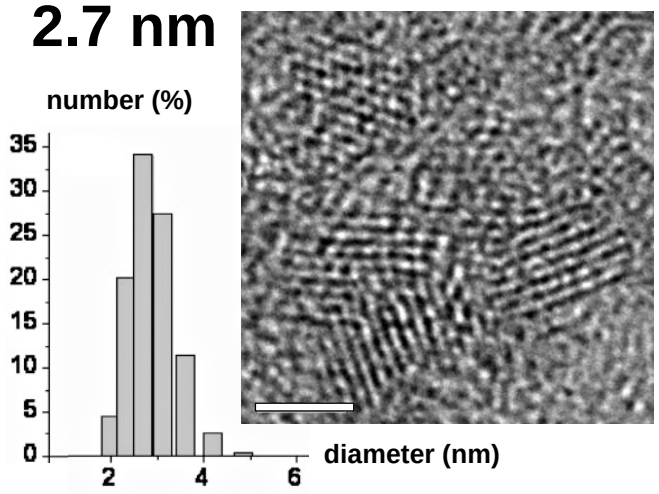
1.1 nm



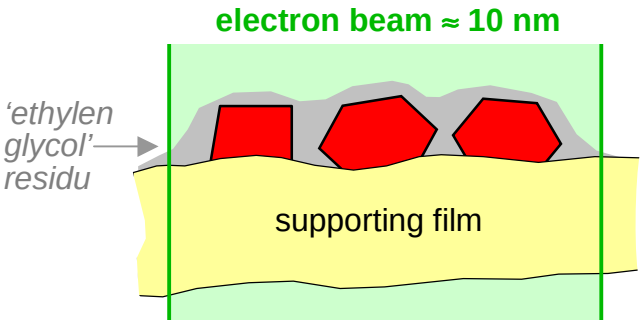
1.5 nm



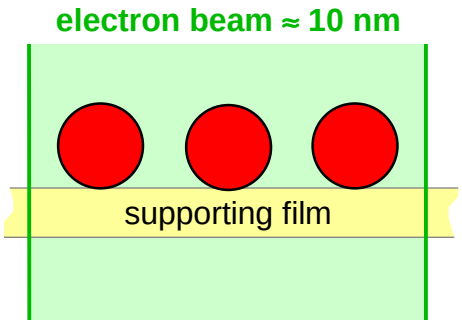
2.7 nm



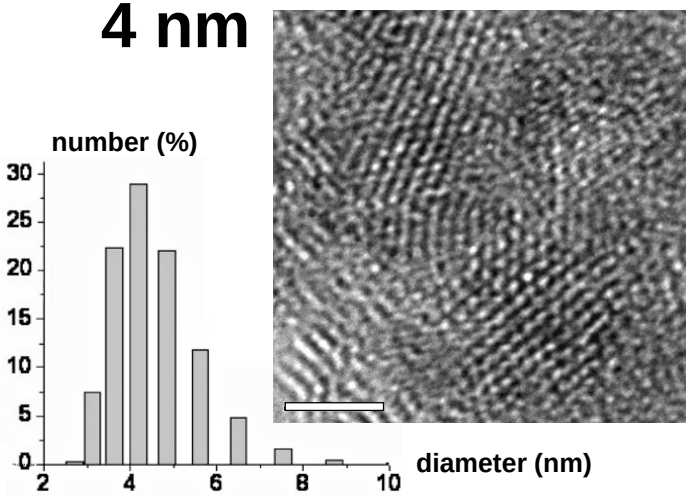
reality as it is (?)



...as we describe it



4 nm



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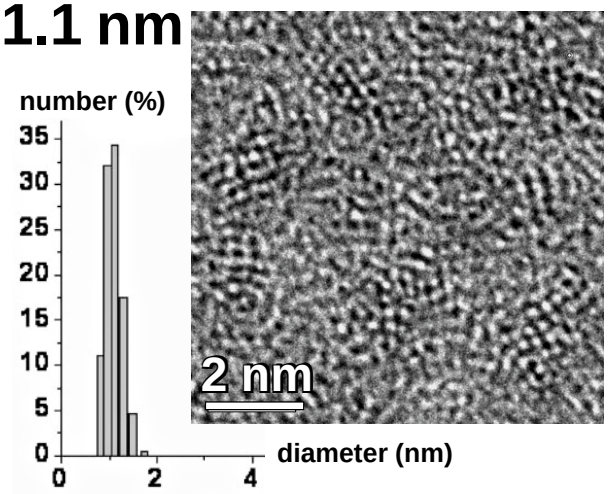
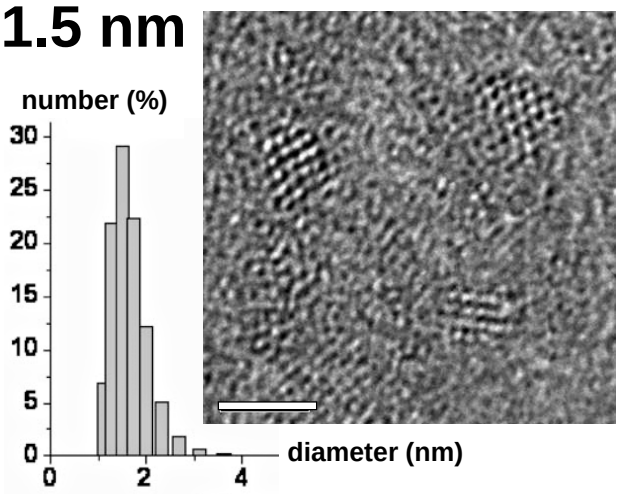
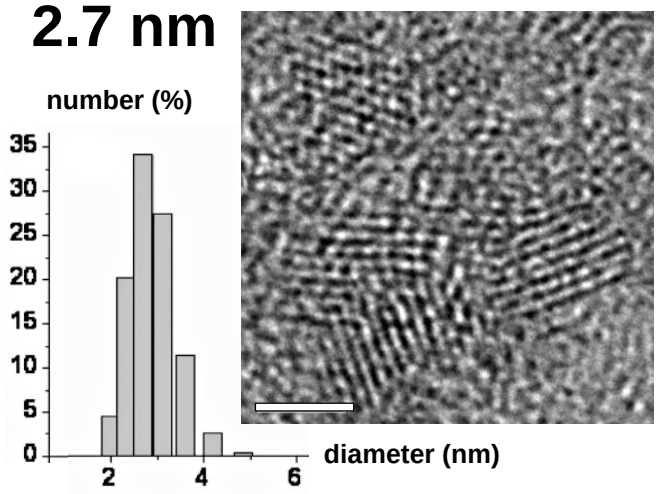
1.1 nm



1.5 nm



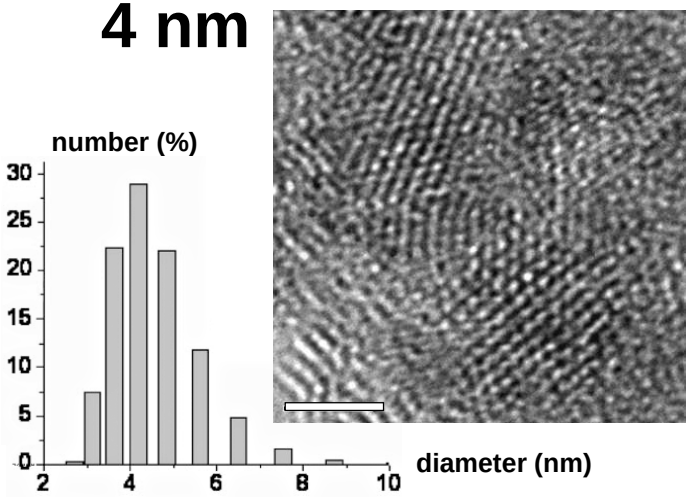
2.7 nm



❑ FEFF* M.S. calculations of the O-K edge

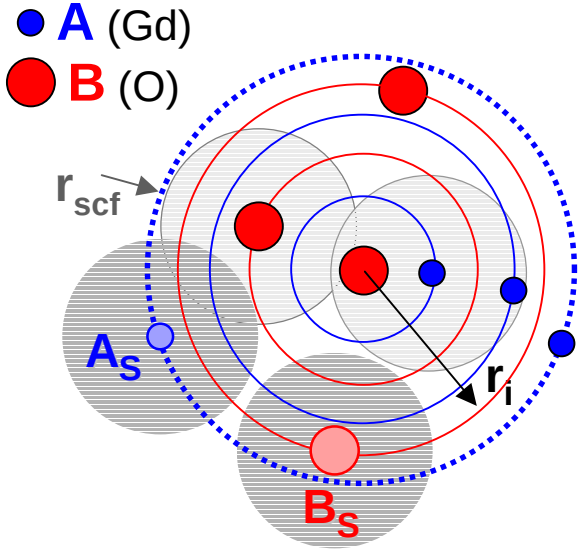
- ***Gd_2O_3 clusters assumed to be stoichiometric, spherical and crystallized***
- ***All surface atoms described in the same way***
- ***No surface relaxation / bond 'reconstruction'***
- ***Magnetism effects (Gd) ignored*** *(no spin-orbit coupling)*

4 nm



*[A.L. ANKUDINOV et al., *Phys. Rev. B*, 58, 7565 (1998)]

FEFF calculation of Gd_2O_3 clusters



atomic shell sequence:

$B_0\ A_1\ B_2 \ldots A_{2k-1}\ B_{2k}$ (distances $r_0 = 0, r_1, \ldots r_n$)

❑ **Bulk: identical *atomic potentials* for all A_i and B_j**

$$\frac{\partial^2\sigma_{total}}{\partial E\,\partial\Omega} = \frac{\partial^2\sigma_{B_0}}{\partial E\,\partial\Omega}$$

❑ **Cluster: *potentials* will depend on *site position* r_i (especially surface A_S and B_S atoms)**

2 steps:

1/2 calculation of each 'site' X-section

2/2 calculation of the weighted total X-section

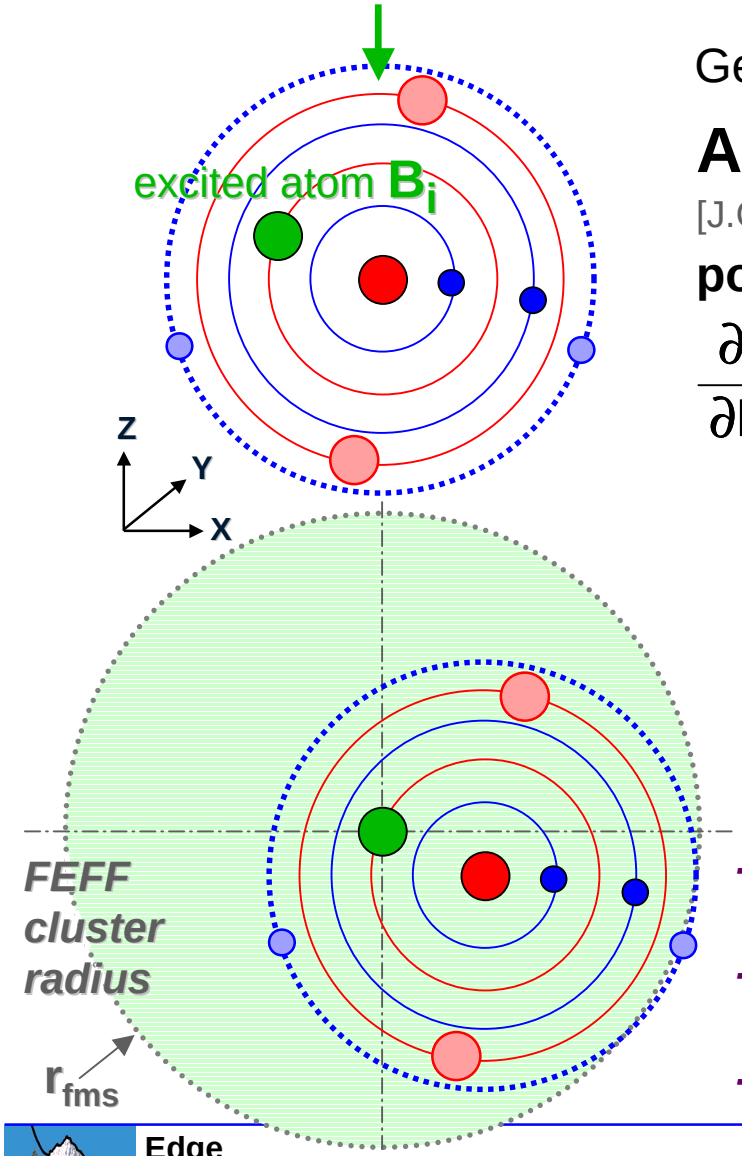
$$\text{2/2}\quad \frac{\partial^2\sigma_{total}}{\partial E\,\partial\Omega} = \frac{1}{N_B}\left[\sum_i N_i \frac{\partial^2\sigma_{B_i}}{\partial E\,\partial\Omega} + \text{1/2}\ N_S \frac{\partial^2\sigma_{B_S}}{\partial E\,\partial\Omega}\right]$$

N_i : number of B_i atoms at distance r_i from centre

N_S : number of *(identical) surface* B_S atoms

N_B : total number of **B** atoms

1/2 calculation of an 'elementary site' cross-section



General case of a B_i atom at distance r_i from centre

Anisotropic effects

POSTER N°65 Le BOSSÉ et al.

[J.C. Le BOSSÉ et al., *Phys. Rev.* **B76**, (2007), 0751271]

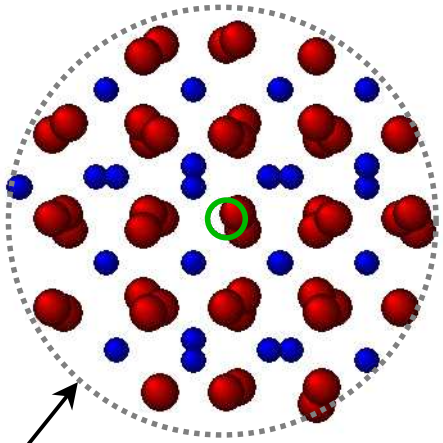
point group $C_1(1)$: *most general c-TRICHROISM* case

$$\frac{\partial^2\sigma_{B_i}}{\partial E\,\partial\Omega} = K^c_{100}\left.\frac{\partial^2\sigma_{B_i}}{\partial E\,\partial\Omega}\right|_{[100]} + K^c_{010}\left.\frac{\partial^2\sigma_{B_i}}{\partial E\,\partial\Omega}\right|_{[010]} + K^c_{001}\left.\frac{\partial^2\sigma_{B_i}}{\partial E\,\partial\Omega}\right|_{[001]} + K^c_{110}\left.\frac{\partial^2\sigma_{B_i}}{\partial E\,\partial\Omega}\right|_{[110]} + \underbrace{K^c_{011}}\left.\frac{\partial^2\sigma_{B_i}}{\partial E\,\partial\Omega}\right|_{[011]} + \underbrace{K^c_{101}}\left.\frac{\partial^2\sigma_{B_i}}{\partial E\,\partial\Omega}\right|_{[101]}$$

weighting factors function of

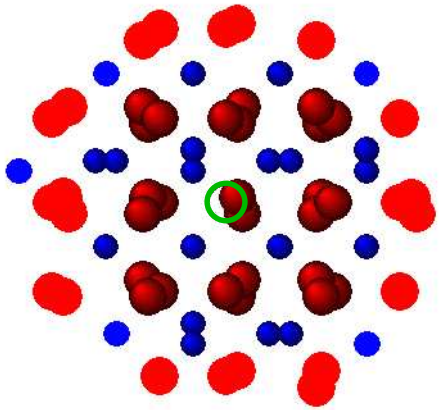
- ***experimental conditions:*** *convergence ½ angle α, collection ½ angle β*
- ***beam vs. crystal orientation:*** *elevation & azimuthal angles δ_0, χ_0*
- ***electron energy*** *(relativisitc effects)*

Illustration: central atom B_0 in a cluster of 1.35 nm



cluster radius = 0.675 nm

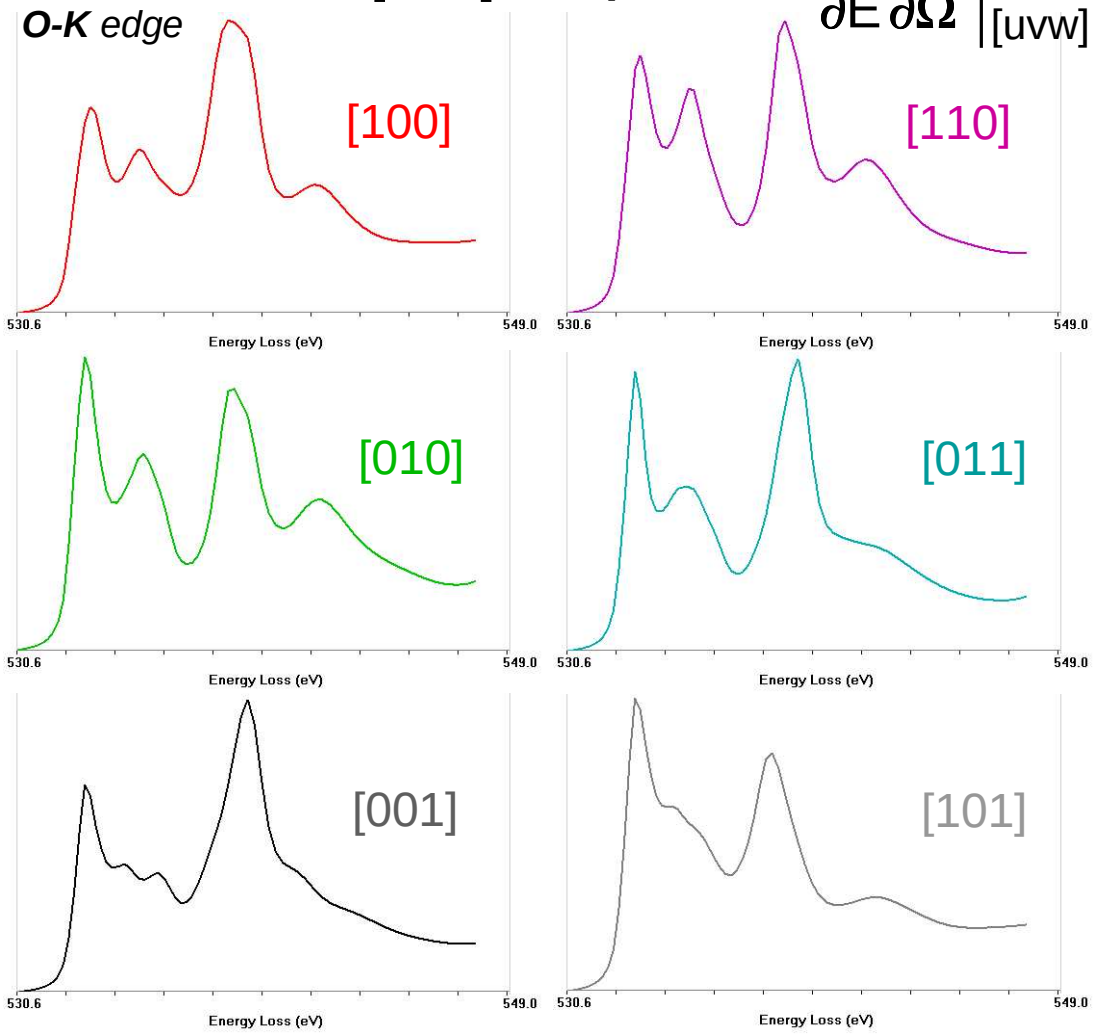
86 atoms, composition $Gd_2O_{3.06}$



38.4 % of "surface atoms"

half-coordinance or less Gd ≤ 3, O ≤ 2

intrinsic [uvw] **components** $\left.\frac{\partial^2\sigma_{B_0}}{\partial E\,\partial\Omega}\right|_{[uvw]}$



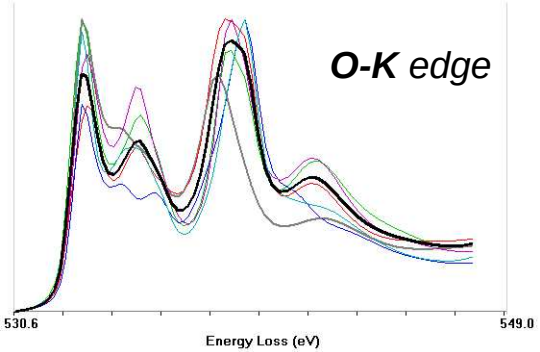
For large convergence & collection angles

$\alpha = 10$ mRad

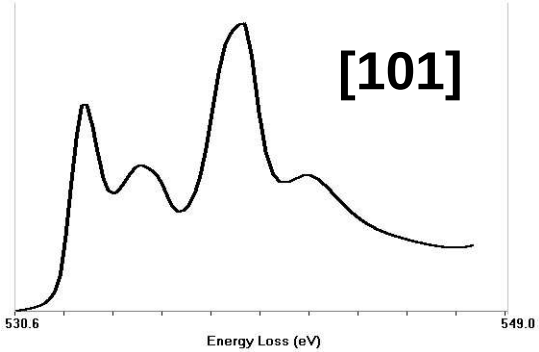
$\beta = 7$ mRad

magic set:
$\alpha_{max} = \beta_{max} \approx 2$ mRad

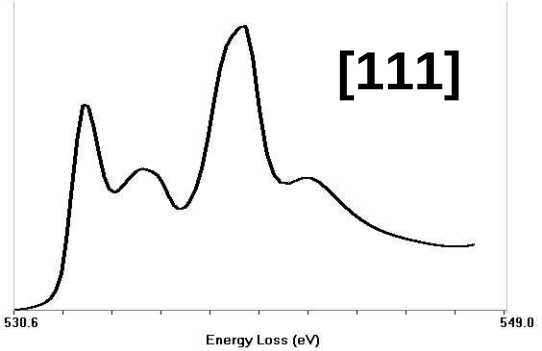
collected current along [001]



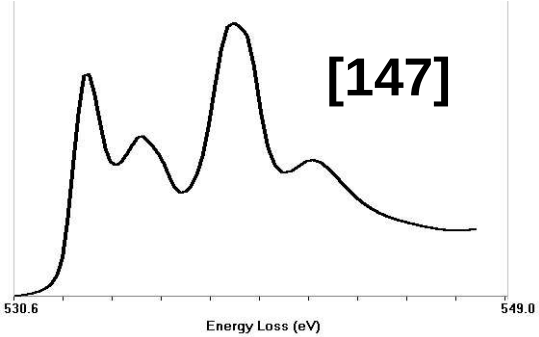
$K_{[100]} = 0.4378$ $K_{[110]} = 0.0$
$K_{[010]} = 0.4378$ $K_{[011]} = 0.0$
$K_{[001]} = 0.1244$ $K_{[101]} = 0.0$



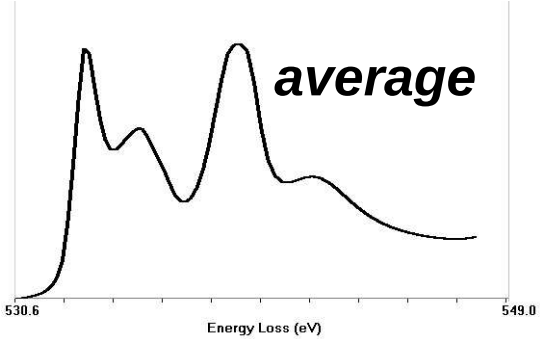
$K_{[100]} = 0.4308$ $K_{[110]} = 0.0$
$K_{[010]} = 0.4308$ $K_{[011]} = 0.0$
$K_{[001]} = 0.4308$ $K_{[101]} = -0.2930$



$K_{[100]} = 0.5282$ $K_{[110]} = -0.1988$
$K_{[010]} = 0.5282$ $K_{[011]} = -0.1988$
$K_{[001]} = 0.5282$ $K_{[101]} = -0.1988$

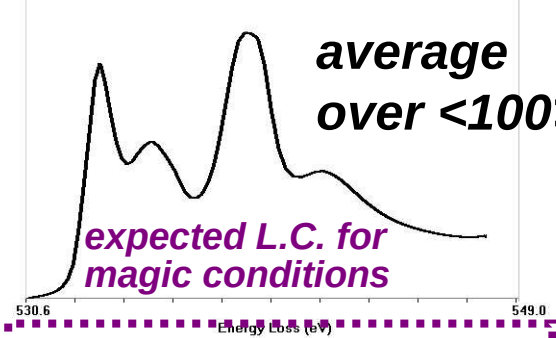


$K_{[100]} = 0.4545$ $K_{[110]} = -0.0184$
$K_{[010]} = 0.4928$ $K_{[011]} = -0.2531$
$K_{[001]} = 0.3557$ $K_{[101]} = -0.0315$



all $K_{[uvw]} = 1/6$

[J.C. Le BOSSÉ et al., *Phys. Rev.* **B76**, (2007), 0751271]



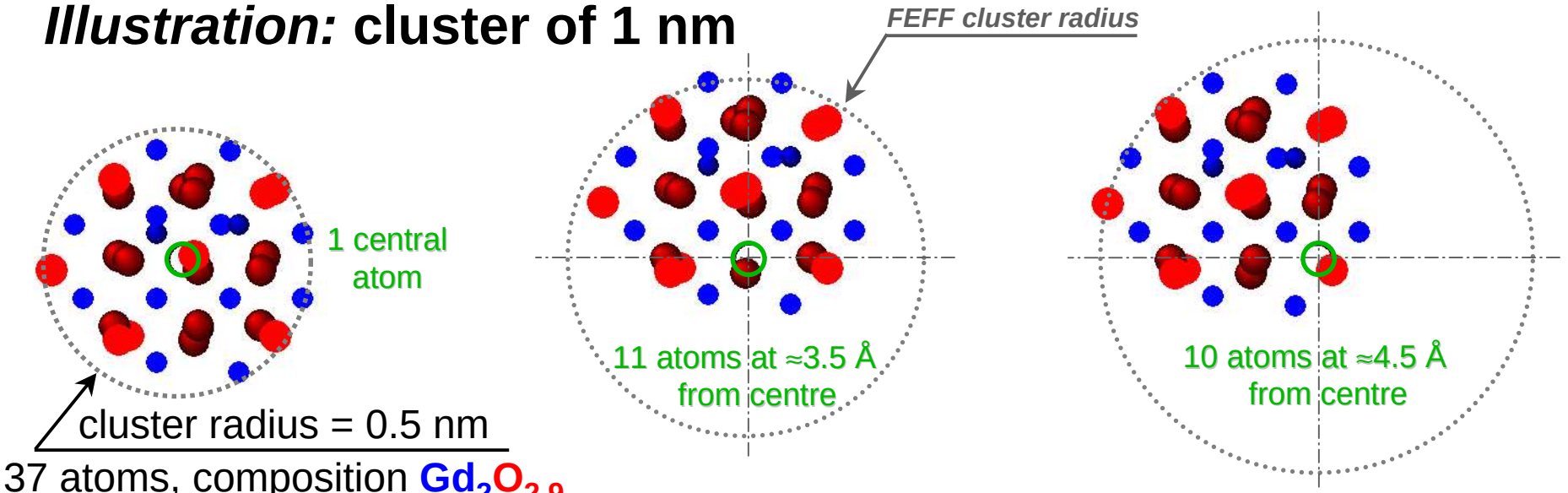
$K_{[100]} = 1/3$ $K_{[110]} = 0.0$
$K_{[010]} = 1/3$ $K_{[011]} = 0.0$
$K_{[001]} = 1/3$ $K_{[101]} = 0.0$

2/2 calculation of the total cluster cross-section

$$\frac{\partial^2\sigma_{total}}{\partial E\,\partial\Omega} = \frac{1}{N_B}\left[\sum_i N_i \frac{\partial^2\sigma_{B_i}}{\partial E\,\partial\Omega} + N_S \frac{\partial^2\sigma_{B_S}}{\partial E\,\partial\Omega}\right]$$

N_i : number of $\mathbf{B_i}$ atoms at distance $\mathbf{r_i}$ from centre
N_S : number of *(identical) surface* $\mathbf{B_S}$ atoms
N_B : total number of **B** atoms

Illustration: cluster of 1 nm



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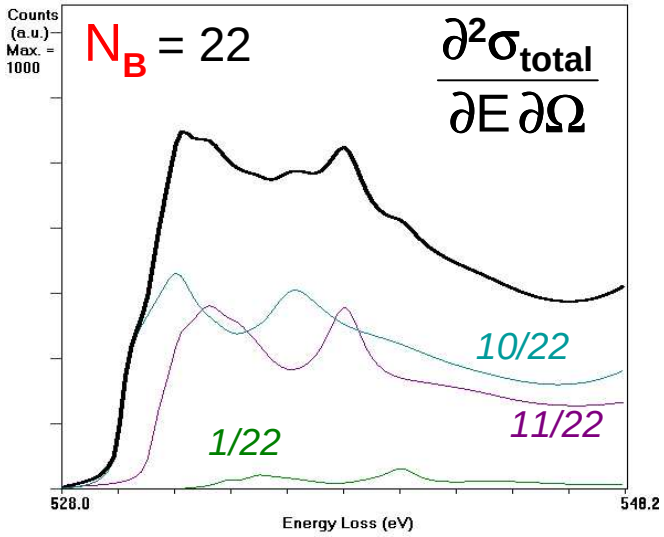

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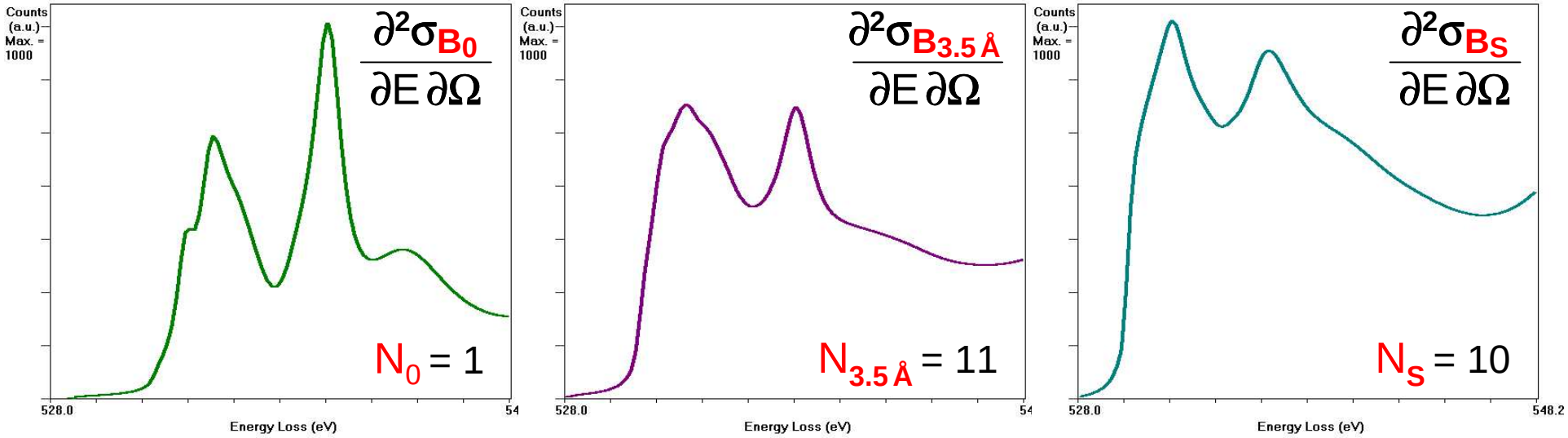
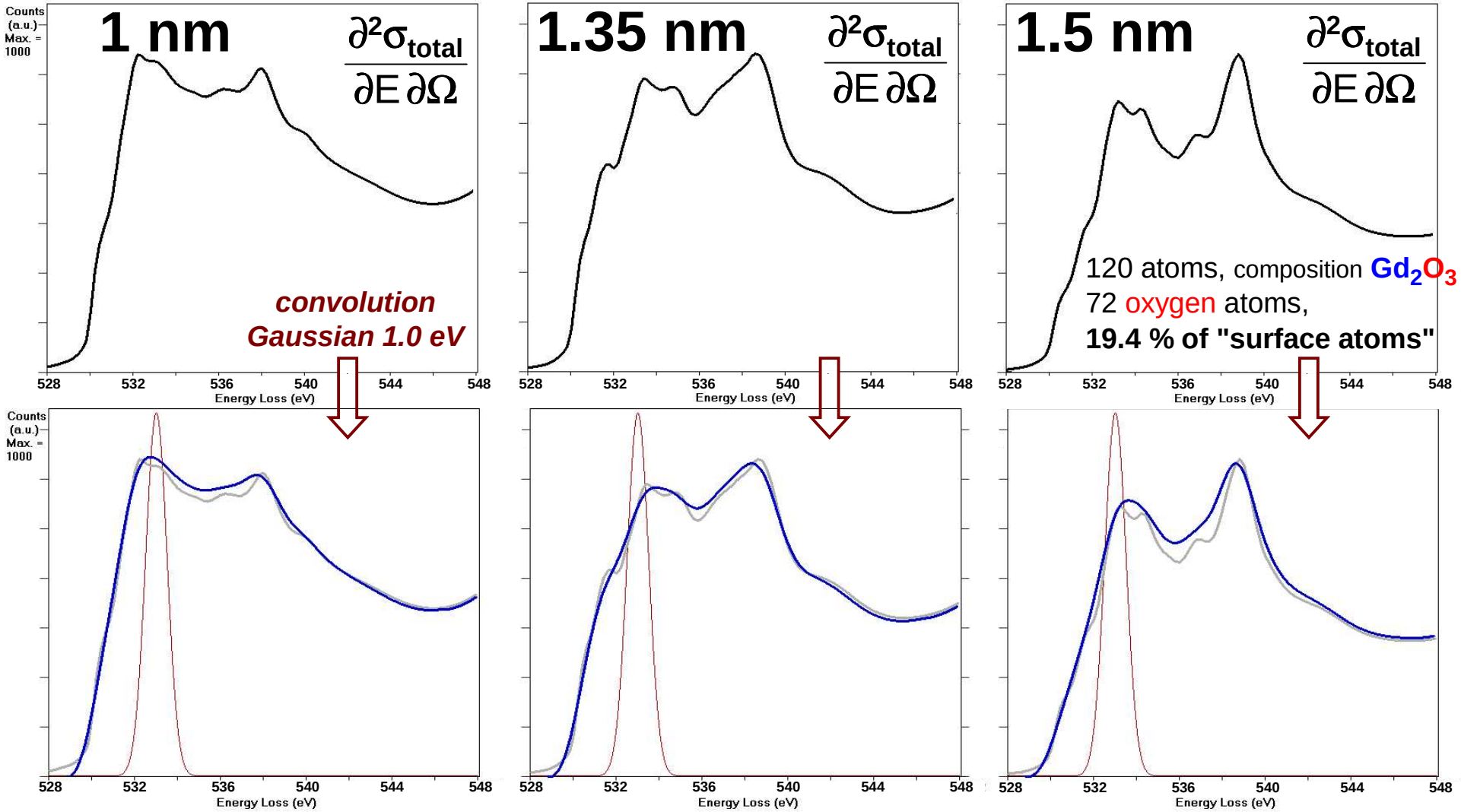
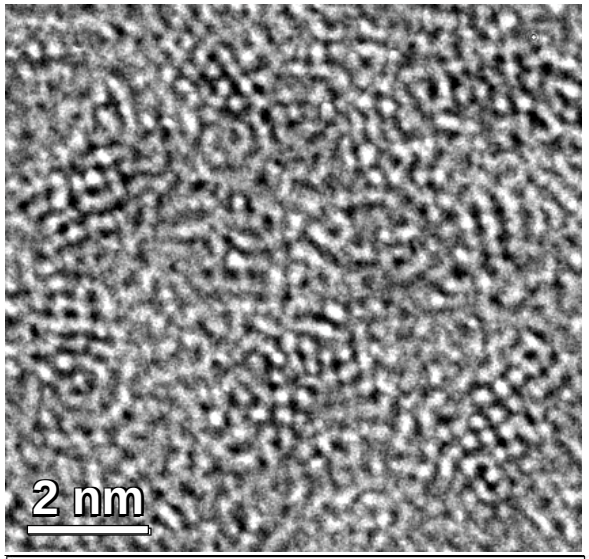


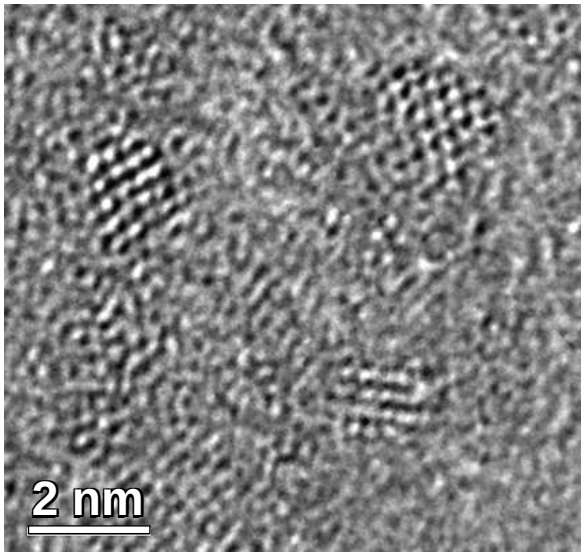
Size effect for clusters of 1, 1.35 and 1.5 nm



Comparison EELS experiments - simulations

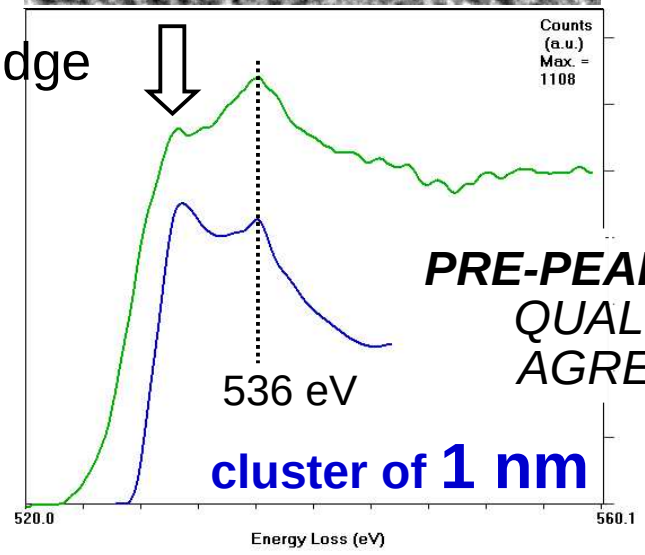
particles ***≈ 1 nm***



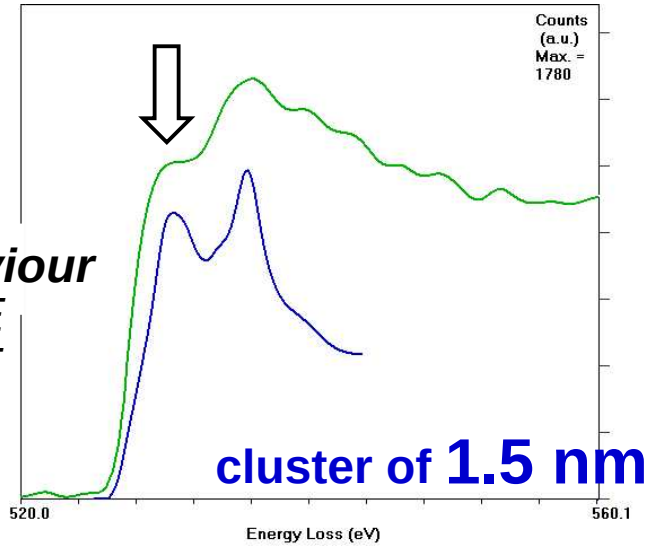


particles ***≈ 1.5 nm***

O-K edge



PRE-PEAK behaviour
QUALITATIVE AGREEMENT



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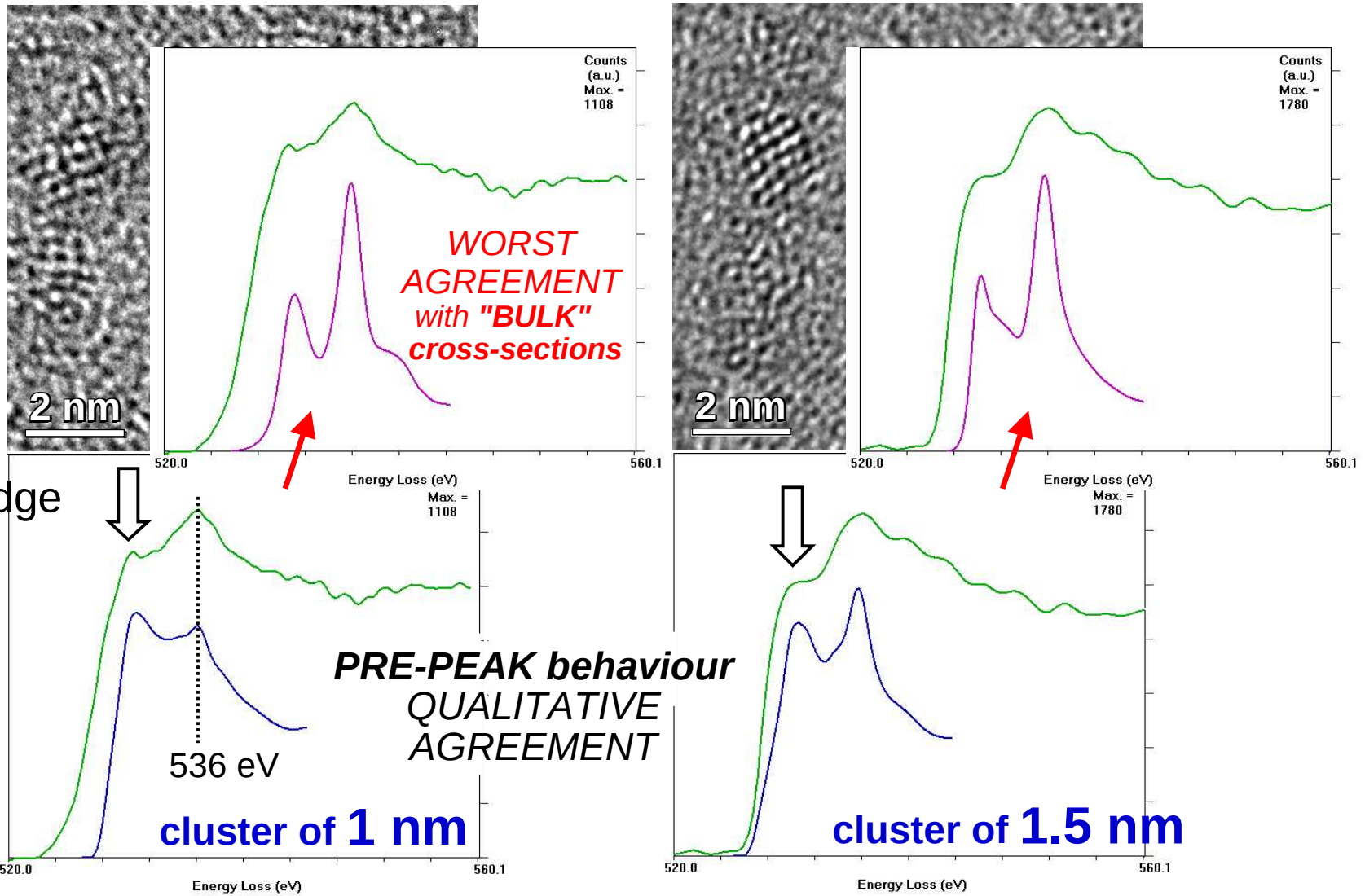
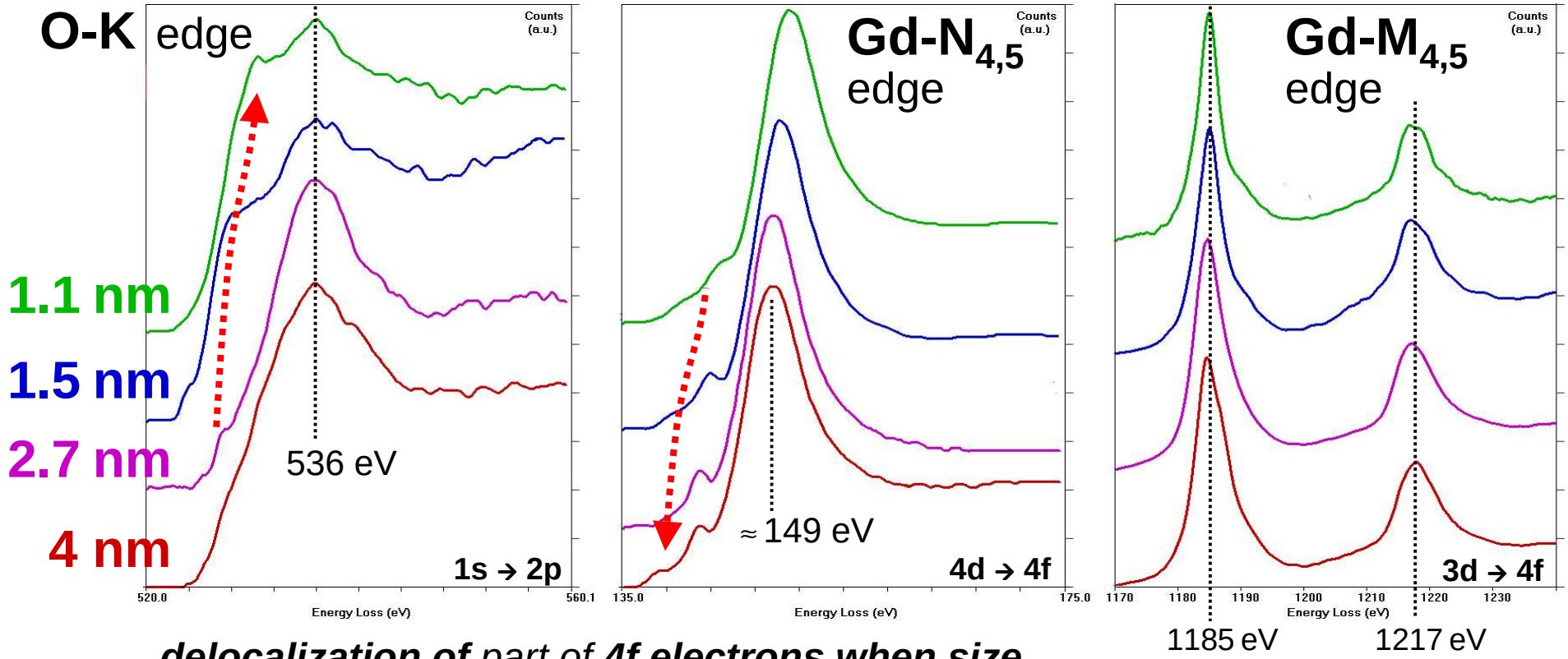


Complete EELS results

[M. OU et al., *J. Phys. Chem. C*, **113**, 10 (2009), 4038]



delocalization of** part of **4f electrons when size decreases: hybridization Gd-4f / O-2p*

for SMALL sizes: PRE-PEAK in O-K INCREASES, PRE-PEAK in Gd-N DECREASES

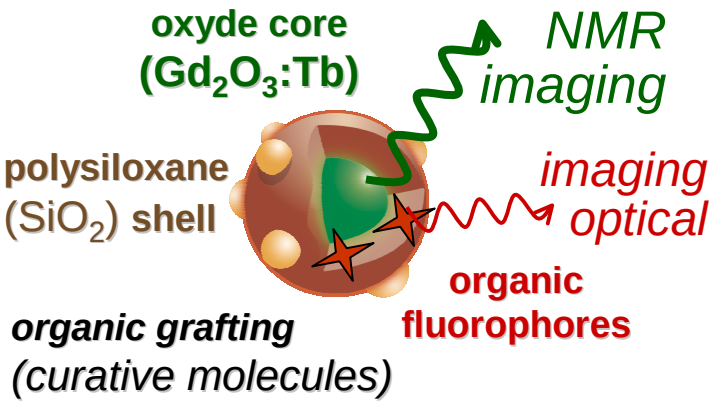
no size effect: NO CHARGE TRANSFER
(no valence change)

* analogy with Ce oxides:

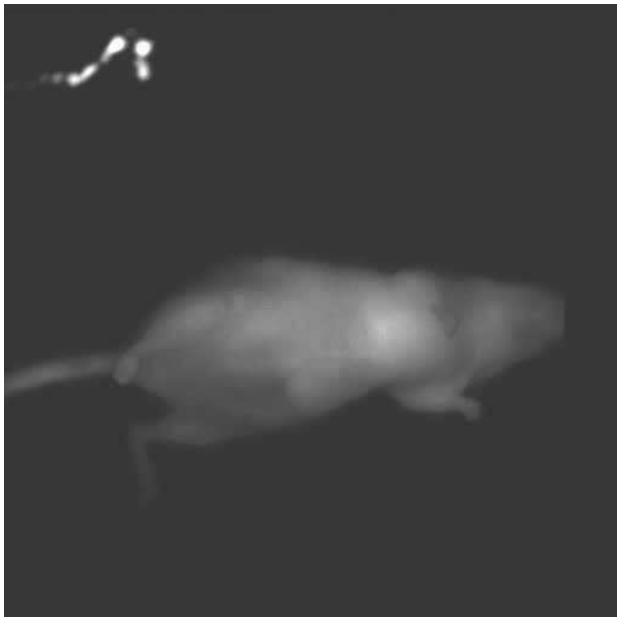
[D. WIELICZKA et al., *Phys. Rev. B,* ***26***, (1982), 7056; R.A..GORDON et al., Eur. *Phys. Lett.* **81**, (2008), 26004]

interest of nano-hybrid Gd_2O_3 *(Au)* based-systems for medical applications

lanthanide-based nanoparticles for cancer diagnostic and therapy

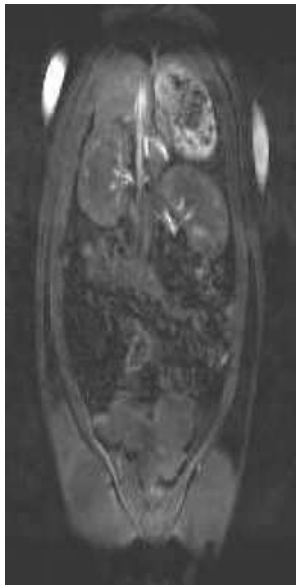


Fluorescence imaging



[collaboration J.L. COLL et al., *INSERM, UJF, F-Grenoble*]

Nuclear Magnetic Resonance imaging



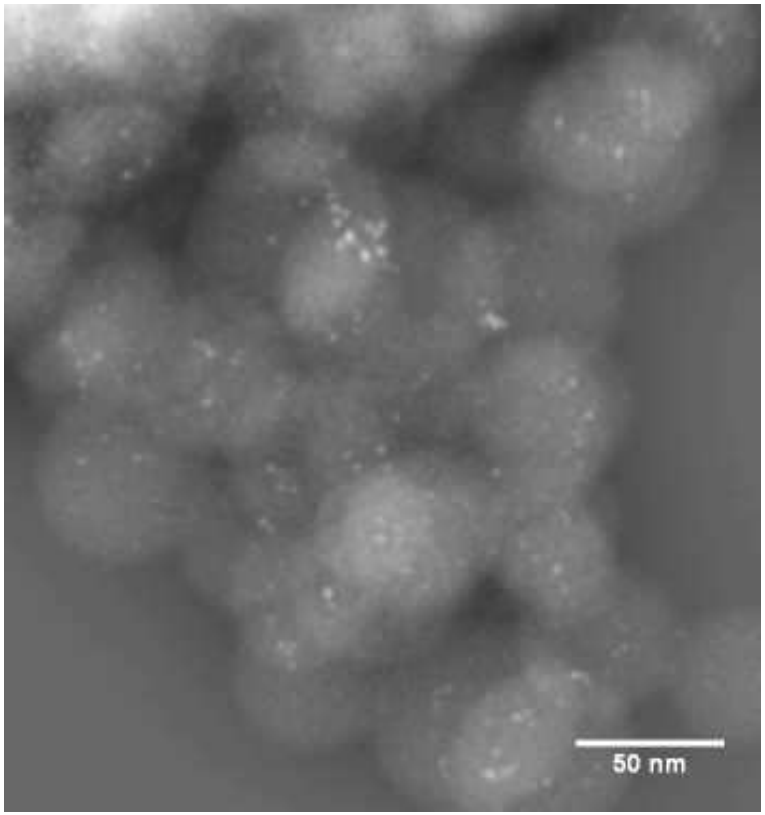
[collaboration C. BILLOTEY et al., *CNRS-INSERM, UCBL, F-Lyon*]

P. PERRIAT, *MATEIS, INSA-Lyon*
C. BILLOTEY, M. JANIER, *CREATIS (INSA-UCB- HCL)*
O. TILLEMENT, S. ROUX, *LPCML (UCB)*
C. LOUIS, *NANO-H SAS*

[J.L. BRIDOT et al., *J. Am. Chem. Soc.*, **129** 16, (2007), 5076]

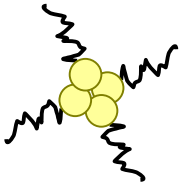
interest of nano-hybrid Gd_2O_3 *(Au)* based-systems for medical applications

Tomography on $Au@SiO_2$ nano-composites

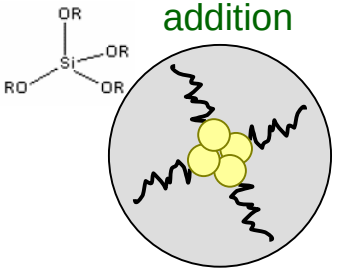


[S. BENLEKBIR, *PhD*, (2009), MATEIS INSA-Lyon]

1 colloïdal solution **Au@DTDTPA**

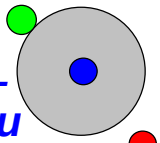


2 **$Si(OEt)_4$** TEOS addition

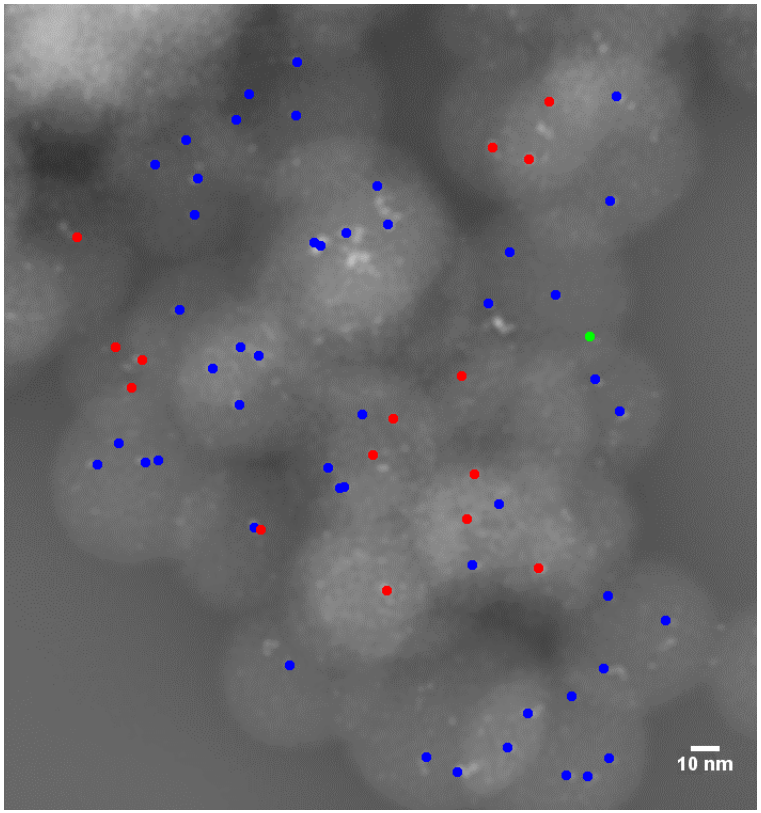


Au at SURFACE

INTERNAL Au

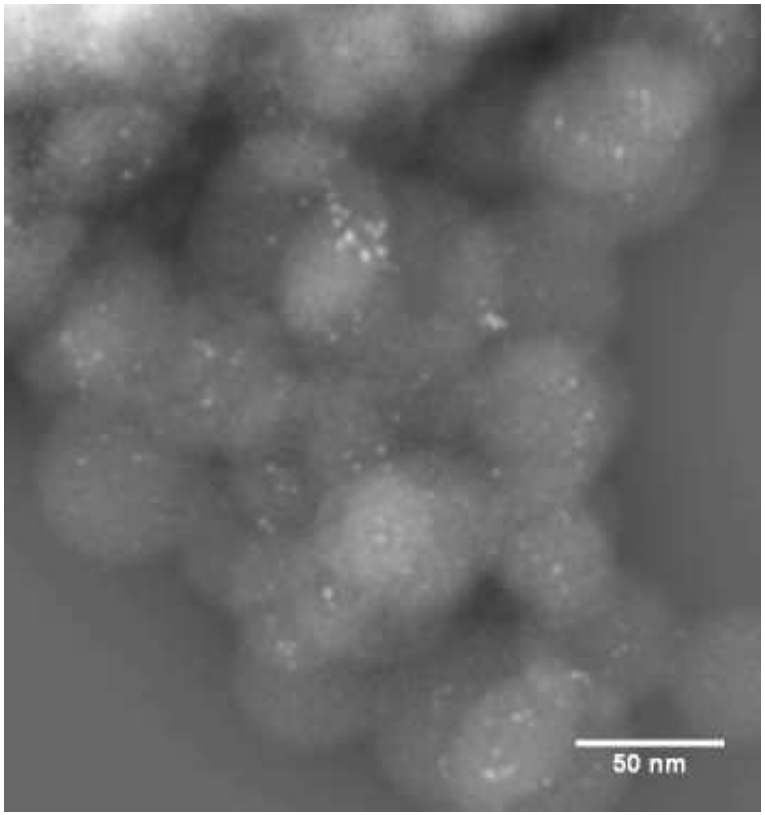


Un-positioned Au



interest of nano-hybrid Gd_2O_3 *(Au)* based-systems for medical applications

Tomography on $Au@SiO_2$ nano-composites



[S. BENLEKBIR, *PhD*, (2009), MATEIS INSA-Lyon]

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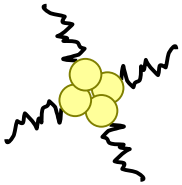

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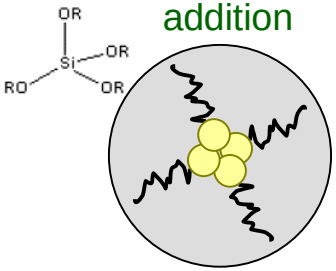
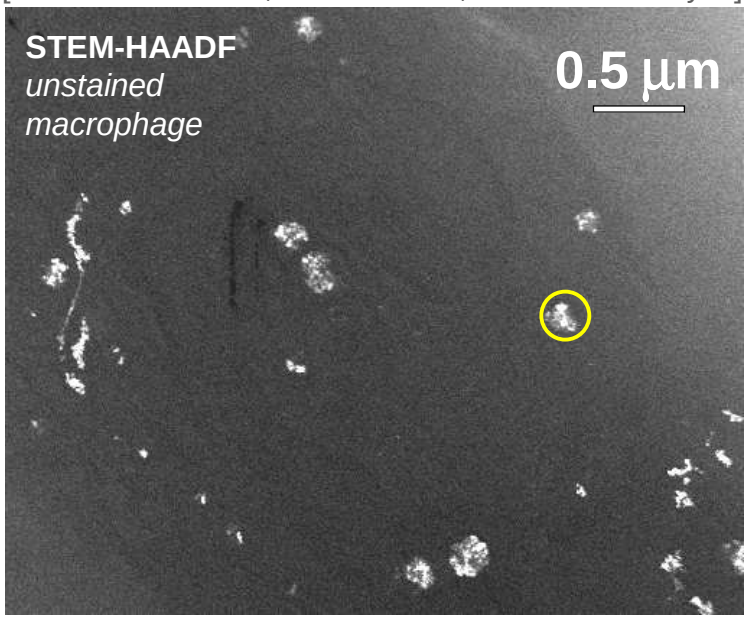


Au-NPs ingestion in cells

[L. JOLY-POTTUZ, P. PERRIAT, *MATEIS* INSA Lyon]



(*sample prep.* C. MANDON, *CREATIS* INSA-Lyon I)