La spectroscopie d'absorption de rayons X dans l'analyse de verres dopés aux terres rares

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dacapito@esrf.fr

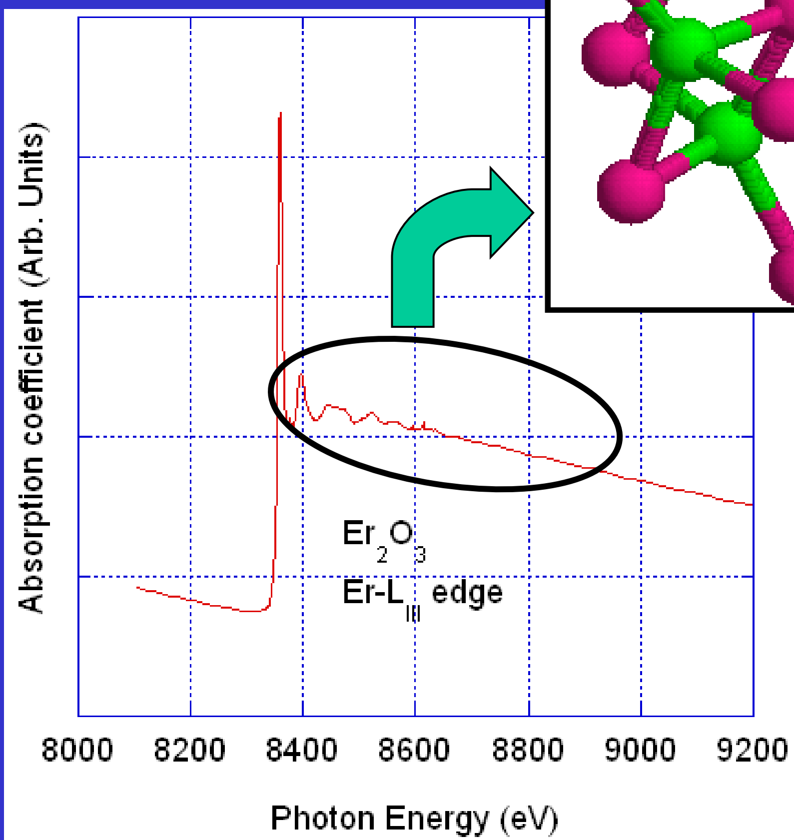
i o m
Istituto Officina dei Materiali

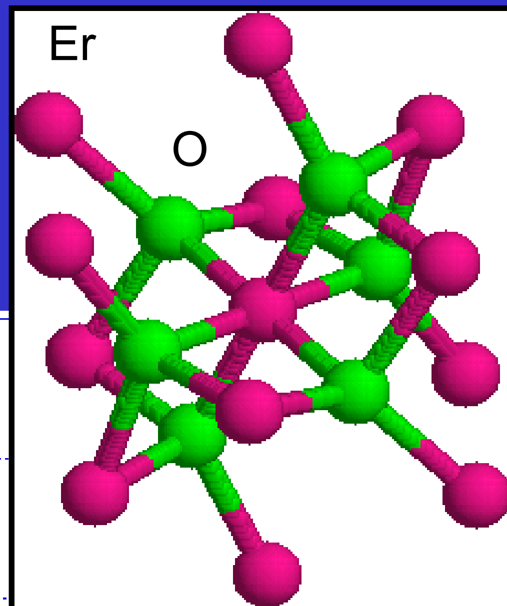
Layout

- Introduction to XAS
- Description of GILDA
- Experimental examples

Introduction to the XAS technique

X-ray Absorption Spectroscopy-XAS



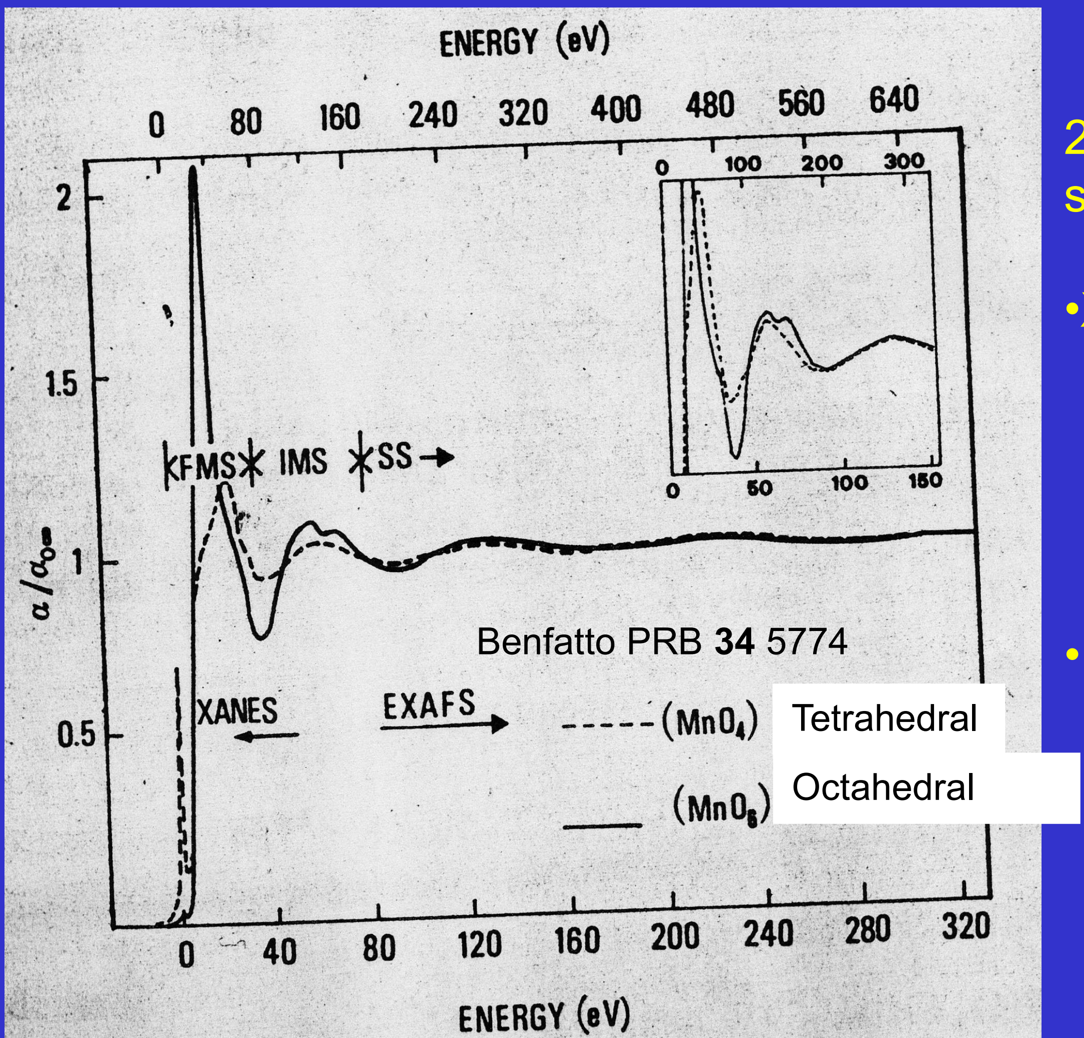


-The information is retrieved from the oscillations above the absorption edge

-Local structural parameters
- N (number of neighbors),
- R (distance),
- σ^2 Debye-Waller factor (disorder)

- No need for long range order
- Typical accuracy 1% R, 10% N, 20% σ^2

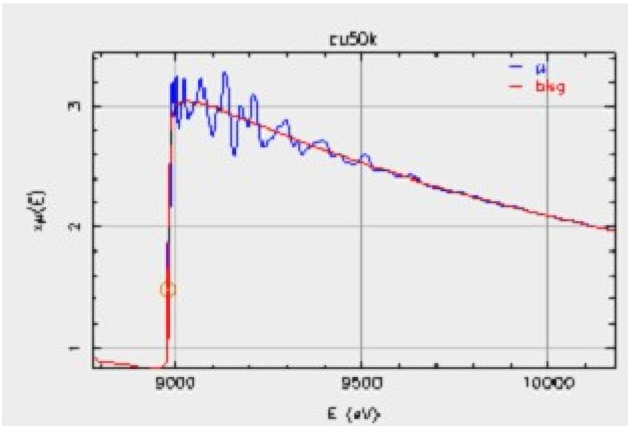
XAS spectrum regions



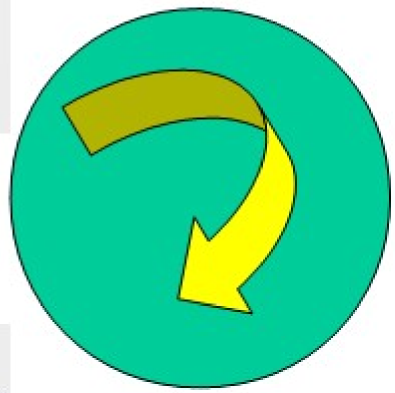
2 regions can be defined in the absorption spectrum

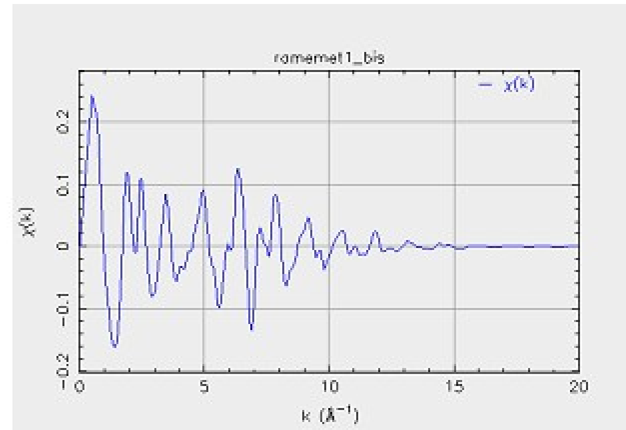
- XANES
  - Up to 50 eV
  - Long photoelectron wavelength
  - Electronic structure
  - Local geometry, symmetry
  - Complex scattering processes
- EXAFS
  - Short photoelectron wavelength
  - Quantitative
  - Dominated by single scattering

EXAFS data analysis

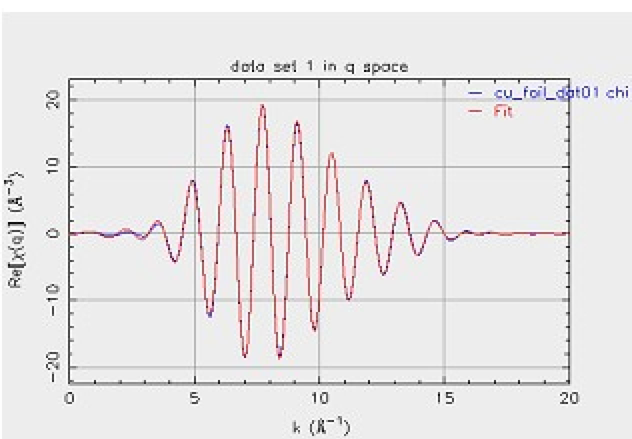


Background subtraction

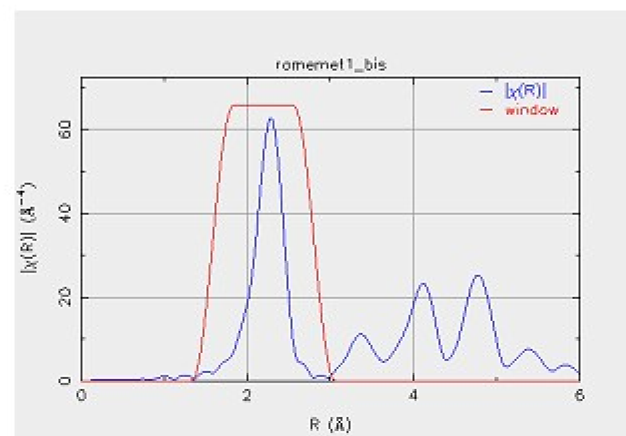




Oscillatory χ function



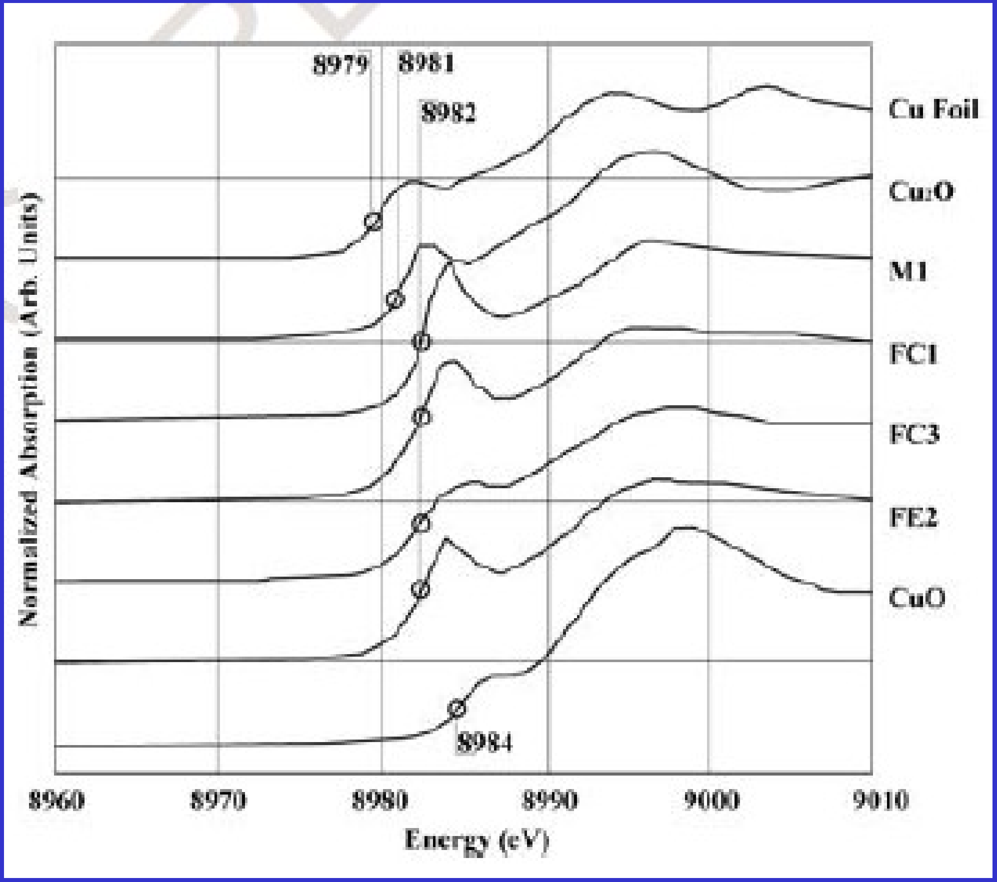
Back-transform and
Multiparameter fit



Fourier Transform

XANES

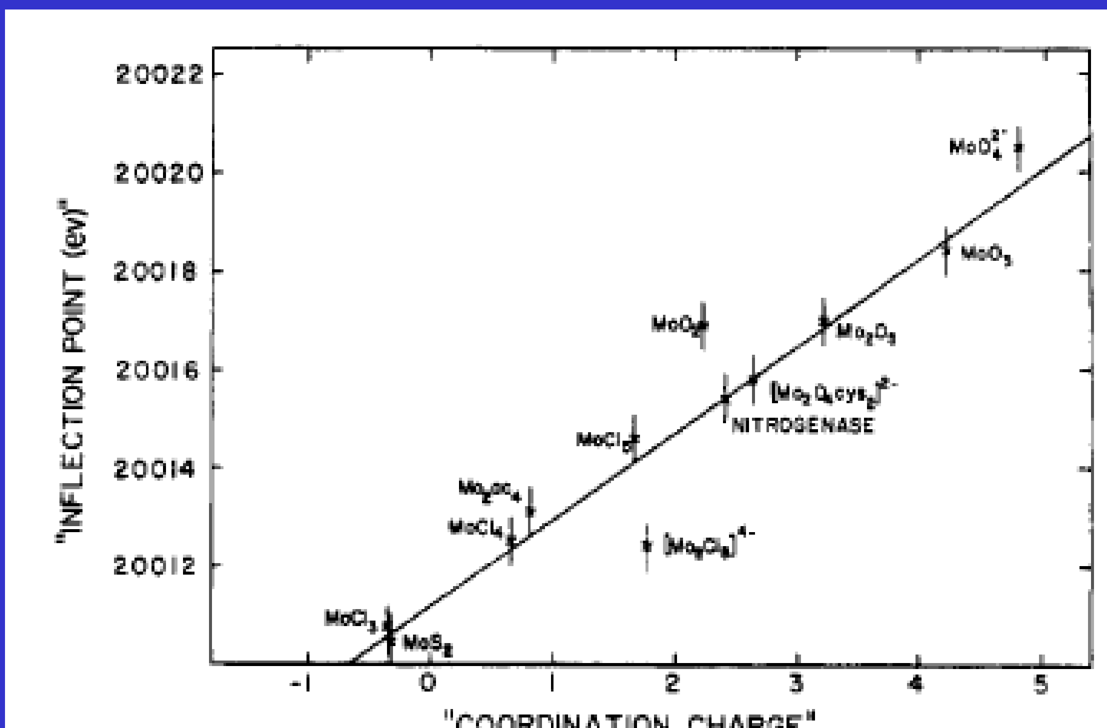
Some fundamental data can be extracted from the near edge region



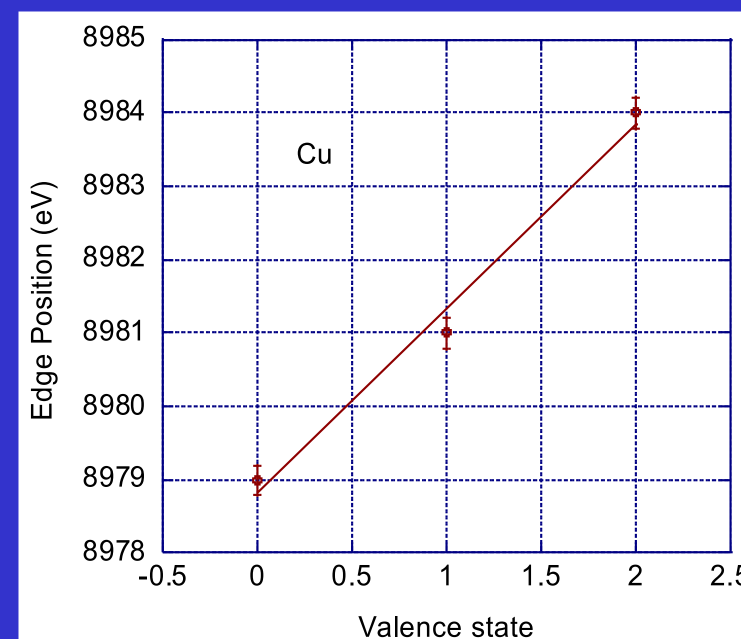
I: Valence state
The position of the edge (1st inflection point) depends on the charge on the ion.

Qualitative XANES data analysis

The valence state of a chemical specie can be derived from the position of the first inflection point of μ(E).



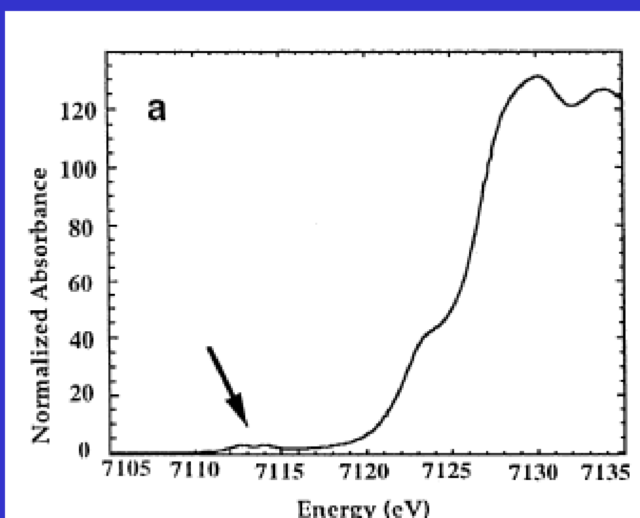
S. P. Cramer, T. K. Eccles, F. W. Kutzler, Keith O. Hodgson
L. E. Mortenson
Journal of the American Chemical Society / 98:5 / March 3, 1976



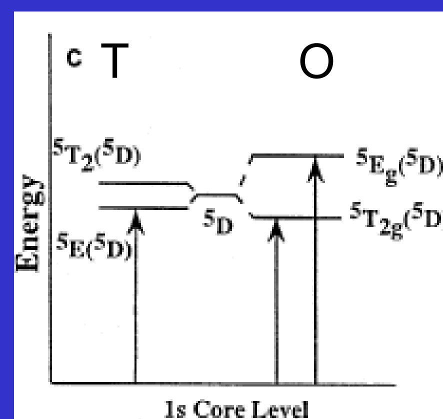
Qualitative XANES data analysis

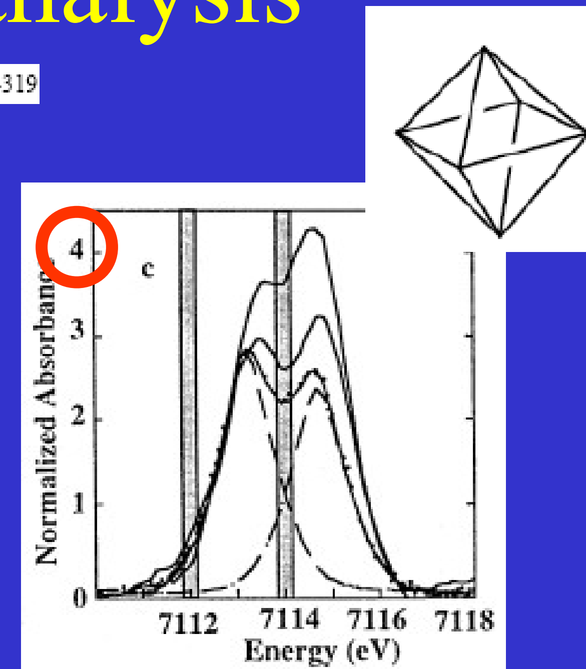
L. Galoisy *, G. Calas, M.A. Arrio Chemical Geology 174 (2001) 307–319

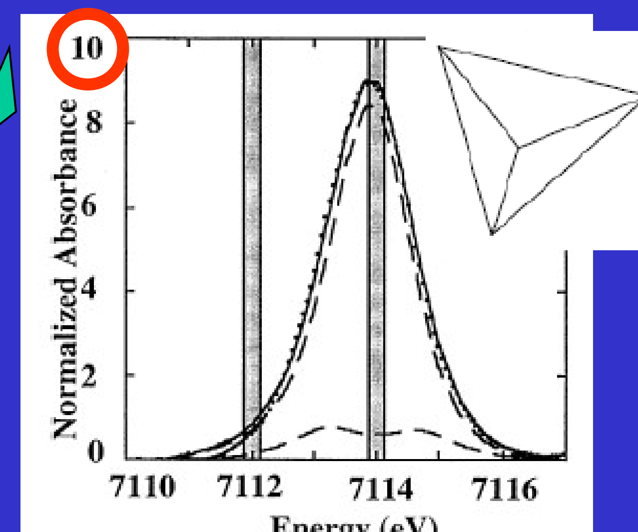
- Octahedral vs Tetrahedral site



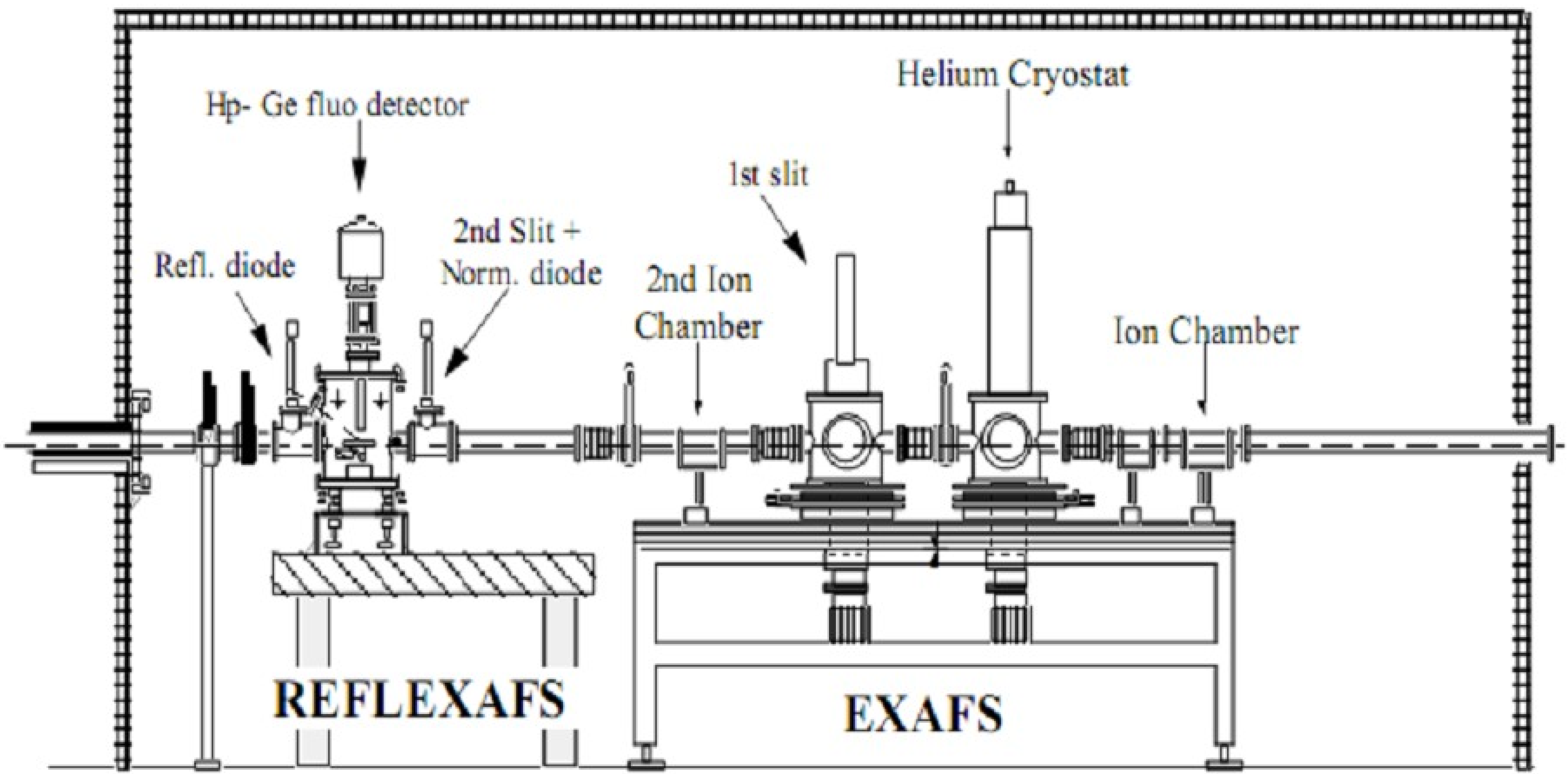
Analysis of the small features before the edge (1s-3d in Fe^{3+} comp.)



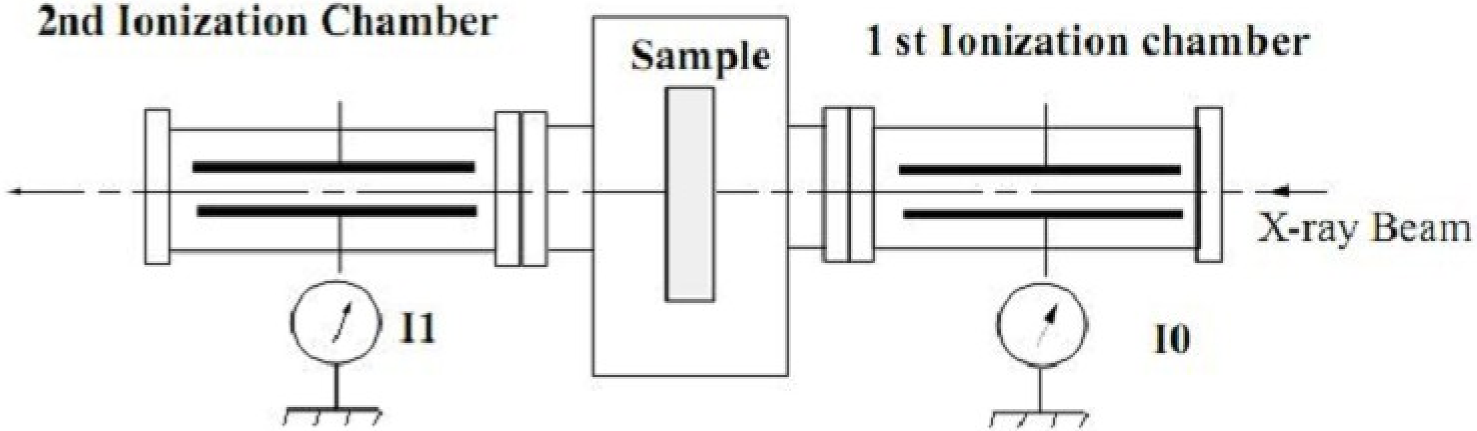




Apparatus for measuring XAS



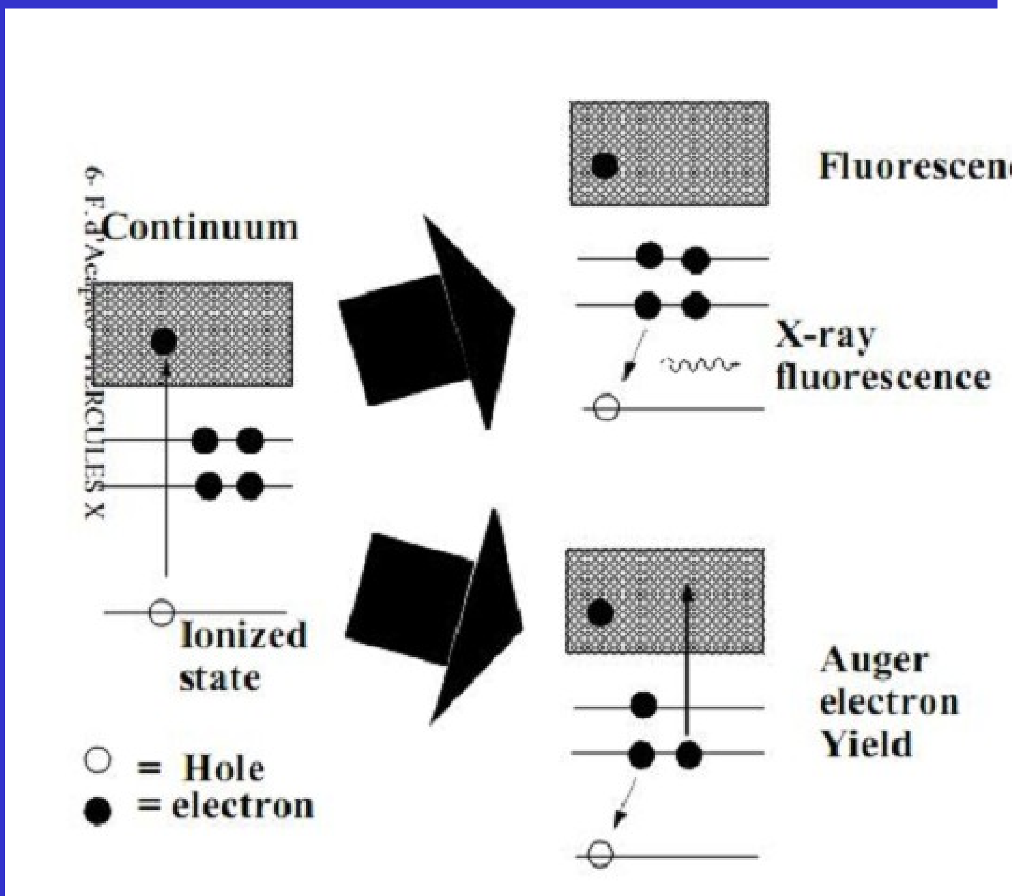
Measuring μ: direct method

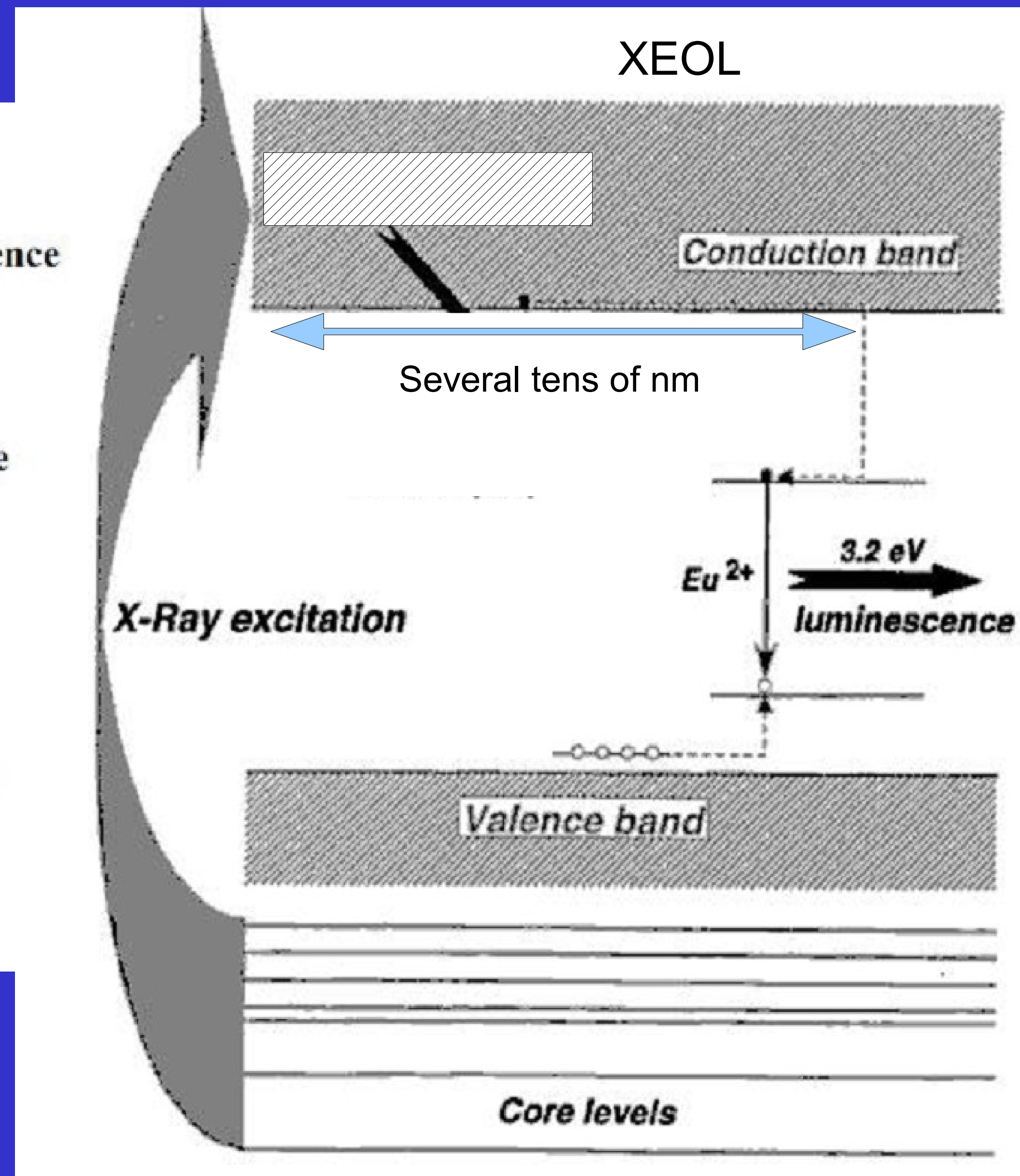


$$I1 = I0 * \exp(-\mu x)$$

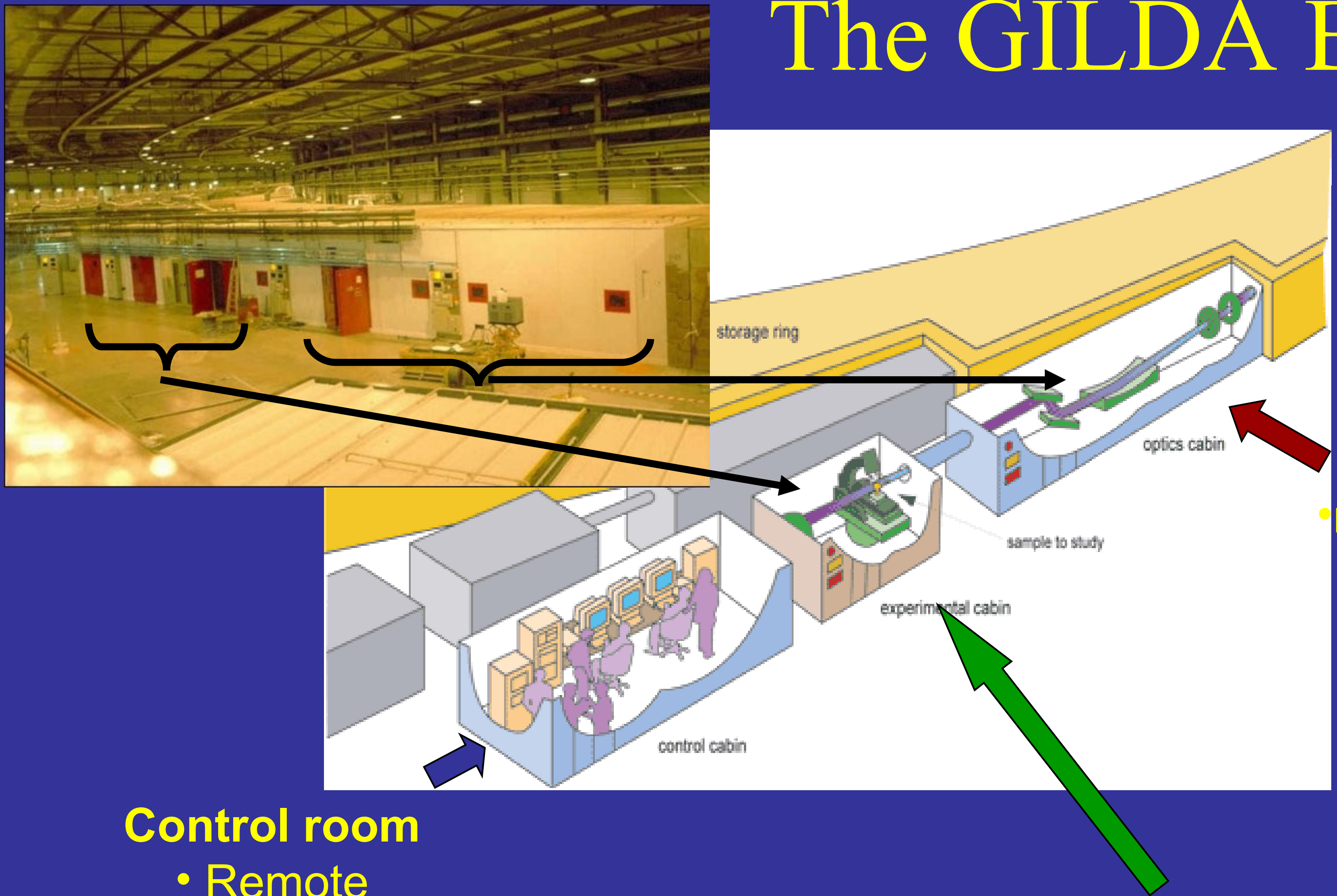
$$\mu = -\ln(I1/I0)$$

Indirect methods





The GILDA Beamline



Optic Hutch
•beam sizing
•mono-chromatization
• focalization

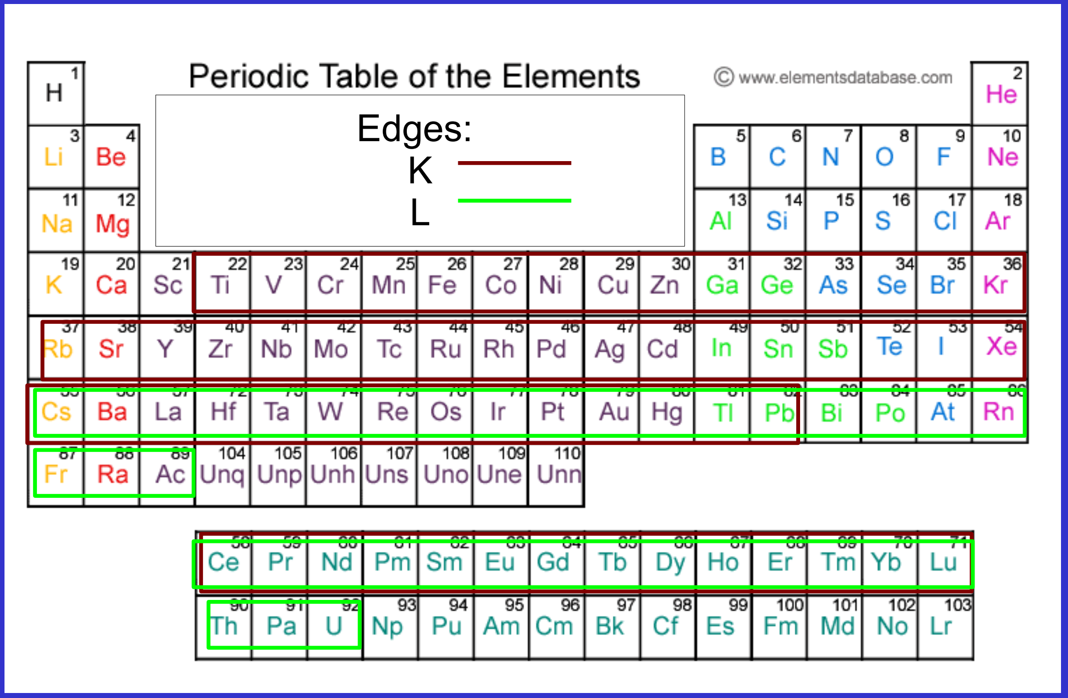
Control room
• Remote instrumentation control
• Data analysis

3 Experimental cabins
• XAS Hutch (Instrumentation for XAS experiments)
• Diffraction Hutch (Instrumentation for XRD experiments)
• "Open Hutch" (Open to user's experimental apparata)

F. d'Acapito et al. ESRF Newsletter **30** (1998), 42

Some figures

- Energy range: 5-90 keV
- Crystals Si(111), (311), (511), (755)
- Beam size 2*1 mm² >> 0.2*0.2 mm²
- Beam intensity 10^{11}-10^{9} ph/s
- HP-Ge detectors for X-ray fluorescence
-



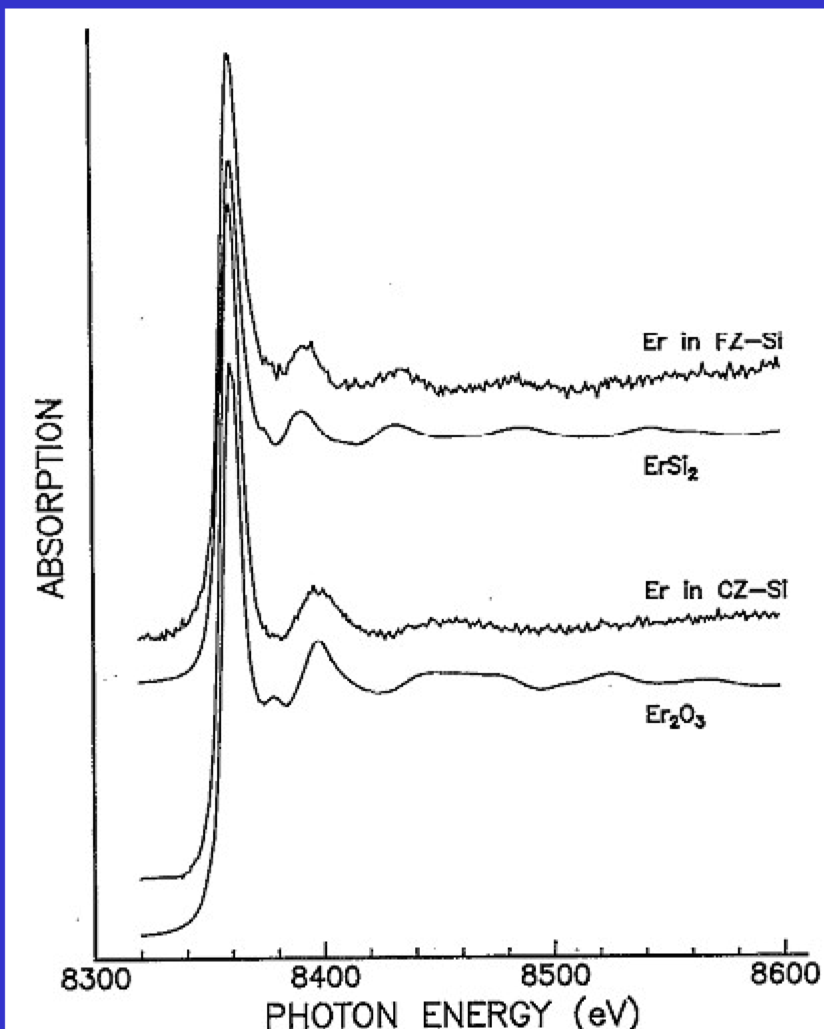
Experimental examples

How the local information from XAS helps in explaining the luminescence properties

Local structure of 1.54-μm-luminescence Er^{3+} implanted in Si

D. L. Adler, D. C. Jacobson, D. J. Eaglesham, M. A. Marcus, J. L. Benton, J. M. Poate, and P. H. Citrin
AT&T Bell Laboratories, Murray Hill, New Jersey 07974

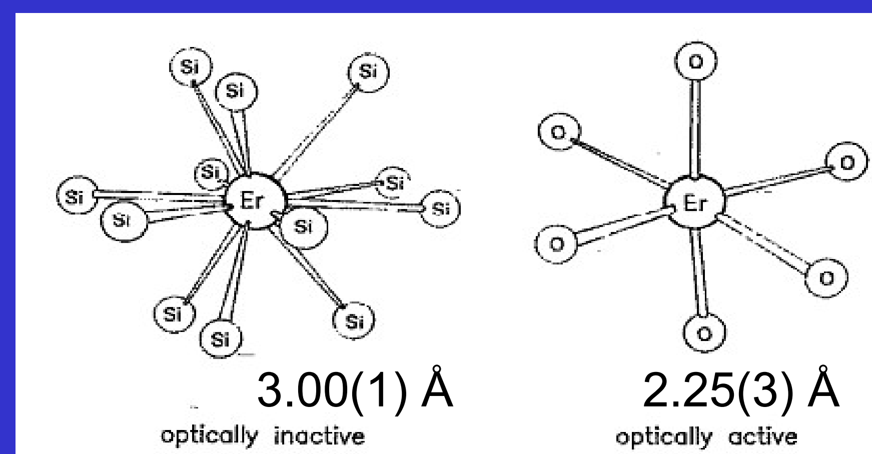
2181 Appl. Phys. Lett. **61** (18), 2 November 1992



1st investigation on link between structure and luminescence

10^{17} Er/cm^3 -implanted Si: FZ vs CZ substrates.

CZ-Si ~100* more luminescent than FZ-Si
CZ-Si contains 10^{18} O/cm^3



Evolution of the local environment around Er upon thermal annealing in Er and O co-implanted Si

A. Terrasi,[a] G. Franzò, and S. Coffa
Consiglio Nazionale delle Ricerche, Istituto Nazionale Metodologie e Tecnologie per la Microelettronica, I-95121 Catania, Italy

F. Priolo
Istituto Nazionale Fisica delle Materia and Dipartimento di Fisica dell'Università, I-95129 Catania, Italy

F. D'Acapito[b]
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S. Mobilio
Istituto Nazionale di Fisica Nucleare and Dipartimento di Fisica, Università di Roma III, I-00146 Rome, Italy

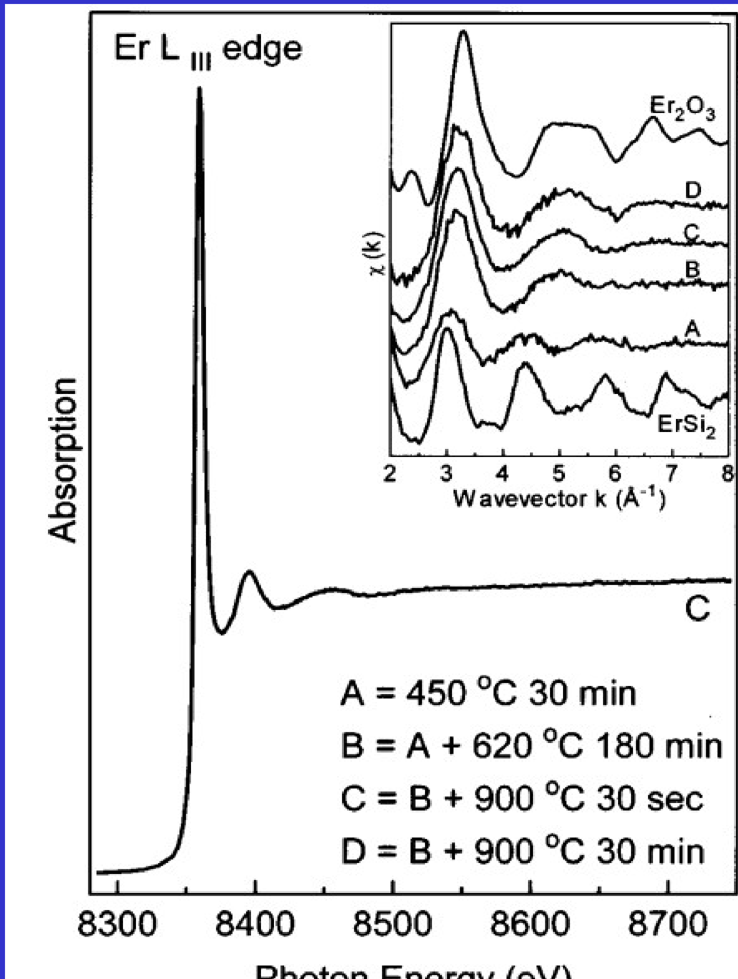
(Received 22 November 1996; accepted for publication 30 January 1997)

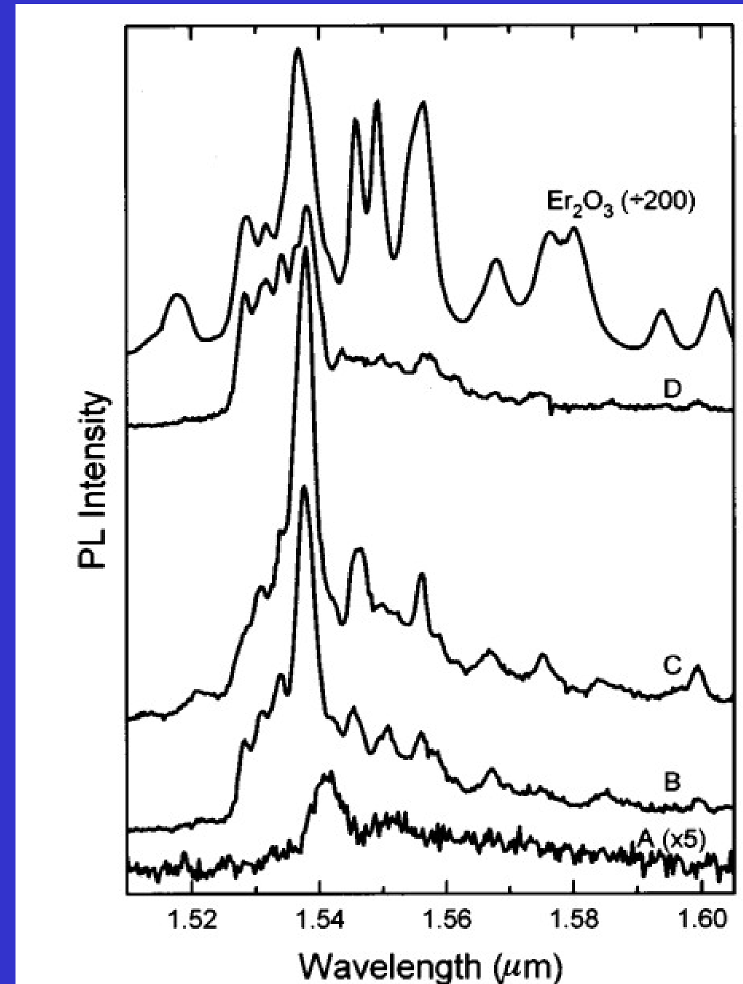
1712 Appl. Phys. Lett. **70** (13), 31 March 1997 0003-6951/97/70(13)/1712/3/$10.00

Er + O implanted FZ Si (resp 10^{19} and 10^{20} /cm^3)

Several Annealing processes to promote re-crystallization and Er-O reaction

Comparison structure-luminescence at each stage





Results

A: Er-Si coordination
B: Er-Si and Er-O
C only Er-O
D only Er-O more ordered

Results

A: barely visible PL
B: presence of PL
C: more intense PL
D: less intense PL respect to C

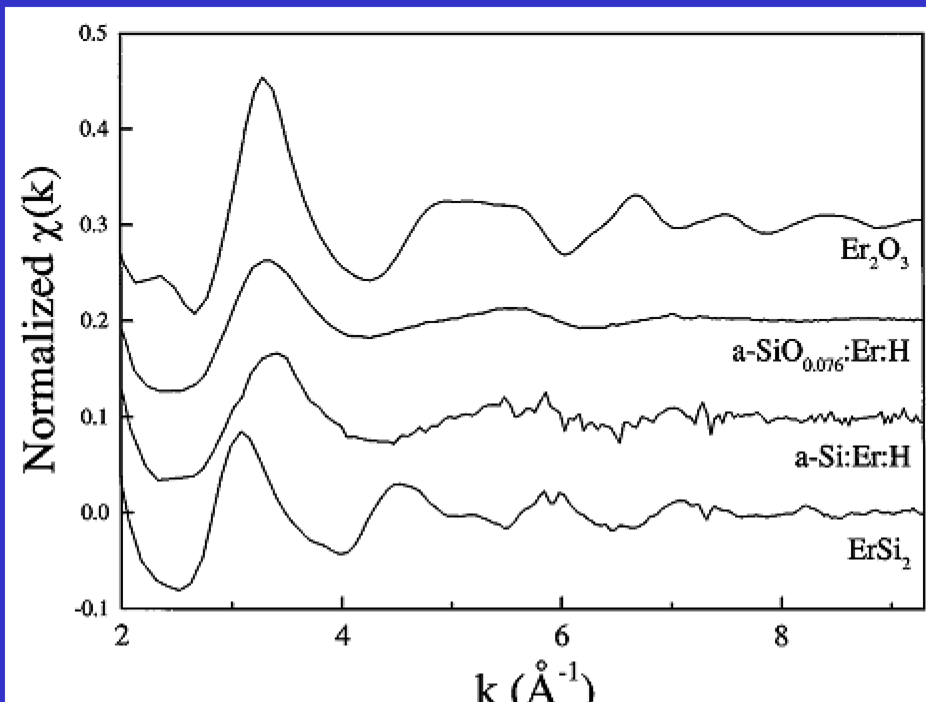
VOLUME 81, NUMBER 21 PHYSICAL REVIEW LETTERS 23 NOVEMBER 1998

Environment of Erbium in *a*-Si:H and *a*-SiO$_x$:H

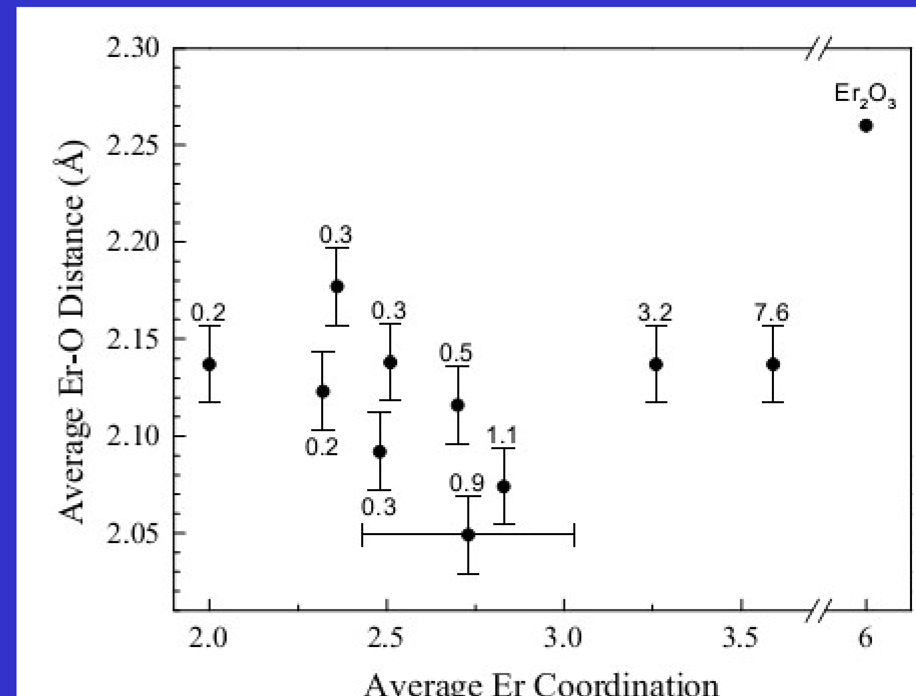
C. Piamonteze, A. C. Iñiguez, and L. R. Tessler
Instituto de Física "Gleb Wataghin," UNICAMP, CP 6165, 13083-970, Campinas, São Paulo, Brazil

M. C. Martins Alves and H. Tolentino
Laboratório Nacional de Luz Síncrotron, CP 6192, 13083-970, Campinas, São Paulo, Brazil
(Received 17 June 1998)

Er:aSi prepared by RF sputtering
Residual O or on purpose O doping at low level.
Creation of ErO_δ complexes with a high luminescence efficiency



EXAFS spectra



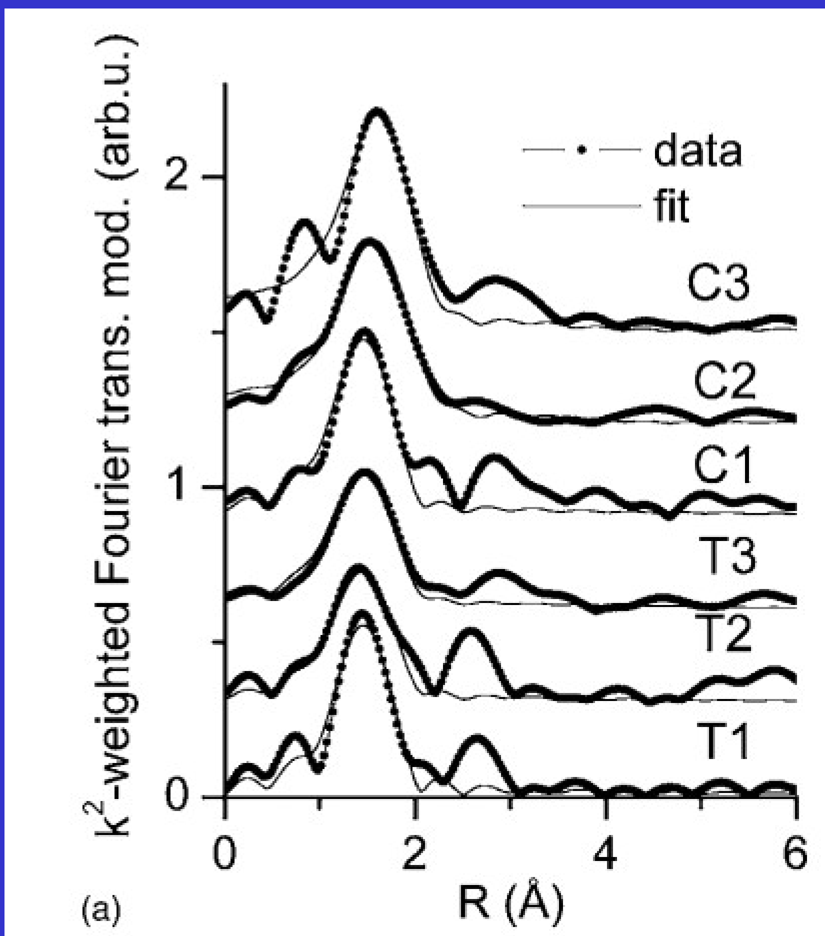
N to R comparison: a lower number of neighbors corresponds to a shorter distance

The non-centrosymmetric environment favours the intra-f emission at 1.54 μm

PHYSICAL REVIEW B **74**, 205428 (2006)

Er site in Er-implanted Si nanoclusters embedded in SiO_2

C. Maurizio,[1,*] F. Iacona,[2] F. D'Acapito,[1] G. Franzò,[3] and F. Priolo[3]
[1]*INFM-CNR, OGG-European Synchrotron Radiation Facility, GILDA-CRG, Boîte Postal 220, F-38043 Grenoble, France*
[2]*CNR-IMM, Sezione di Catania, stradale Primosole 50, I-95121 Catania, Italy*
[3]*MATIS CNR-INFM and Dipartimento di Fisica e Astronomia, Università di Catania, via Santa Sofia 64, I-95123 Catania, Italy*
(Received 12 July 2006; revised manuscript received 11 September 2006; published 22 November 2006)

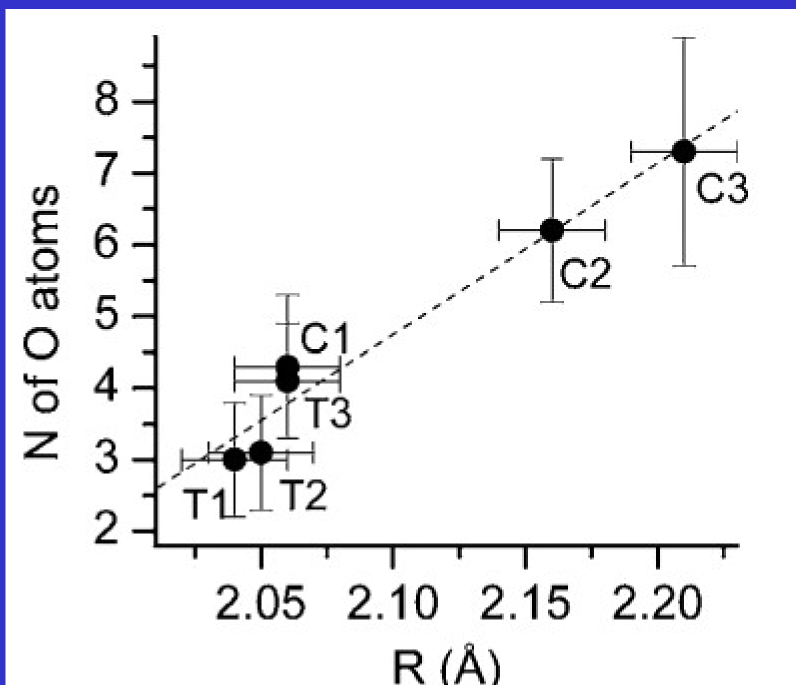


Er-implanted sub-stoichiometric Silica.
Formation of Si nanoclusters (nc)

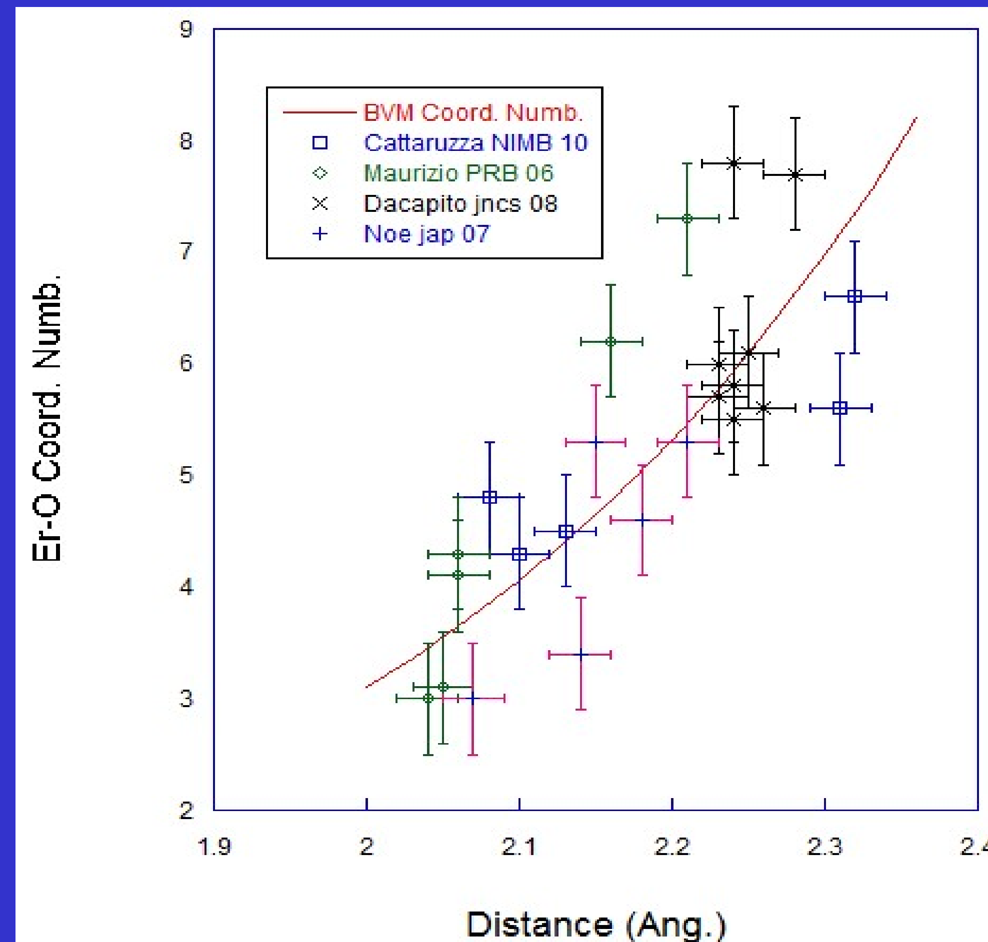
T1-T3 different Si-nc size
C1-C2 like T3 different Er content.

sample	Preimplantation annealing temperature (°C)	Er concentration (cm^{-3})
*T*1		5.3×10^{19}
*T*2	800	5.3×10^{19}
*T*3	1250	5.3×10^{19}
*C*1	1250	4.5×10^{19}
*C*2	1250	1.6×10^{20}
*C*3	1250	1.0×10^{21}

Neighbors vs bond length

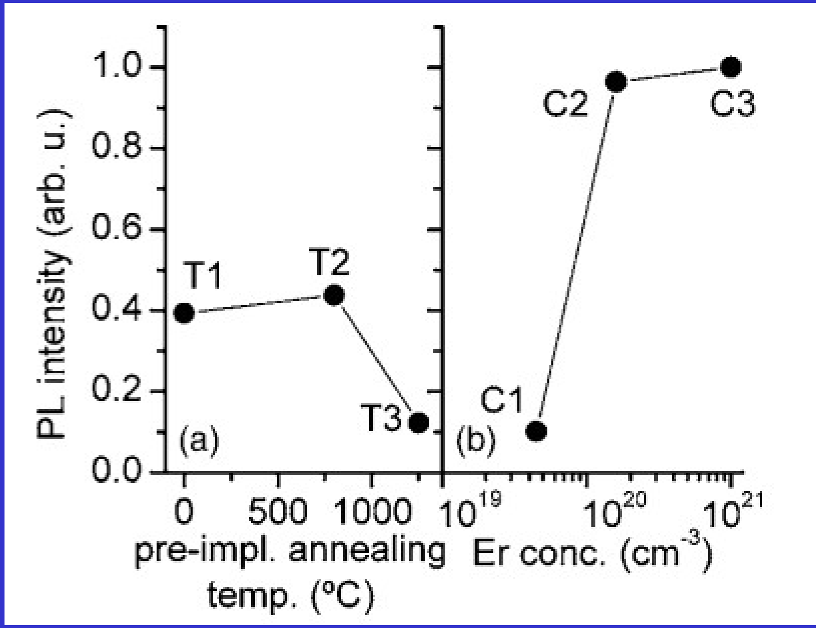


Experimental data

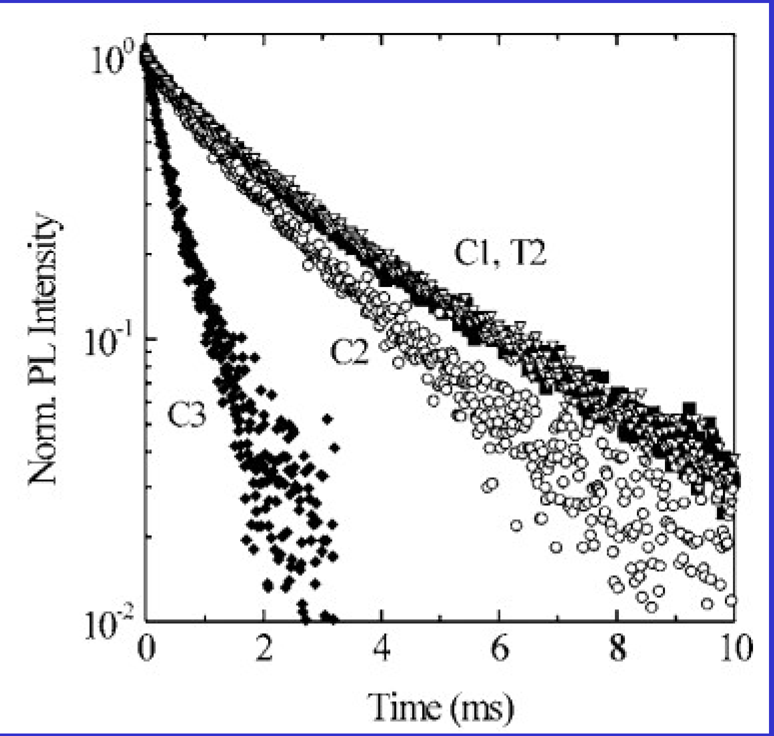


Experimental data vs prediction of Bond Valence Method

PL properties



Intensity



Life time

Low-O-coordinated Er plus small NC enhance the PL response

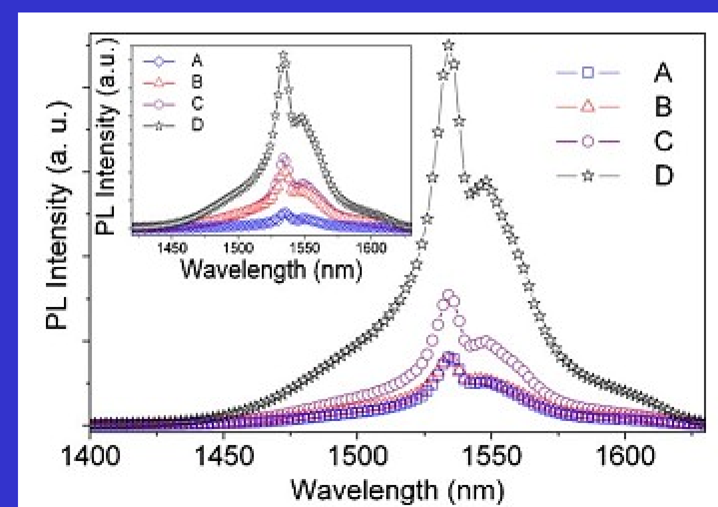
JOURNAL OF APPLIED PHYSICS **102**, 103516 (2007)

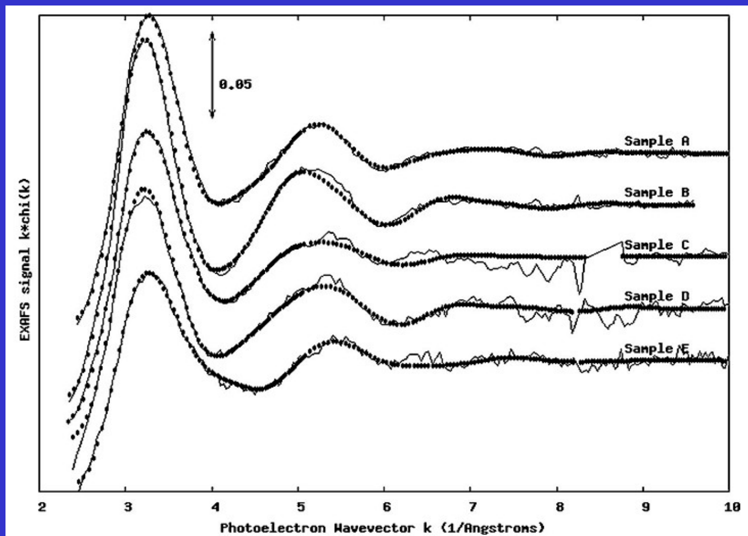
Effect of the Er-Si interatomic distance on the Er^{3+} luminescence in silicon-rich silicon oxide thin films

P. Noé,[a] B. Salem,[b] E. Delamadeleine, D. Jalabert, and V. Calvo
Laboratoire Silicium Nanoélectronique Photonique et Structure, DRFMC/SP2M, Commissariat à l'Energie Atomique, 17 rue des Martyrs, F-38054 Grenoble Cedex, France

C. Maurizio and F. D'Acapito
CNR-INFM-OGG c/o ESRF, GILDA-CRG, 6, Rue Jules Horowitz, F-38043 Grenoble, France

Er:SiO layers obtained by coevaporation
Different atmosphere for the process: vacuum (A), O2 (B), NH3 (C, D, E).

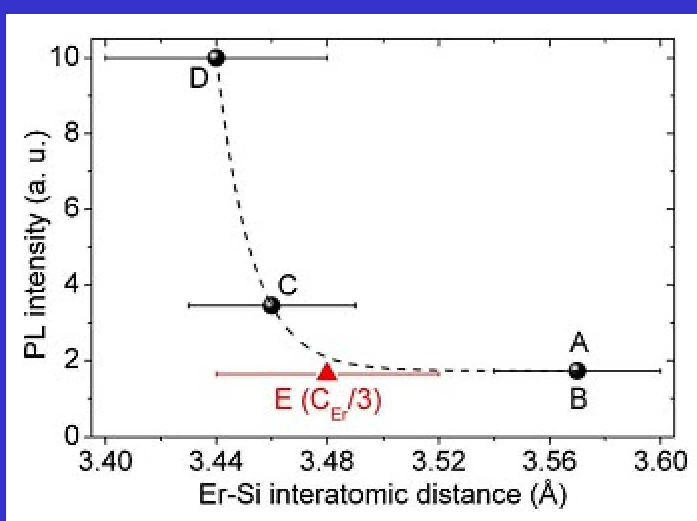




EXAFS experimental data + modelization

Sample	N	$R_{Er\text{-}O}$ (Å)	$R_{Er\text{-}Si}$ (Å)
A	4.6(2)	2.18(1)	3.57(3)
B	5.3(3)	2.21(1)	3.57(3)
C	5.3(3)	2.15(1)	3.46(3)
D	3.4(1)	2.14(2)	3.44(4)
E	3.0(2)	2.07(2)	3.48(4)

Quantitative results



Effect of the local order on the PL intensity
Again, the lowest coordinated Er has shorter Er-O and Er-Si bonds and presents the more intense PL

X-ray absorption fine structure determination of the local environment of Er^{3+} in glass

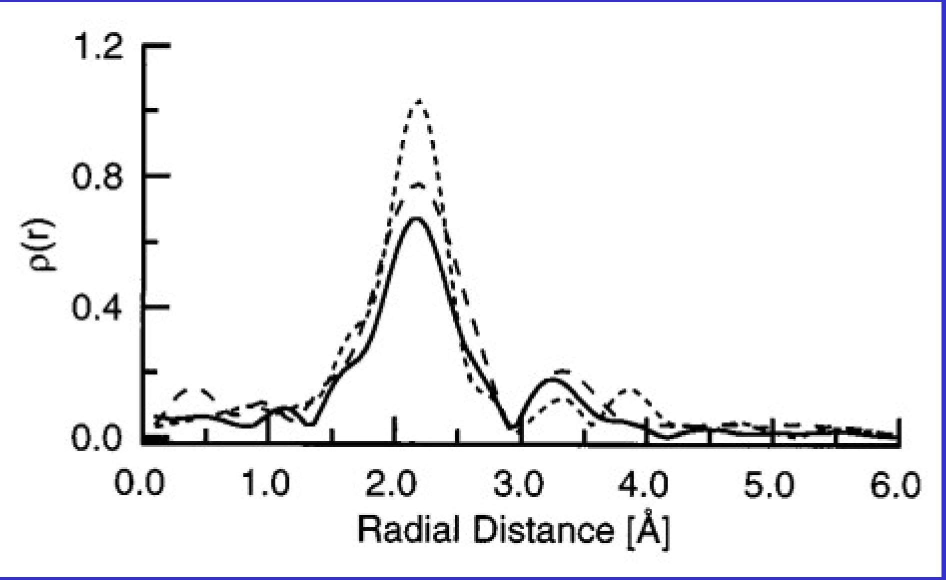
Appl. Phys. Lett. **70** (5), 3 February 1997

P. M. Peters[a)] and S. N. Houde-Walter
The Institute of Optics, University of Rochester, Rochester, New York 14627

Looking for the origin of concentration quenching

Various glasses: Aluminosilicate, (AS) Fluorosilicate (FS), Phosphate(P)

Er concentration between 0.08mole% and 3 mole%



FT of the highest Er glasses: AS (line),FS (long dashes), P (short dashes)

The second shell can be explained with Er-(SI, Al , O, P...)
No evidence of Er-Er coordination

JOURNAL OF APPLIED PHYSICS VOLUME 90, NUMBER 1 1 JULY 2001

Luminescent properties of local atomic order of Er^{3+} and Yb^{3+} ions in aluminophosphate glasses

F. d'Acapito[a)]
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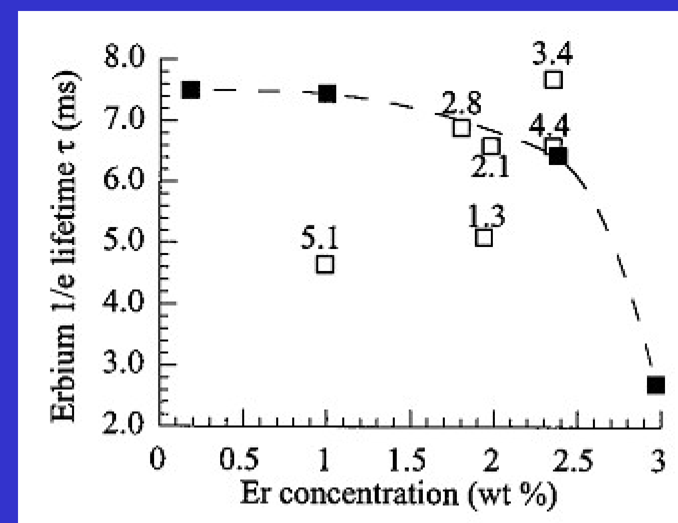
S. Mobilio
Università Roma Tre' Via della Vasca Navale 84, I-00146 Roma, Italy

P. Bruno, D. Barbier, and J. Philipsen
Teemphotonics 13, Chemin du Vieux Chêne, F-38240 Meylan, France

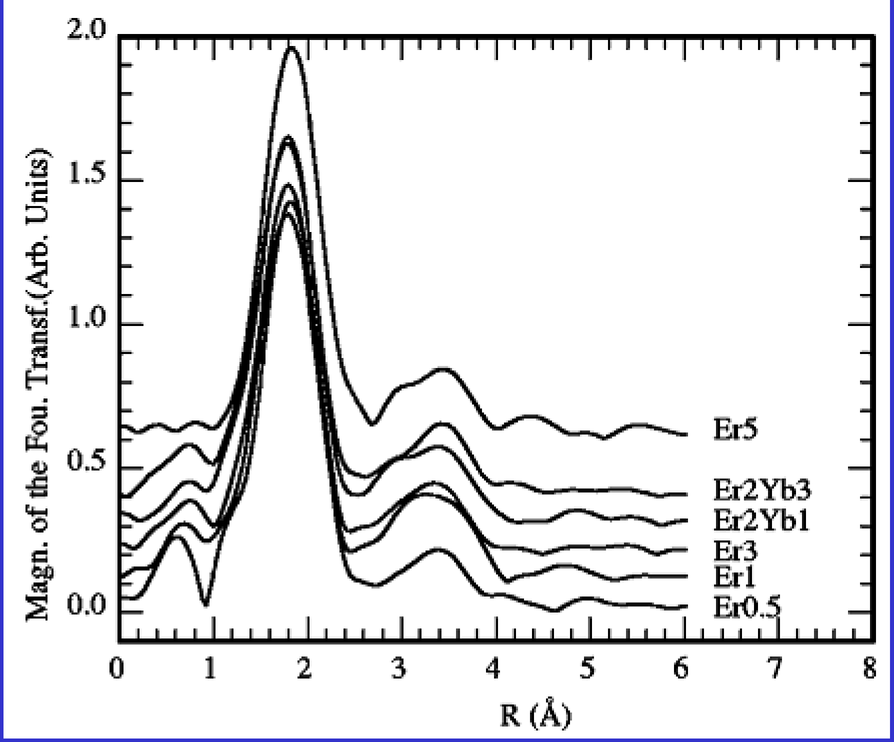
Looking for the origin of concentration quenching

Er Phosphate glasses obtained by melt

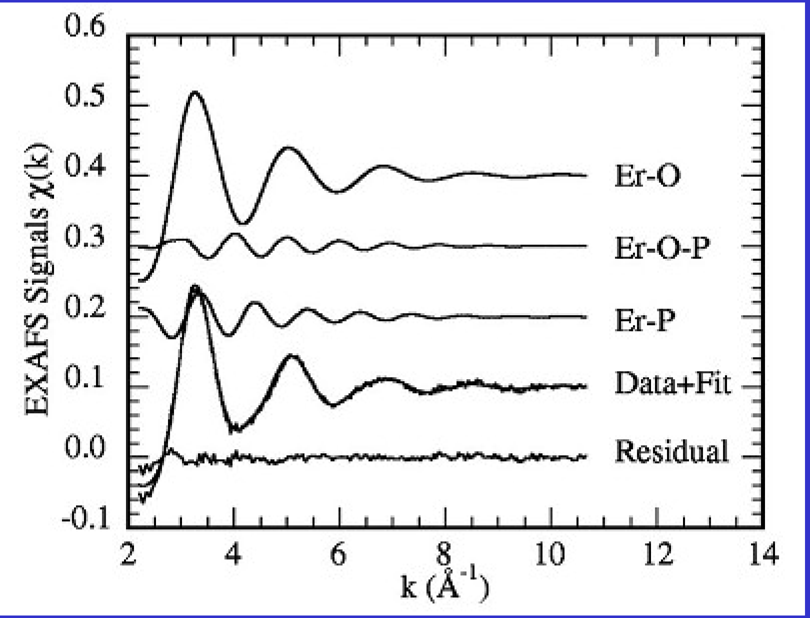
Is concentration quenching due to a direct Er-Er bond ?



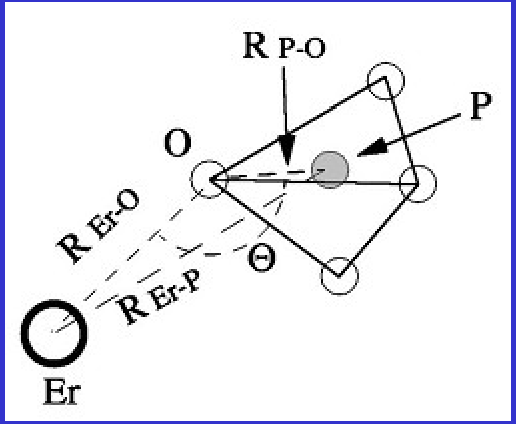
PL lifetime as a function of the Er concentration



Fourier Transforms of the EXAFS data.
A second shell is clearly visible but it is present on all the samples



Data fitting with the proposed structural model



The second shell is due to Er-P coordination bridged by an O. Er-O-P angle well defined

PHYSICAL REVIEW B **69**, 153310 (2004)

Structure of Er-O complexes in crystalline Si

F. d'Acapito*
INFM-OGG, c/o GILDA CRG-ESRF, Boîte Postale 220, F-38043 Grenoble, France

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Dipartimento di Fisica, Universitá Roma Tre, Via della Vasca Navale 84, I-00146 Roma, Italy

S. Scalese
CNR-IMM, Stradale Primosole 50, I-95121 Catania, Italy

A. Terrasi, G. Franzó, and F. Priolo
INFM and Dipartimento di Fisica, Universitá di Catania, Corso Italia 57, I-95129 Catania, Italy

Sample	N_{Er-O} ± 0.6	R_{Er-O} ± 0.02 Å	$\Theta_{Er-O-Si}$ ± 4 deg	R_{Er-Si} ± 0.03 Å
33	5.7	2.22	134	3.55
33C	5.6	2.22	137	3.59
33D	5.7	2.23	135	3.62
33E	5.5	2.23	137	3.60
49	5.0	2.23	135	3.58
49C	5.8	2.22	136	3.58
49D	5.8	2.23	137	3.59
49E	4.8	2.24	136	3.59
145AD	5.5	2.23	138	3.62
92AB	5.9	2.25	136	3.63

ELSEVIER Journal of Non-Crystalline Solids 293–295 (2001) 118–124
www.elsevier.com/locate/jnoncrysol

Local order around Er^{3+} ions in SiO_2–TiO_2–Al_2O_3 glassy films studied by EXAFS

F. d'Acapito [a,*], S. Mobilio [b], P. Gastaldo [c], D. Barbier [d], Luís F. Santos [e], Orlando Martins [e], Rui M. Almeida [e]

Sample	N_{Er-O} ± 0.6	$R_{Er-O} \pm 6 \times 10^{-4}$ (nm)	$\Theta_{Er-O-SNN}$ ± 3 (deg)	$R_{Er-SNN} \pm 1 \times 10^{-3}$ (nm)
0A0.2	6.8	0.2269	140	0.359
0A0.5	6.7	0.2271	141	0.363
9A0.2	6.4	0.2245	135	0.361
9A0.5	6.6	0.2265	135	0.365
9A1.0	6.2	0.2257	136	0.364
9A1.75	6.1	0.2256	138	0.362
0A0.25	6.7	0.2275	142	0.360
2A0.25	6.7	0.2277	140	0.361
5A0.25	6.6	0.2266	138	0.362
7A0.25	6.7	0.2265	137	0.365
9A0.25	6.5	0.2260	137	0.363
11A0.25	6.6	0.2258	136	0.365
17A0.25	6.6	0.2251	133	0.365

Er-O-NN angle well defined, about 138 ± 4 deg

APPLIED PHYSICS LETTERS VOLUME 78, NUMBER 18 30 APRIL 2001

Local environment of rare-earth dopants in silica–titania–alumina glasses: An extended x-ray absorption fine structure study at the *K* edges of Er and Yb

F. d'Acapito[a)]
Istituto Nazionale per la Fisica della Materia—OGG, 6 Rue Jules Horowitz, F-38043 Grenoble, France

S. Mobilio
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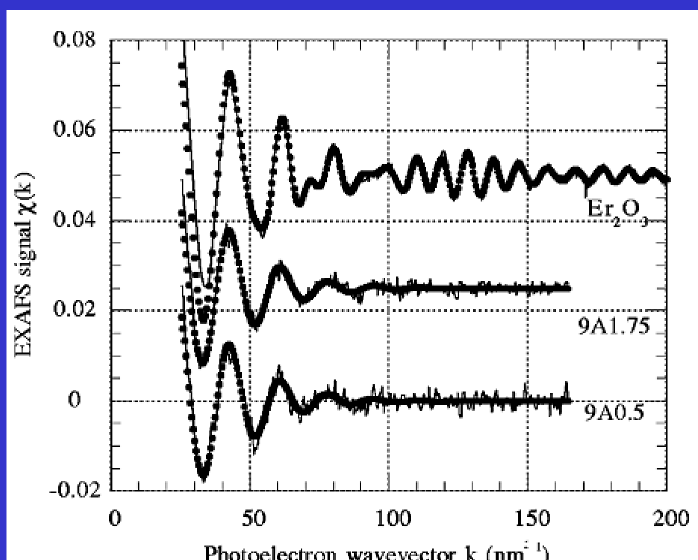
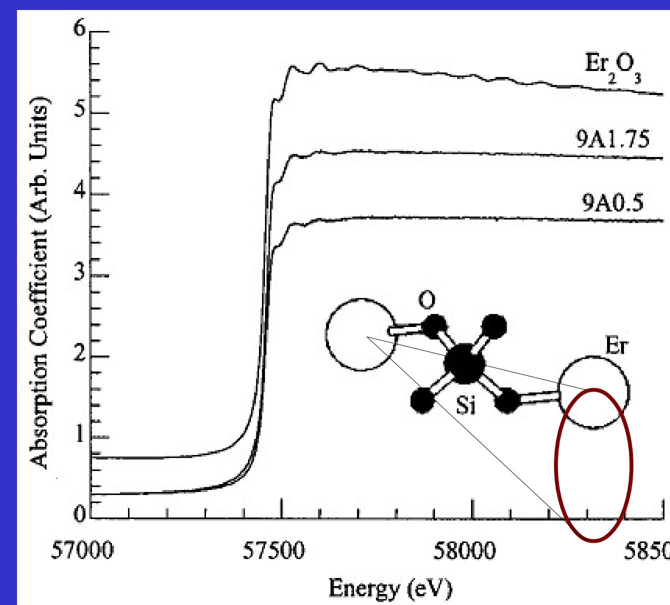


EXAFS data



Proposed model for Er clustering: two ions bound to the same SiO4 tetrahedron

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Materials Science and Engineering B 146 (2008) 167–170

Role of CaO addition in the local order around Erbium in SiO_2–GeO_2–P_2O_5 fiber preforms

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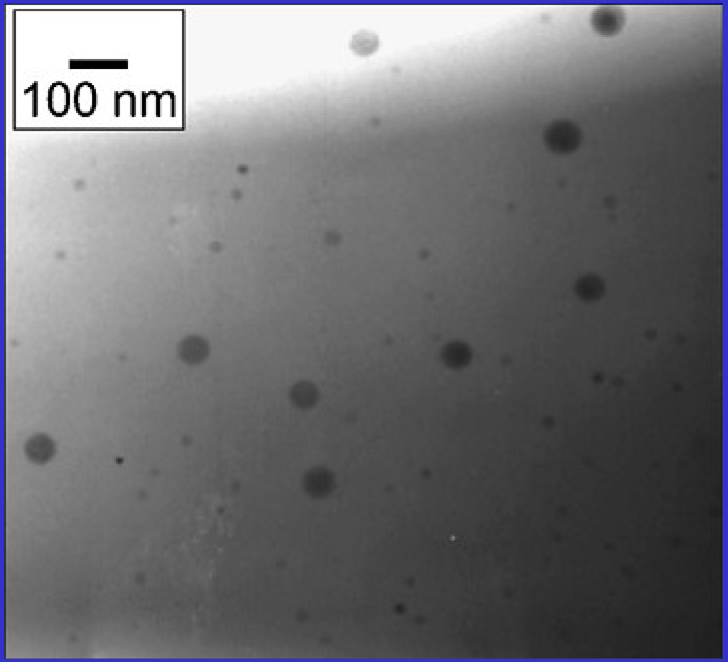
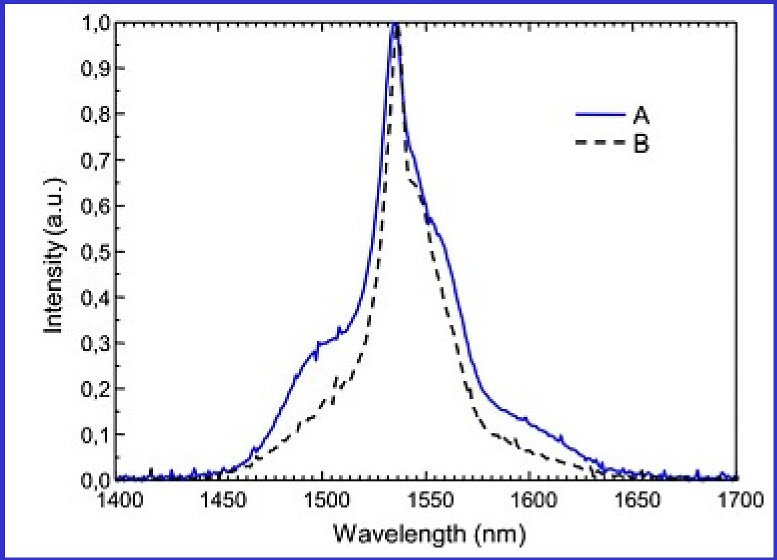
Investigation on fibre preforms (diam. ~500 µm)
Glass: SiO2–GeO2–P2O5–Er2O3 with (A) and without (B) CaO



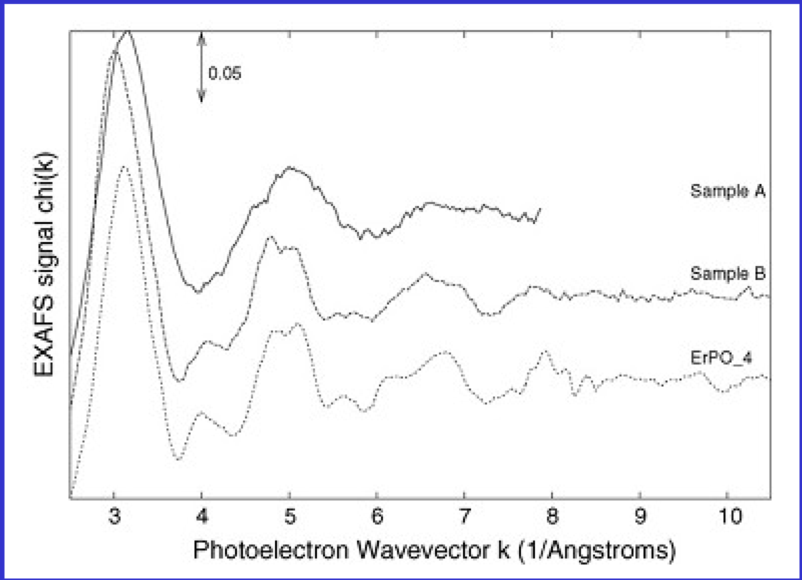
TEM of an A sample

- The addition of Ca promotes the formation of nanoparticles
- NP rich in Ca, P, Er
- NP amorphous

PL and local structure



PL of A and B samples: the former is broader and less structured



EXAFS
A: glassy like spectrum (only a single frequency)
B: modulated spectrum identical to ErPO4.

Conclusion
Er has a strong affinity with P to form ErPO4 and the addition of Ca helps in dispersing Er

Journal of Non-Crystalline Solids 354 (2008) 4940–4943

Contents lists available at ScienceDirect

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journal homepage: www.elsevier.com/locate/jnoncrysol

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EXAFS study of the Er^{3+} ion coordination in SiO_2–TiO_2–HfO_2 sol–gel films

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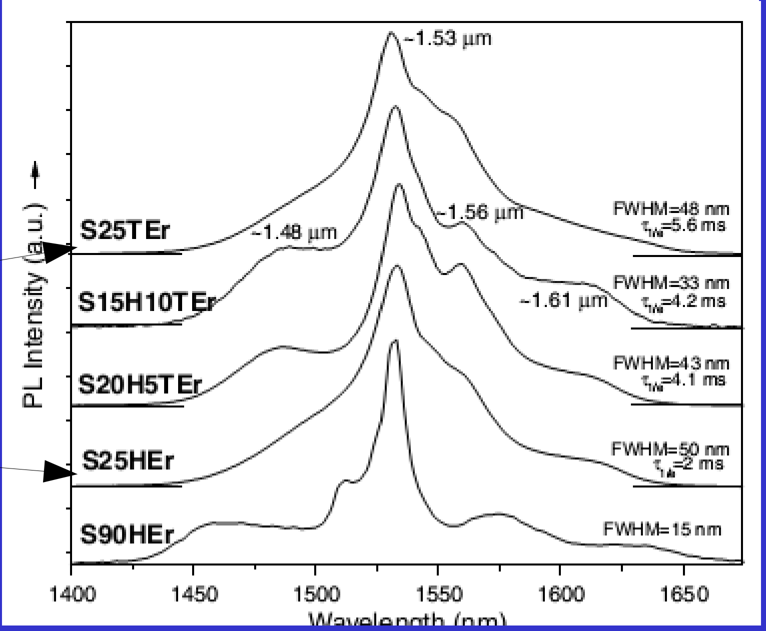
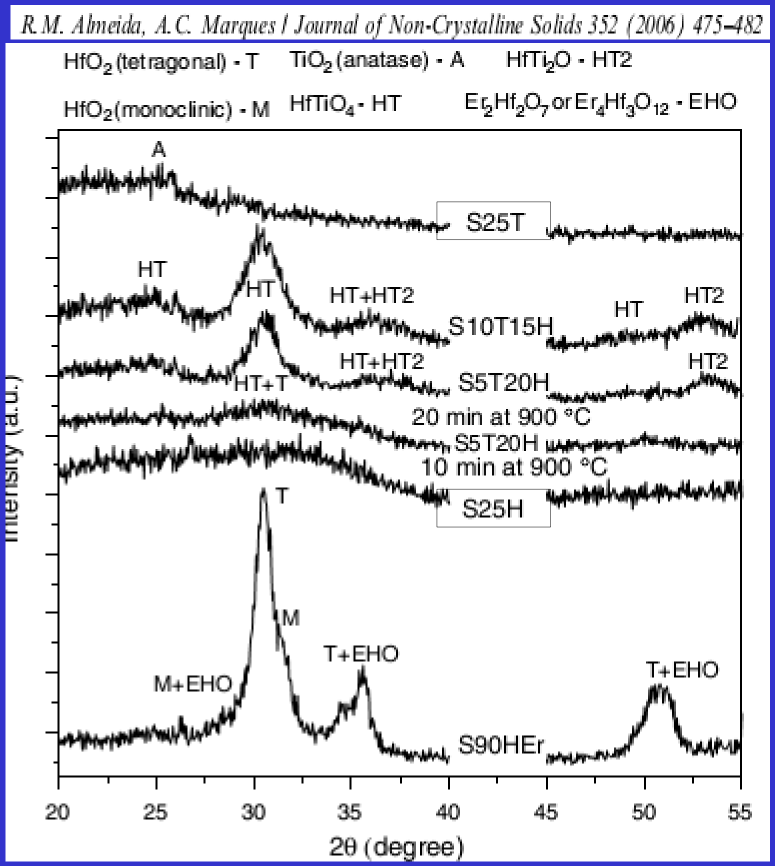
Silica-Titania-Hafnia layers produced by sol-gel

Several annealing treatments

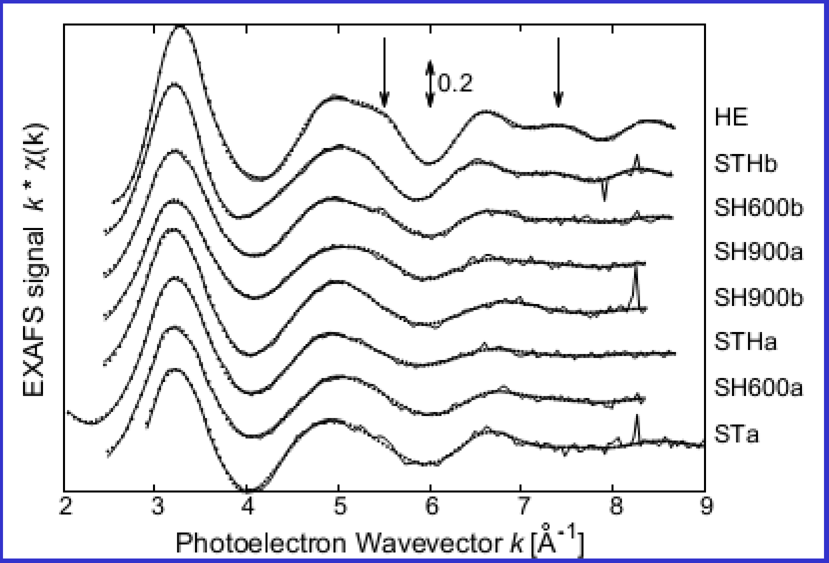
Acronym	Composition (molar ratio)	Densification heat-treatment	Post-implantation heat-treatment
STa	75 SiO_2–25 TiO_2	5 min @ 600 °C	10 min @ 600 °C
STHa	75 SiO_2–10 TiO_2–15 HfO_2	5 min @ 600 °C	10 min @ 600 °C
STHb	75 SiO_2–10 TiO_2–15 HfO_2	5 min @ 600 °C	5 min @ 900 °C
SH600a	75 SiO_2–25 HfO_2	5 min @ 600 °C	10 min @ 600 °C
SH600b	75 SiO_2–25 HfO_2	5 min @ 600 °C	5 min @ 900 °C
SH900a	75 SiO_2–25 HfO_2	5 min @ 900 °C	10 min @ 600 °C
SH900b	75 SiO_2–25 HfO_2	5 min @ 900 °C	5 min @ 900 °C

R.M. Almeida, A.C. Marques / Journal of Non-Crystalline Solids 352 (2006) 475–482





XRD from samples



No evidence of crystallization
PL remains broad
Evidence of Er-Hf
coordination upon annealing

Optical Materials 34 (2012) 660–664

Contents lists available at SciVerse ScienceDirect

Optical Materials

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Incorporation of Yb^{3+} ions in multicomponent phase-separated fibre glass preforms

C.I. Oppo [a], R. Corpino [a], P.C. Ricci [a], M.C. Paul [b], S. Das [b], M. Pal [b], S.K. Bhadra [b], S. Yoo [c], M.P. Kalita [c], A.J. Boyland [c], J.K. Sahu [c], P. Ghigna [d], F. d'Acapito [e,*]

Phase separated fibers: a way to insert Yb in crystalline environment
Yb-doped Yttria-Alumina-Silica with P2O5. Target: obtain Yb-doped Y2O3.

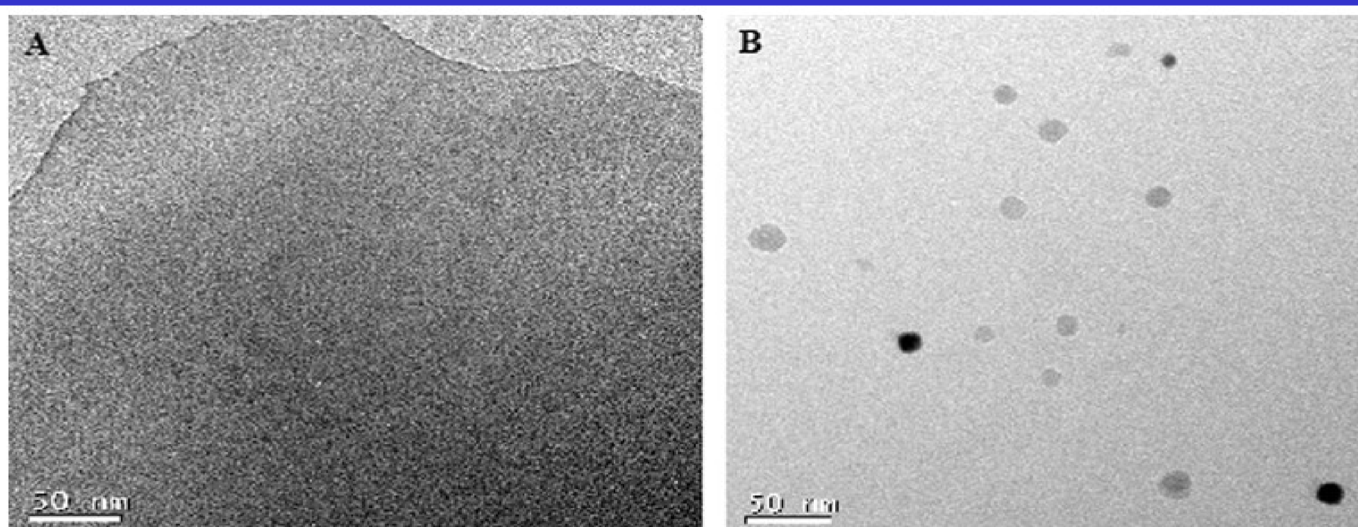
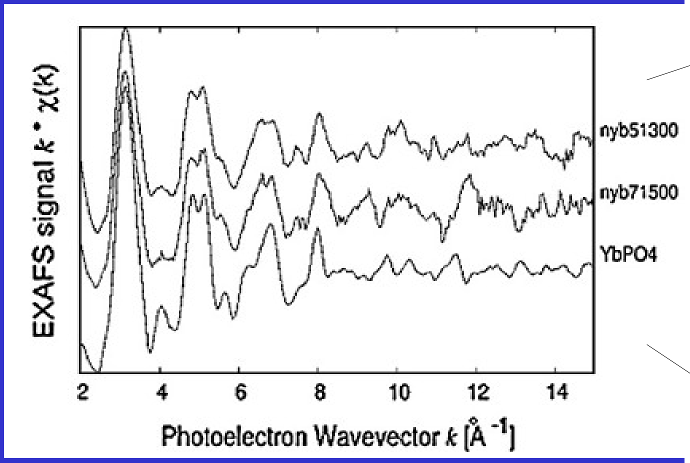
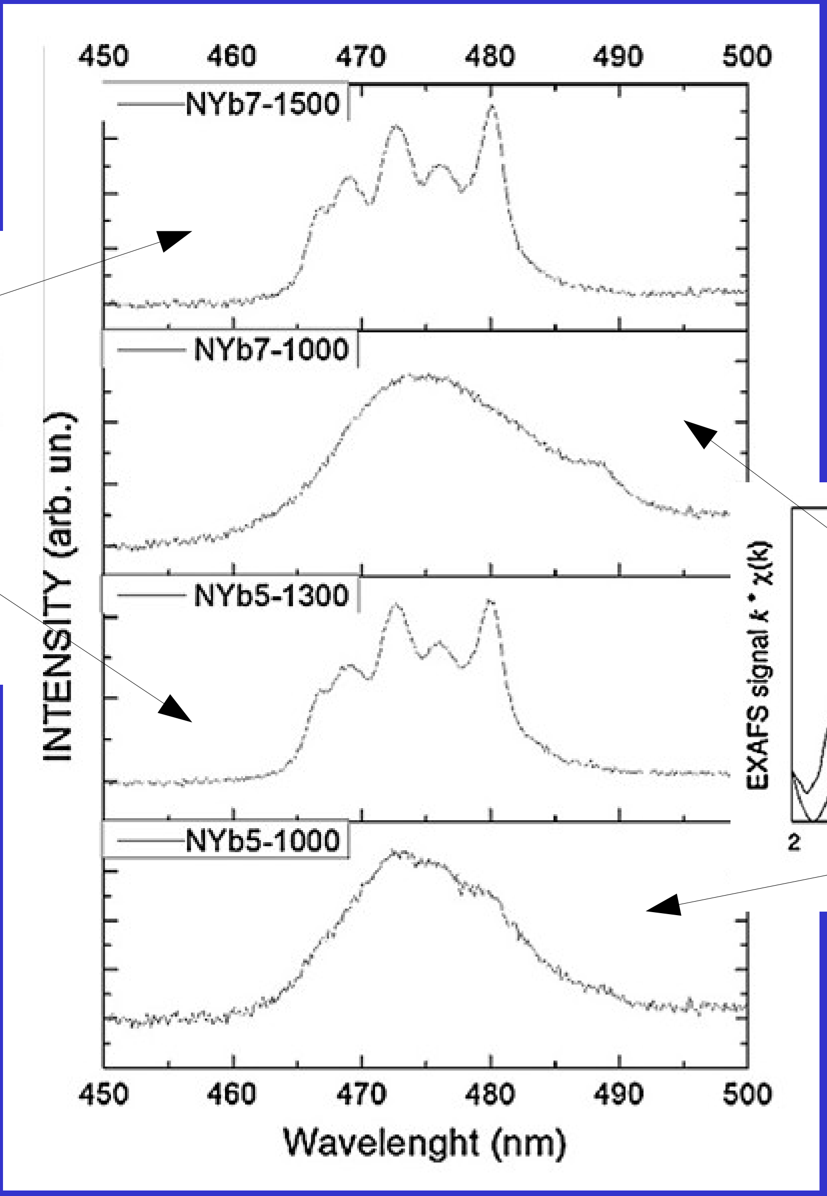


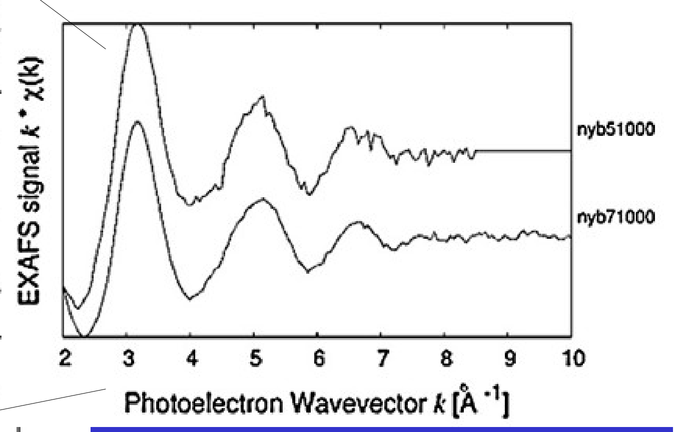
Fig. 1. TEM pictures two annealed preform samples (A) NYb5-1000 annealed at 1000 °C and (B) NYb5-1300 annealed at 1300 °C.

Structure & PL



EXAFS high temp samples





EXAFS low temp samples

Anti-stokes PL, λ_{exct} = 978 nm

Conclusion

XAS is a tool for accessing the local structure of dopants in glassy matrices.

REs in glasses: clear link between structure and optical properties.