The GILDA project

http://www.esrf.eu/UsersAndScience/Experiments/CRG/BM08/

F. d'Acapito

CNR-IOM-OGG

dacapito@esrf.fr

LAYOUT

- Beamline Description
- Facts and figures
- Scientific Highlights
- Perspectives

Description

Where ?

Grenoble
(France)

ESRF
European Synchrotron
Radiation Facility

ILL
Institut Laue-Langevin
Neutron Source

The landscape

Surrounded by world-class institutes

General infos

Funding
CNR + INFN

Operative since
1994

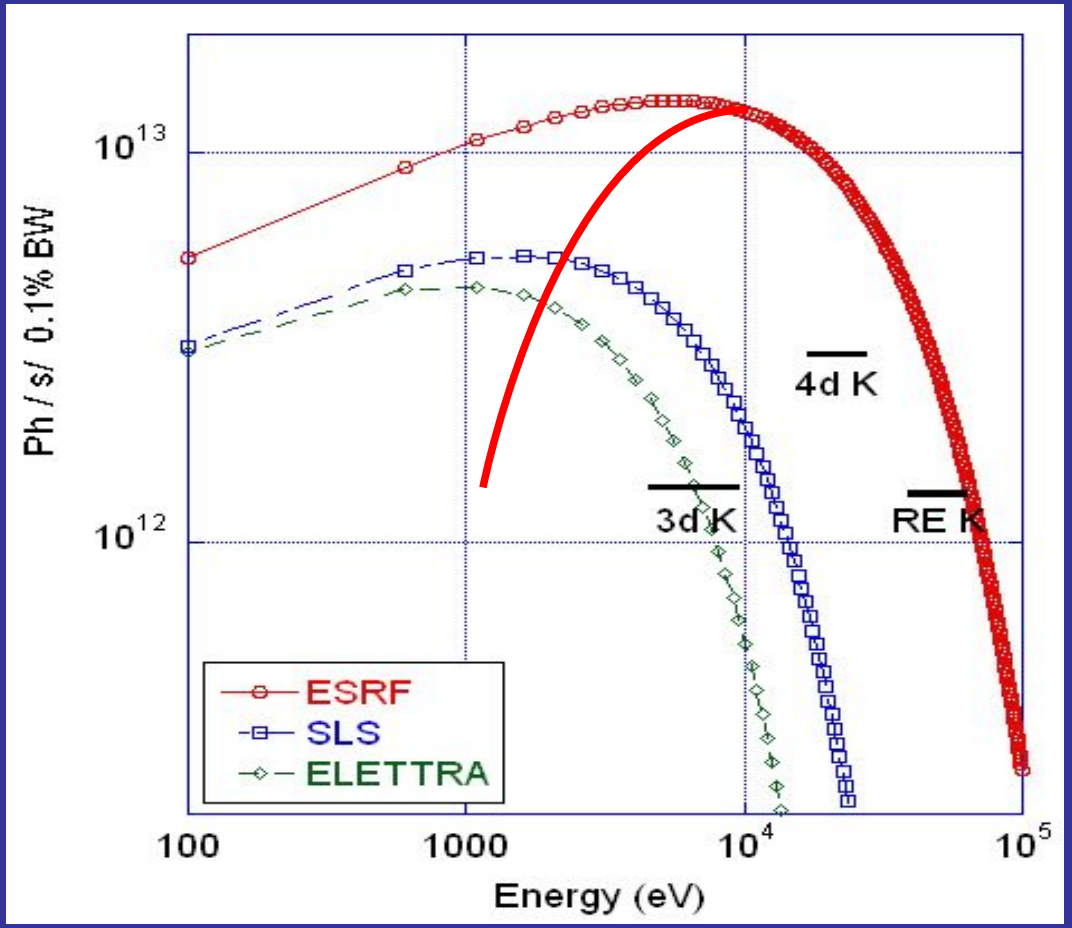
Scientific goal
Study of the structure of materials
and its relation with their mocroscopic properties

Experimental techniques
- X-ray absorption spectroscopy
- X-ray powder diffraction

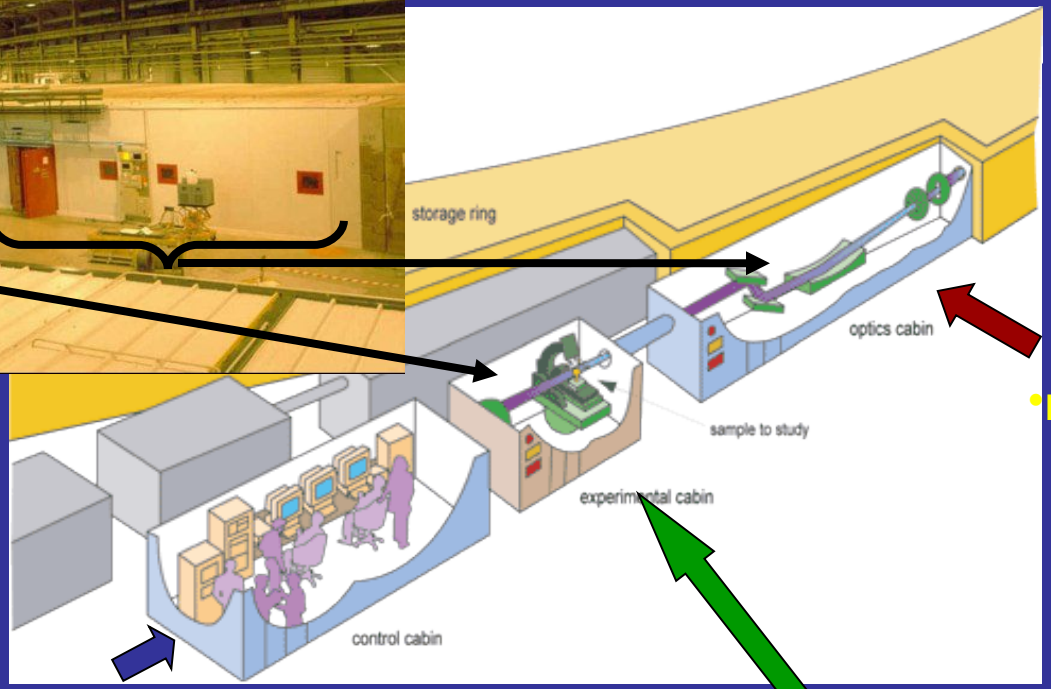
General Features

Source: bending Magnet

- Energy range **complementary** to ELETTRA
- Energy range 4 – 85 keV
- Resolution $\Delta E/E = 10^{-4}$-10^{-5}
- Flux on the sample 10^{9} – 10^{11} ph/s
- Spot size 1*1 > 0.1*0.1 mm^2



Beamline layout



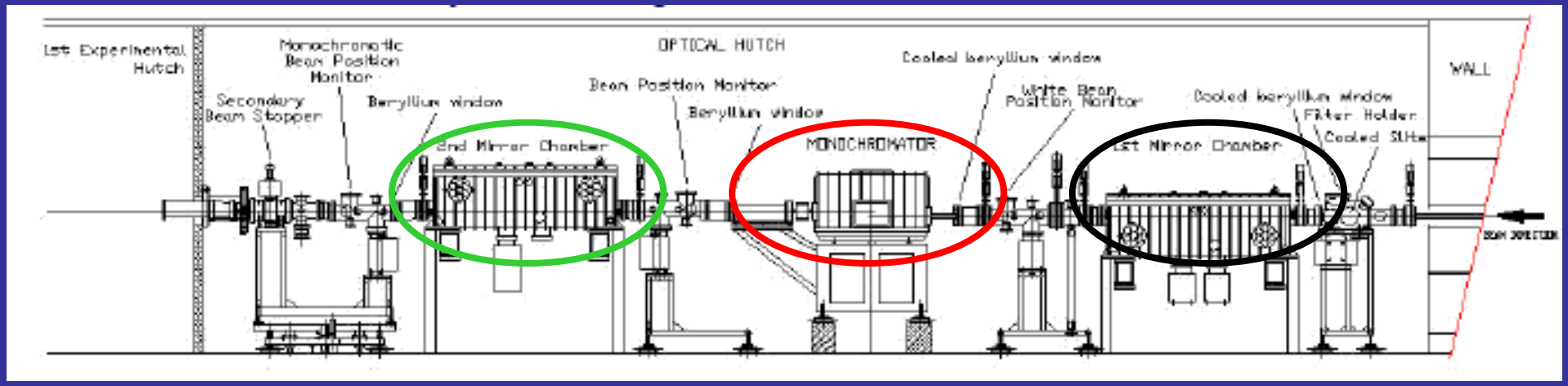
Optic Hutch
- beam sizing
- mono-chromatization
- focalization

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

X-ray optics

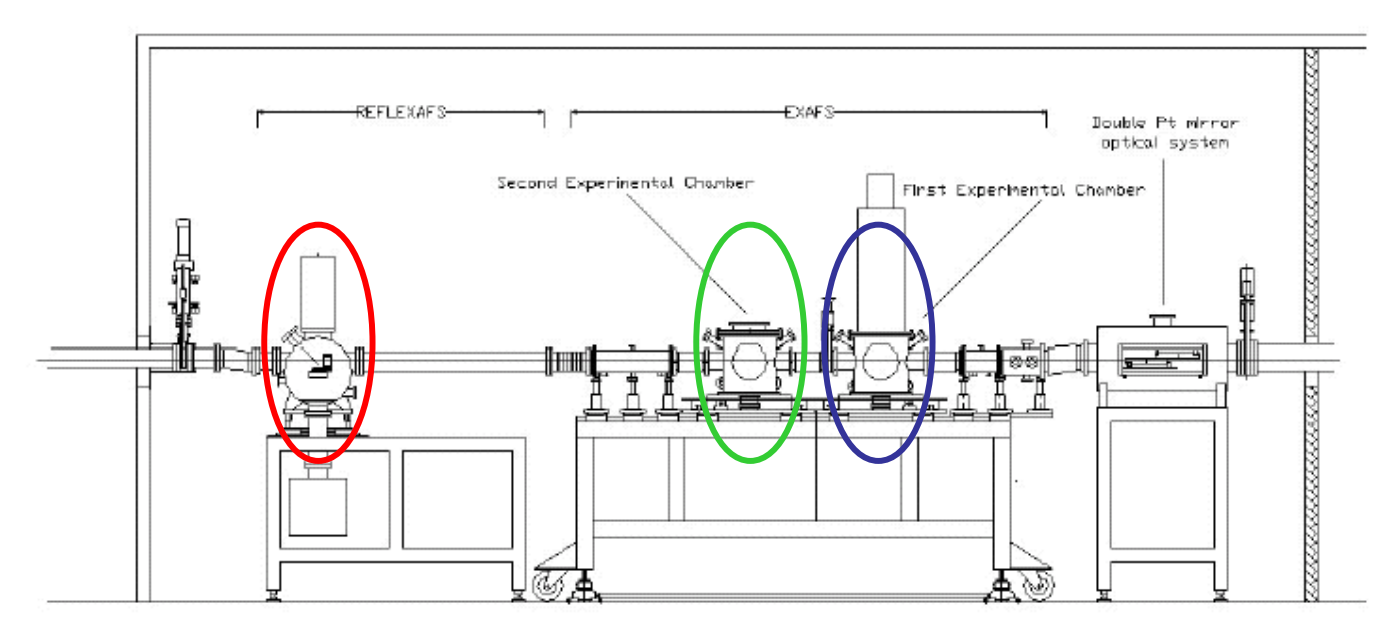


1st collimating mirror (Pd or Pt)

Sagittally focusing monochromator

2nd vertically focusing mirror (Pd or Pt)

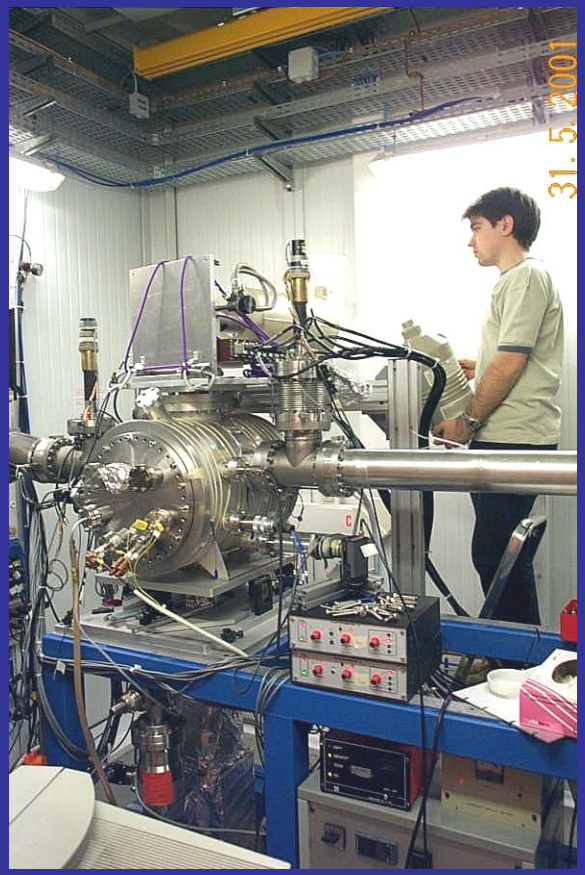
XAS



3 experimental chambers

- Standard sample environment
- User's sample environment
- ReflEXAFS

ReflEXAFS



The ReflEXAFS chamber

F. d'Acapito et al. JSR (2003). **10**, 260–264.

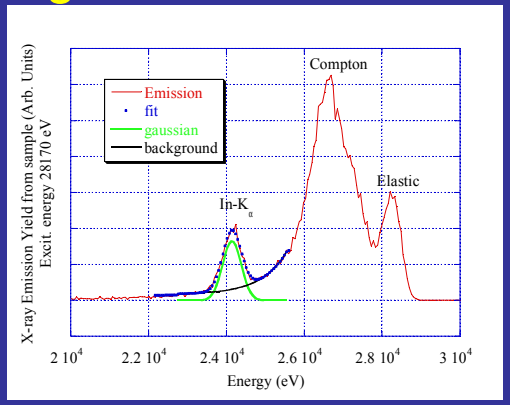
- Operative between 5.8 and 28 keV.
- Record dilution: $5*10^{13}$ at/cm^2 at the In-K edge.
- Program for data analysis (*)

Contact mode *AFM*

(*) F. Benzi et al. REV. OF SCI. INSTRUM. **79**, 103902 (2008).

Fluorescence detectors

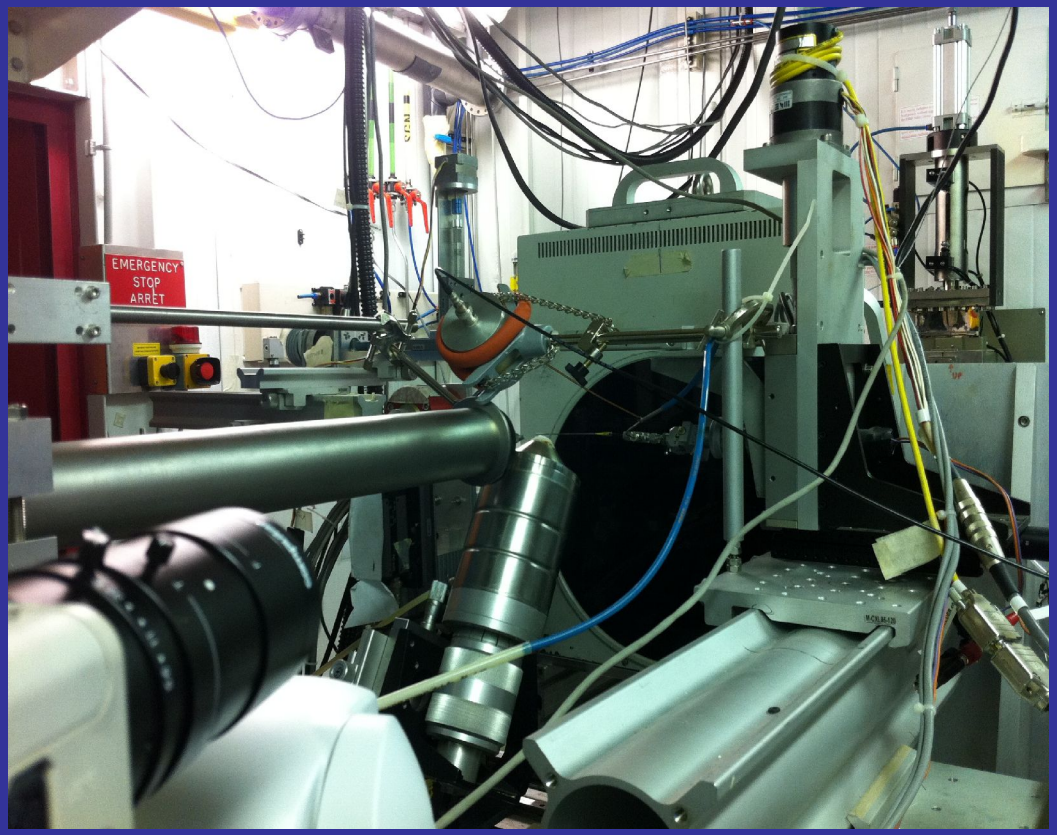
- 2* 13 elements HP-Ge
- Resolution 200 eV @ 6.4 keV
- Max CR 80kcps/element
- Digital data collection



- Automatic refill

G. Ciatto et al. JSR **11** (2004), 278-283

Time Resolved XRD



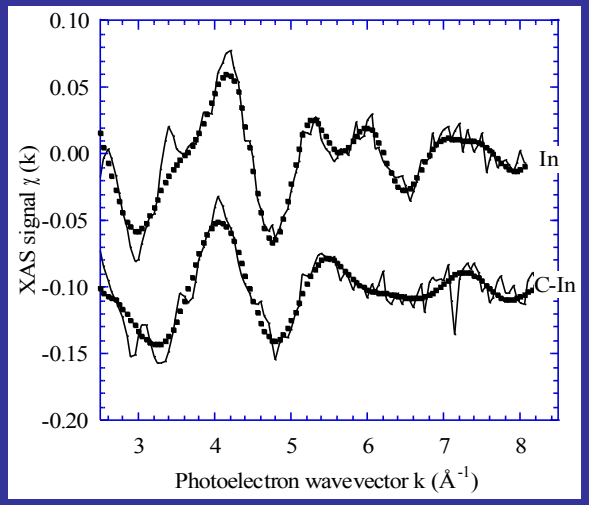
- MAR 345 2D detector
- Si PIN photodiodoe for XAS collection
- sample holders: Capillaries, flat cell, translating slices

Sample conditioning:

- Heating Gun (RT-900 °C)
- Cryo-cooler (LN-RT),
- Reaction chamber
  - Automatic gas distribution system_
  - Mass spectrometer

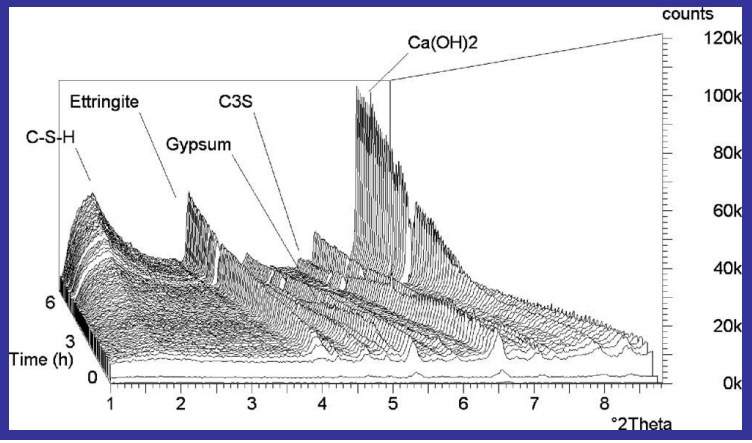
Experimental keypoints

Diluted samples
Grazing Incidence



10^{13} In/cm^2 in Si. In-K edge
Reflexafs
*F. d'Acapito et al. APL **88***
(2006) 212102

In situ treatments
Time resolution a few min.



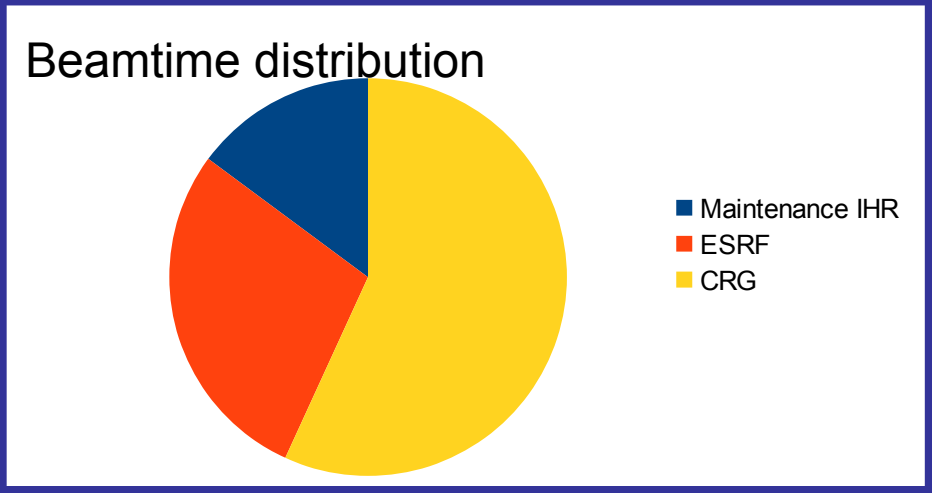
Isothermal XRD spectra of hydratation of cements
M. Merlini et al. Pow. Diff. 22 (2007), 201.

Facts and figures

Legal stuff

5 years **contract with ESRF**
Evaluation **just before the end of the contract**
Contract *constraints*
- **Provide to ESRF 1/3 of the total beamtime**
- **Support users on the ESRF beamtime**
- **Minimal staff 3 people 1 scientist 1 technician**

CNR-INFN *agreement* 2/3 – 1/3 contribution

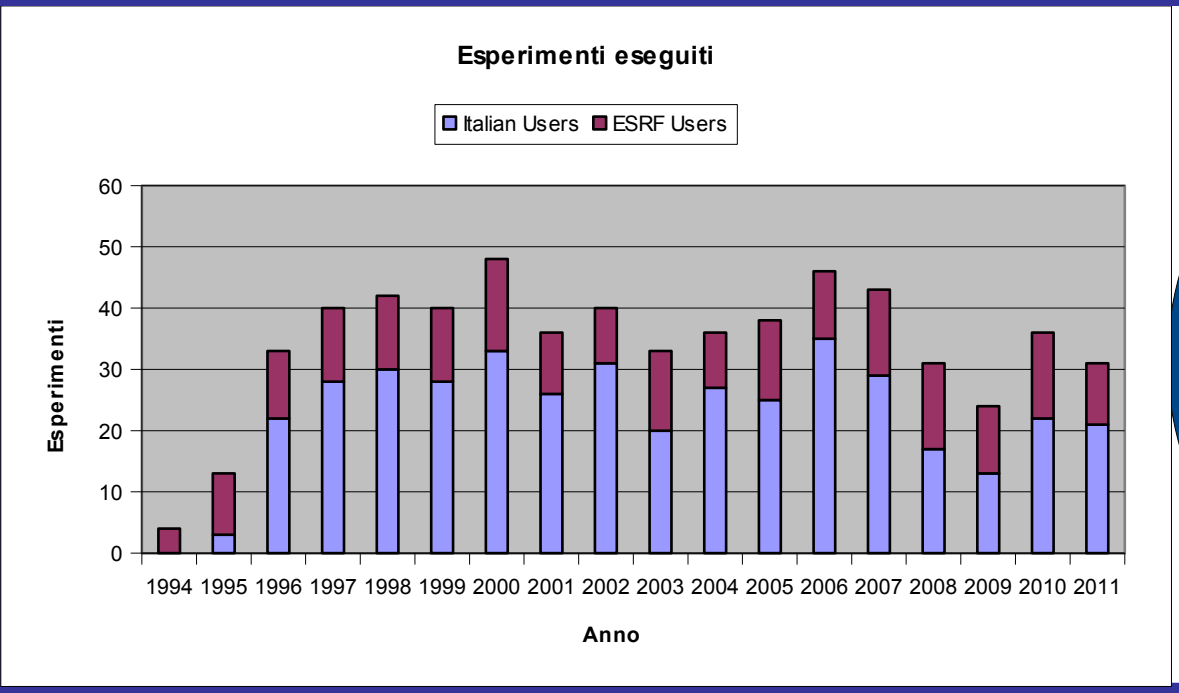


ESRF beamtime: attributed by ESRF committees

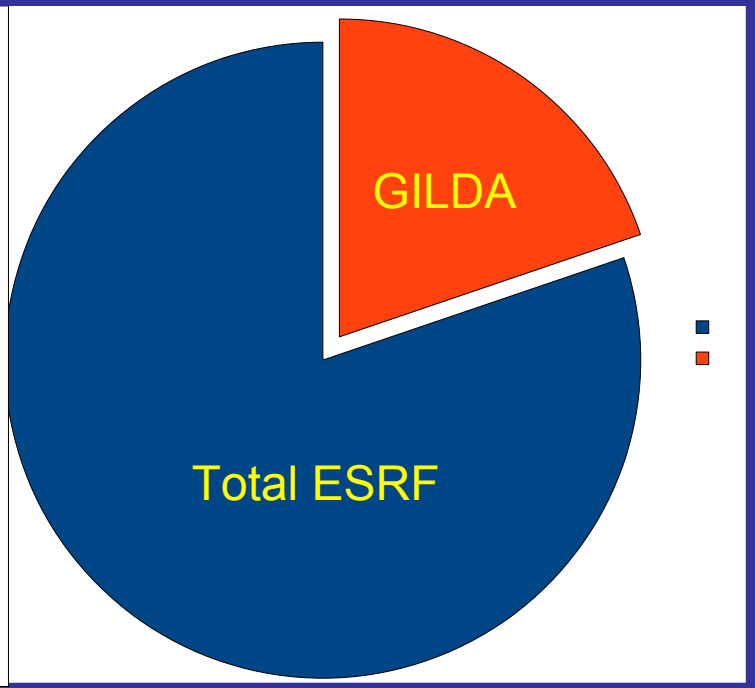
CRG beamitime Attributed by the italian committee

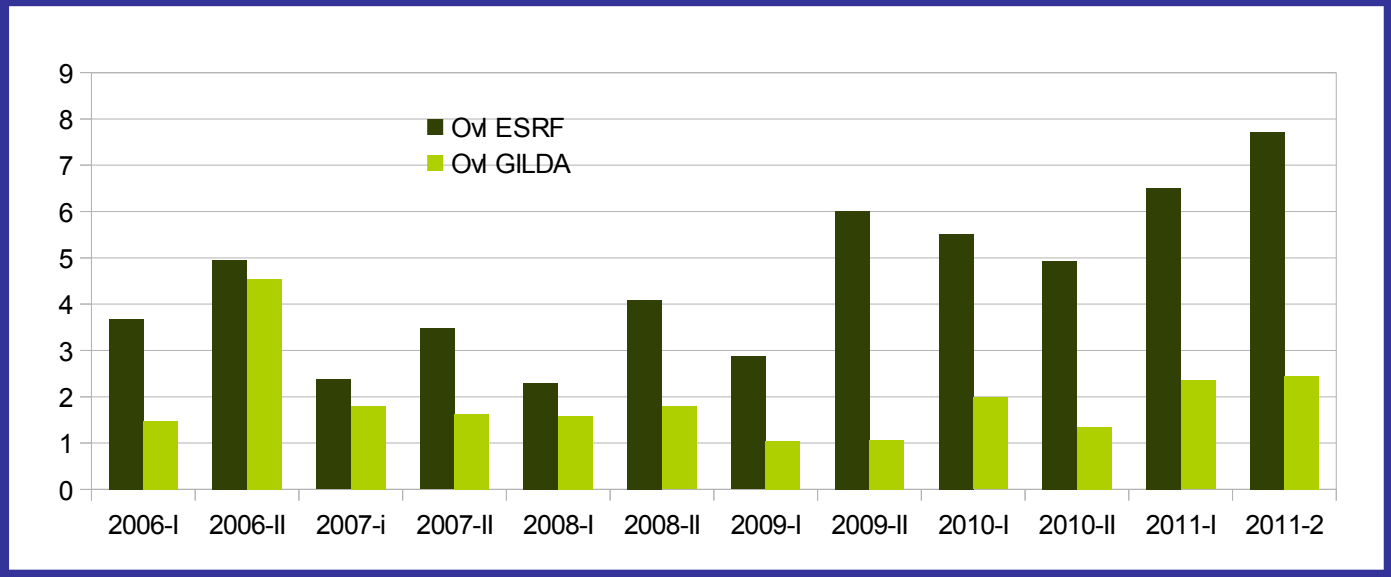
Impact of GILDA on the italian activities at ESRF

Number of experiments @ GILDA

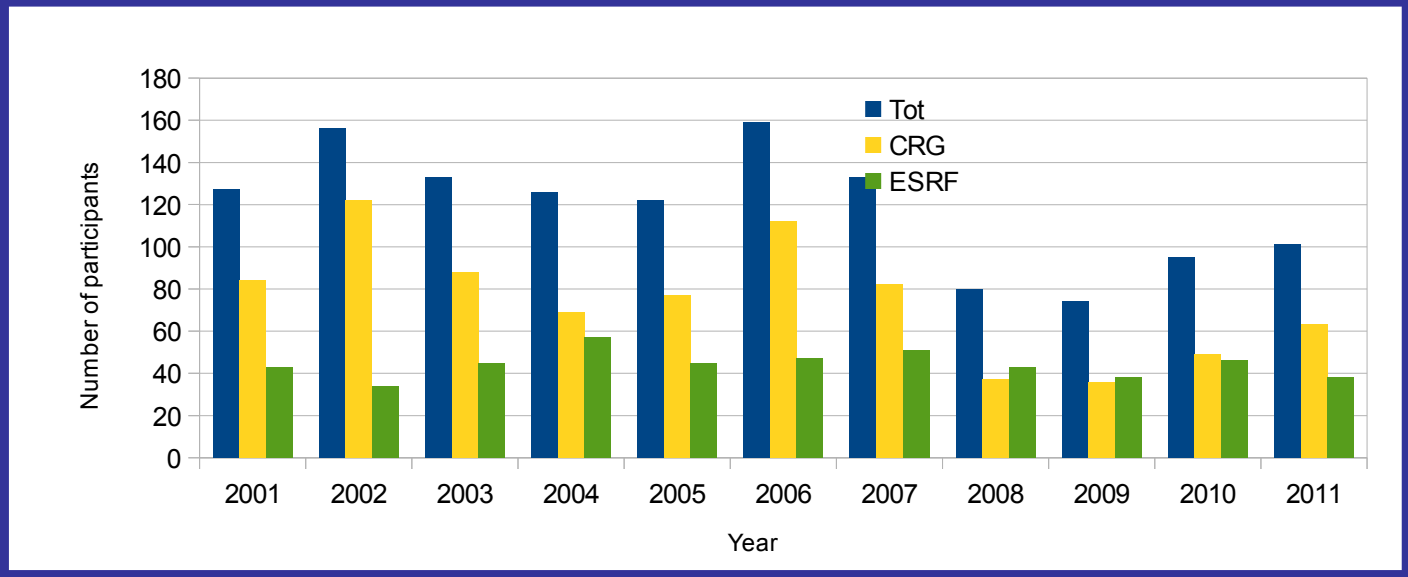


Beamtime for italian users





Beamtime overload



Participants

GILDA user community

GILDA is a fundamental **infrastructure** for the italian scientific community

Universities INFN CNR

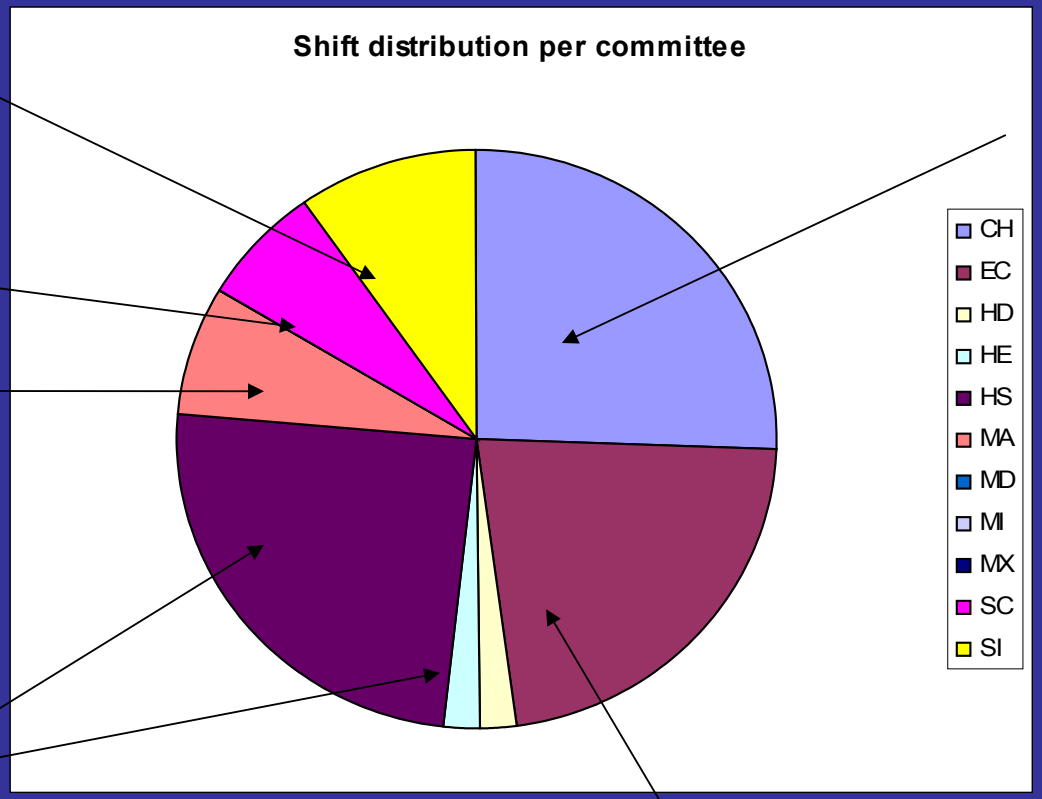
Investigation fields

Surface Science

Life science

Materials Engineer.

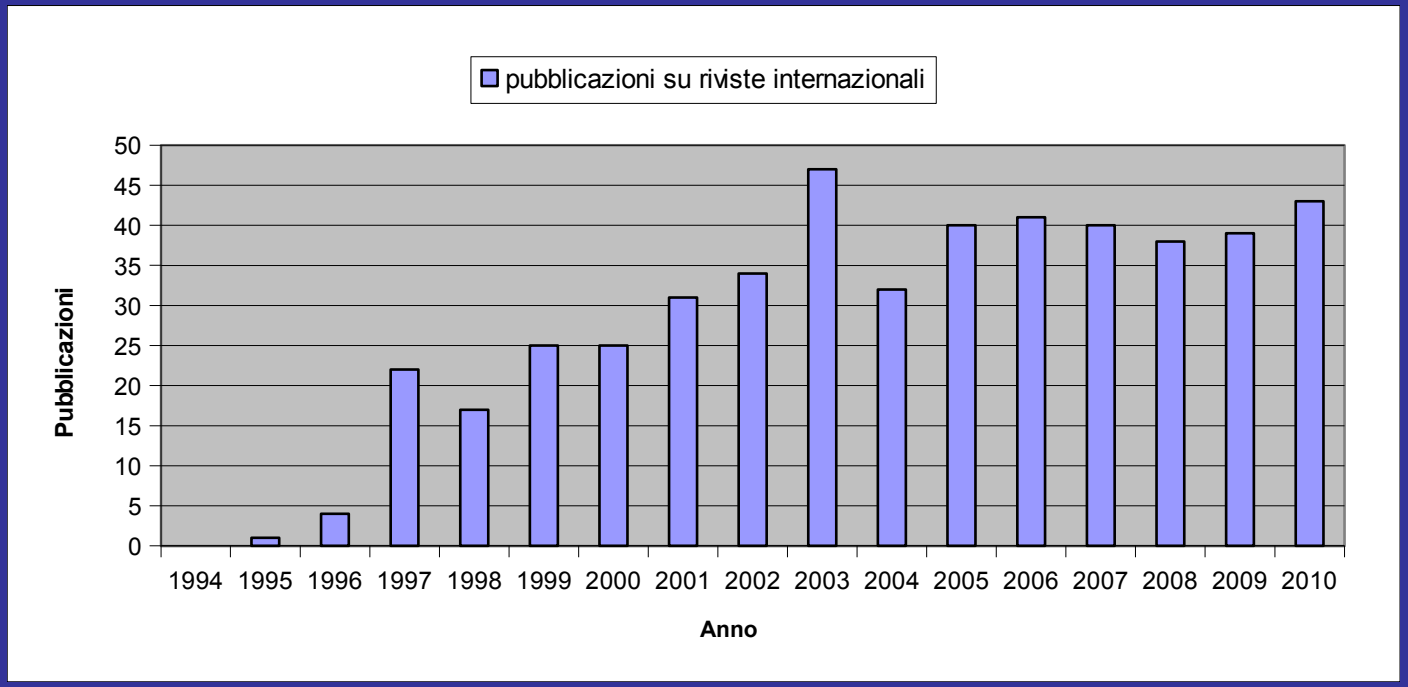
Hard Cond. Matter

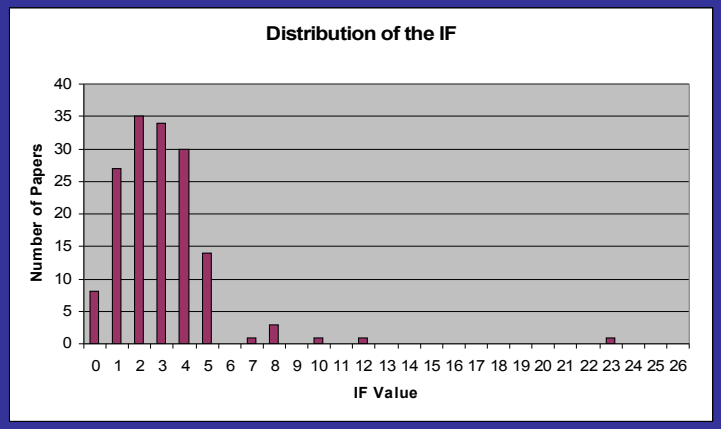


Chemistry

Environm. & Cult. Herit.

GILDA Publications





- About 510 **publications** on International journals in 17 years of activity

- Current performance: about 40 **articles/year** !

Personnel & Budget

Staff
1 responsible II lev Permanent
1 scientist III lev Permanent
1 technician VI lev Fixed Term

Capital	**3 M€**
Budget	**120 K€/y**
Decommissioning	**0.3 M€**

Evaluation

Timely evaluation (5y) via international Review Panels

ESRF Beamline Review Panel 2009

General note: The panel were impressed with the remarkable quality and quantity of science that the beamline has delivered over the reviewed period of operations.

The panel recognises that GILDA plays an essential role for a large user community. It provides valuable and much needed general spectroscopy and diffraction capabilities and the continuation of this provision has to be ensured. The multi-purpose beamline GILDA offers access to high-energy spectroscopy, which is only readily accessible at the ESRF.

ESRF Beamline Review Panel 2004

groups.
The scientific output of the staff and collaborating groups on this beamline is of high quality, as was demonstrated in their excellent presentations.

The beamline is an excellent facility for XAS studies in the wide energy range from 4 keV to well above 50 keV, particularly in dilute systems, including the capability to undertake experiments under UHV conditions and in the grazing incidence geometry. The performance of the beamline in this type of experiments is comparable to that of similar facilities on 3rd generation sources.

A fast lane to international science

S. Pascarelli
Permanent position
ESRF

P. L. Solari
Permanent position
Soleil

M. Rovezzi
Post Doc
ESRF

G. Ciatto
Permanent position
Soleil

H. G. Pais
Permanent position
Soleil

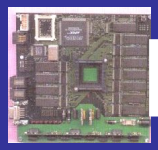
L. Giachini
Post Doc.
Australian Synch.

Sonia PIN
Post Doc
SLS

G. Veronesi
Post Doc
ESRF

Scientific Highlights

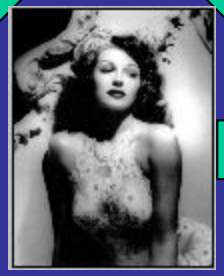
Fields of activity



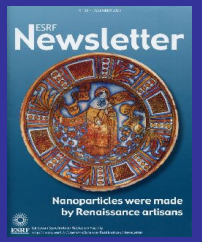
Semiconductors

Superconductors

Environmental Science

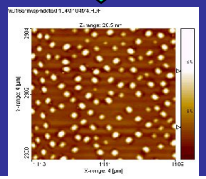


Earth Science



Cultural Heritage

Biology
Food Science



Nanotechnology

Energy
Catalysis

Environmental science

ENVIRONMENTAL Science & Technology

ARTICLE

Environ. Sci. Technol., 2011, 45 (24), pp 10492–10500
DOI: 10.1021/es201002g

pubs.acs.org/est

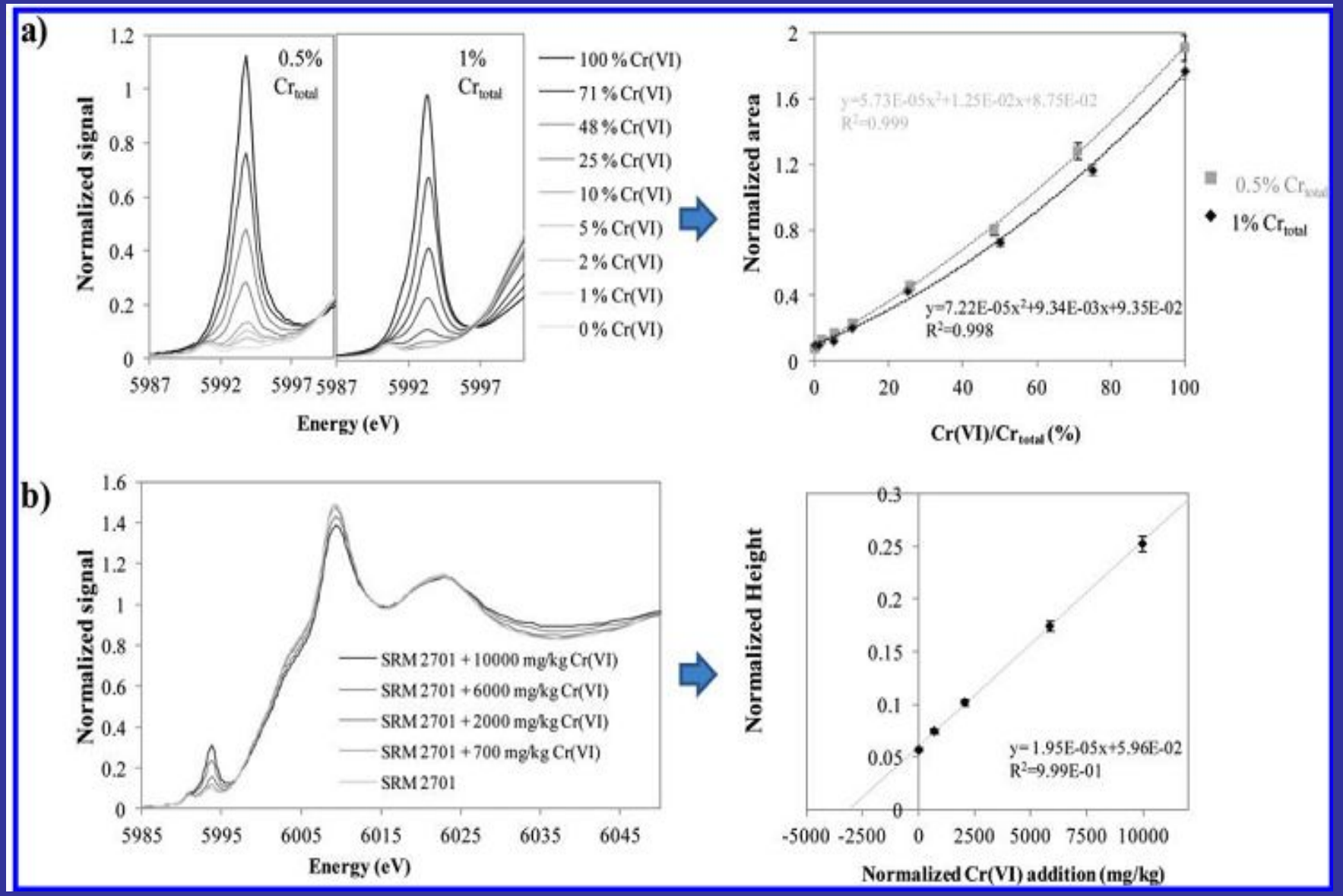
Evaluation of Hexavalent Chromium Extraction Method EPA Method 3060A for Soils Using XANES Spectroscopy

Julien Malherbe,[*,†,‡] Marie-Pierre Isaure,[†] Fabienne Séby,[§] Russell P. Watson,[‡] Pablo Rodriguez-Gonzalez,[∥] Paul E. Stutzman,[⊥] Clay W. Davis,[‡] Chiara Maurizio,[#] Nora Unceta,[▽] John R. Sieber,[‡] Stephen E. Long,[‡] and Olivier F. X. Donard[†]

Hexavalent chromium (Cr(VI)) in soils is a major contaminant. It is generally quantified using an extraction step to transfer it to the liquid phase.

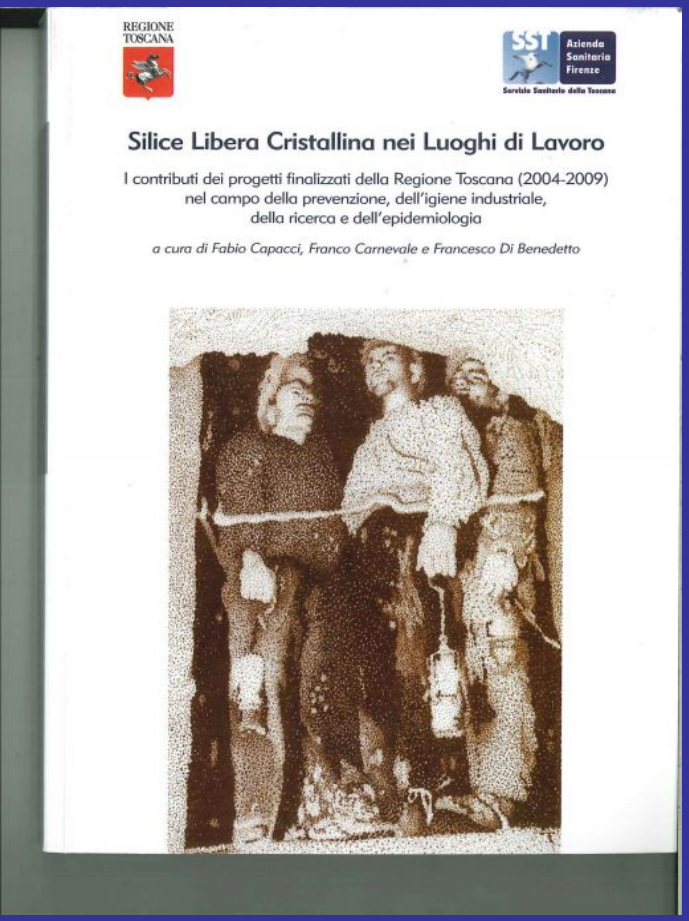
The performance of the most common extraction procedure (EPA Method 3060A) is evaluated using X-ray absorption near edge structure spectroscopy (XANES) on 3 soil samples.

The EPA Method 3060A procedure underestimated the Cr(VI) content in all studied samples



Definition of a calibration curve for the quantification of Cr^{VI} in soil samples

Breathable SiO_2 particles


REGIONE TOSCANA

SST Azienda Sanitaria Firenze
Servizio Sanitario della Toscana

Silice Libera Cristallina nei Luoghi di Lavoro

I contributi dei progetti finalizzati della Regione Toscana (2004-2009) nel campo della prevenzione, dell'igiene industriale, della ricerca e dell'epidemiologia

a cura di Fabio Capacci, Franco Carnevale e Francesco Di Benedetto

Caratterizzazione della SLC: proprietà e alterazioni chimico-fisiche

Maurizio Romanelli, Laura Bartali, Francesco Di Benedetto, Massimo Innocenti, Silvia Tesi
Dipartimento di Chimica, Università di Firenze

Enzo Bafaro, Gabriele Fornaciai
Agenzia Regionale per la Protezione Ambientale della Toscana (ARPAT), Dipartimento di Firenze

Francesco D'Acapito
Istituto Officina dei Materiali, Operative Group in Grenoble, Consiglio Nazionale delle Ricerche (IOM-OGG-CNR) c/o European Synchrotron Radiation Facility, Grenoble (France)

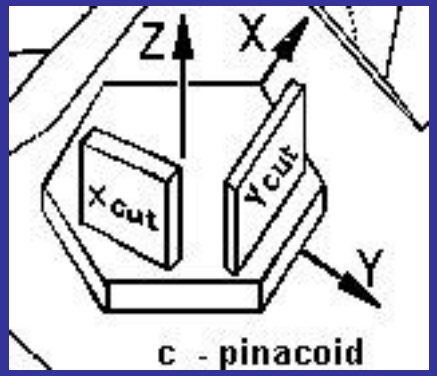
Giordano Montegrossi
Istituto Geoscienze e Georisorse, Consiglio Nazionale delle Ricerche (IGG-CNR)

Luca A. Pardi
Istituto Processi Chimico-Fisici, Consiglio Nazionale delle Ricerche (IPCF-CNR)

Fe on surface analysis

Campione		N	R(Å)	DW(Å²)
XA + Fe(II)	X-cut	2.8(7)	1.93(3)	0.006(4)
XA + Fe(III)		5.1(7)	1.99(2)	0.012(3)
XB + Fe(II)	Y-cut	3.3(7)	1.89(3)	0.005(4)
XB + Fe(III)		4.8(7)	1.98(3)	0.010(5)
XC + Fe(II)	Z-cut	4.5(7)	2.02(3)	0.012(4)
XC + Fe(III)		3.0(7)	2.06(3)	0.005(4)

Model surfaces
X, Y, Z cut
Reflexafs



Shannon 69	Tetra (Å)	Octa (Å)
Fe^{2+}	2.03	2.17
Fe^{3+}	1.89	2.05

Work in progress

Fe in breathable SiO2 powders from work site

Materials science

PRL 103, 046403 (2009) PHYSICAL REVIEW LETTERS week 24 JUL

HIGHLIGHTS 2009

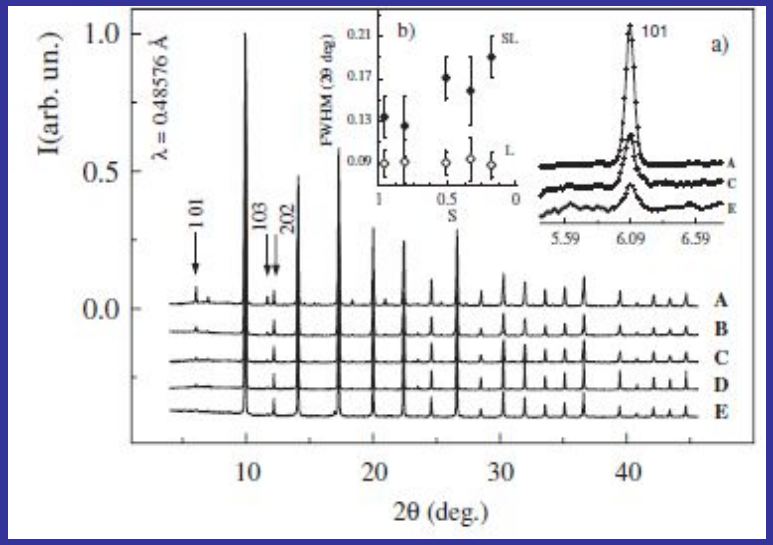
Nature of "Disorder" in the Ordered Double Perovskite Sr_2FeMoO_6

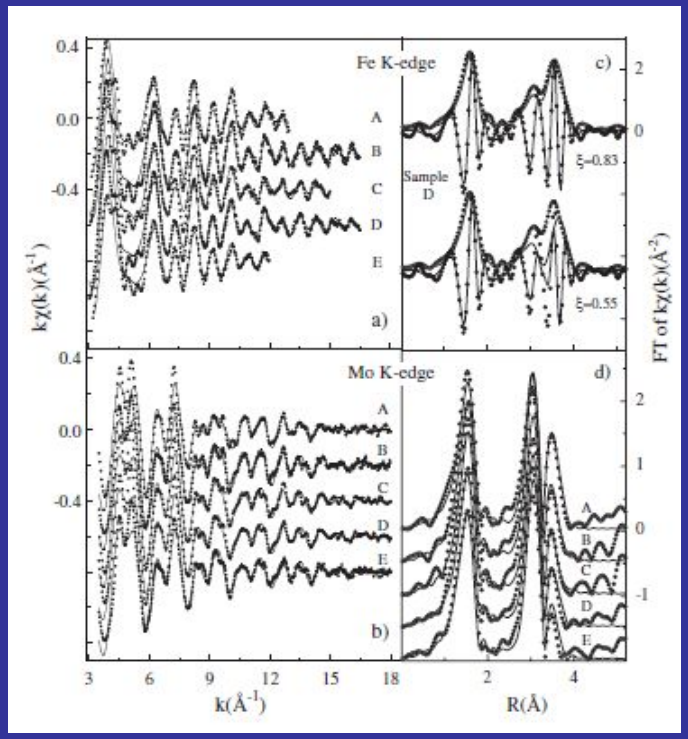
C. Meneghini,[1,2] Sugata Ray,[3,4,5] F. Liscio,[1] F. Bardelli,[1,2] S. Mobilio,[1,2,6] and D. D. Sarma[3,5]

Double perovskites $Sr_2Fe_xMo_yO_6$

Study on the nature of Fe/Mo disorder

Comparison XAS/Diffraction

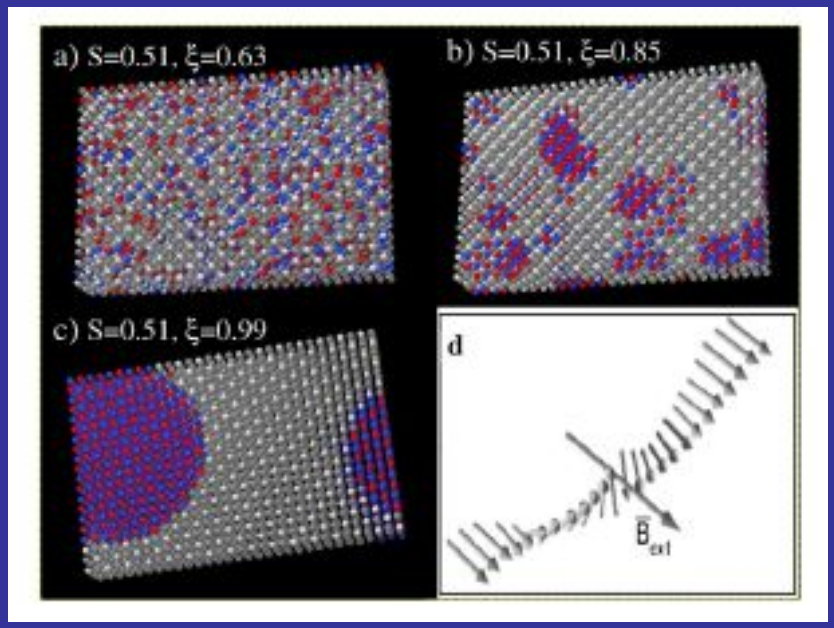




PRL 103, 046403 (2009) PHYSICAL REVIEW LETTERS week endin 24 JULY 20

Nature of "Disorder" in the Ordered Double Perovskite Sr_2FeMoO_6

C. Meneghini,[1,2] Sugata Ray,[3,4,5] F. Liscio,[1] F. Bardelli,[1,2] S. Mobilio,[1,2,6] and D. D. Sarma[3,5]



- High cation order (XAS) even in disordered samples (XRD)
- Clustering of the antiphase domains
- Explanation of the magnetic properties

APPLIED PHYSICS LETTERS **99**, 121909 (2011)

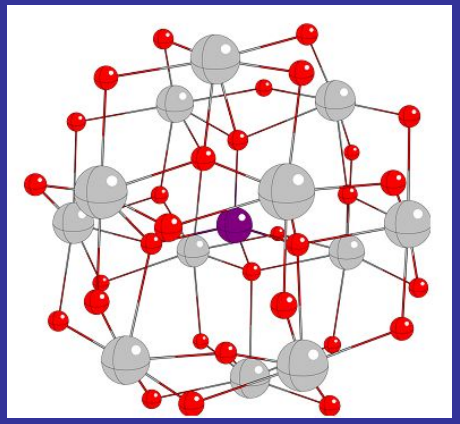
Atomic scale mechanism for the Ge-induced stabilization of the tetragonal, very high-κ, phase of ZrO_2

F. Boscherini,[1,2,a)] F. D'Acapito,[2] S. F. Galata,[3,4] D. Tsoutsou,[3] and A. Dimoulas[3]
[1]*Department of Physics, University of Bologna, viale C. BertiPichat 6/2, 40127 Bologna, Italy*
[2]*I.O.M. - C.N.R. - O.G.G., c/o E.S.R.F., BP 220, 38043 Grenoble, France*
[3]*MBE Laboratory, Institute of Materials Science, NCSR DEMOKRITOS, 153 10 Athens, Greece*
[4]*Department of Electronics, Technological Educational Institution of Athens, 12210 Athens, Greece*

Hi dielectric constant materials needed for device scale reduction
ZrO2 in tetragonal (unstable) form has κ=47
T-ZrO2 is stabilized by adding Ge. Why ?

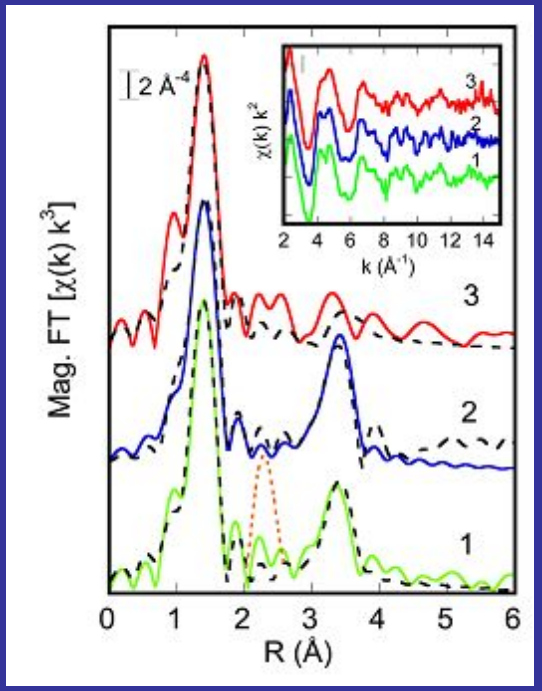
Look at the environment of Ge
Compare XAS data with structural modelization with DFT and MD

Ge-doped zirconia



Ge in t-ZrO2
substitutes for Zr

Ge creates 4 short
Ge-O bonds



XAS analysis

XAS data in agreement with theoretical
predictions for Ge in t-ZrO2

Chemistry

JACS
JOURNAL OF THE AMERICAN CHEMICAL SOCIETY

J. Am. Chem. Soc. 2011, 133, 8982–8994

ARTICLE

pubs.acs.org/JACS

Supramolecular Aggregation of Block Copolymers in the Solid State As Assisted by the Selective Formation of Inclusion Crystals

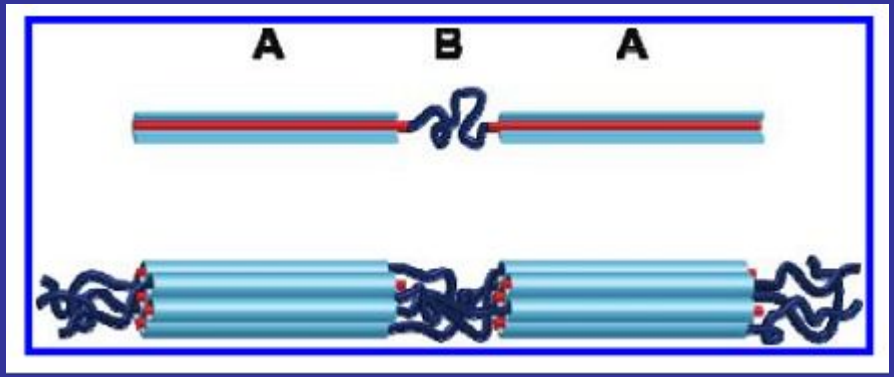
Silvia Bracco, Angiolina Comotti,* Lisa Ferretti, and Piero Sozzani

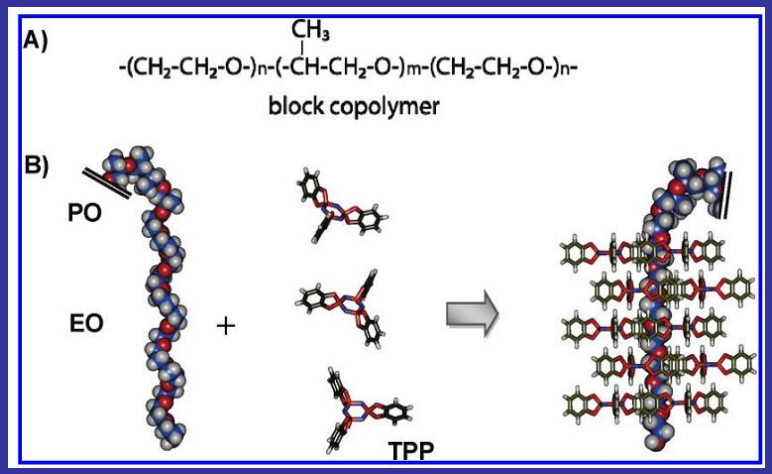
Department of Materials Science, University of Milano Bicocca, Via R. Cozzi 53, 20125 Milano, Italy

Production of supramolecular materials

Process in the solid state, no solvent involved

Alternance of crystalline and amorphous (polymers) regions

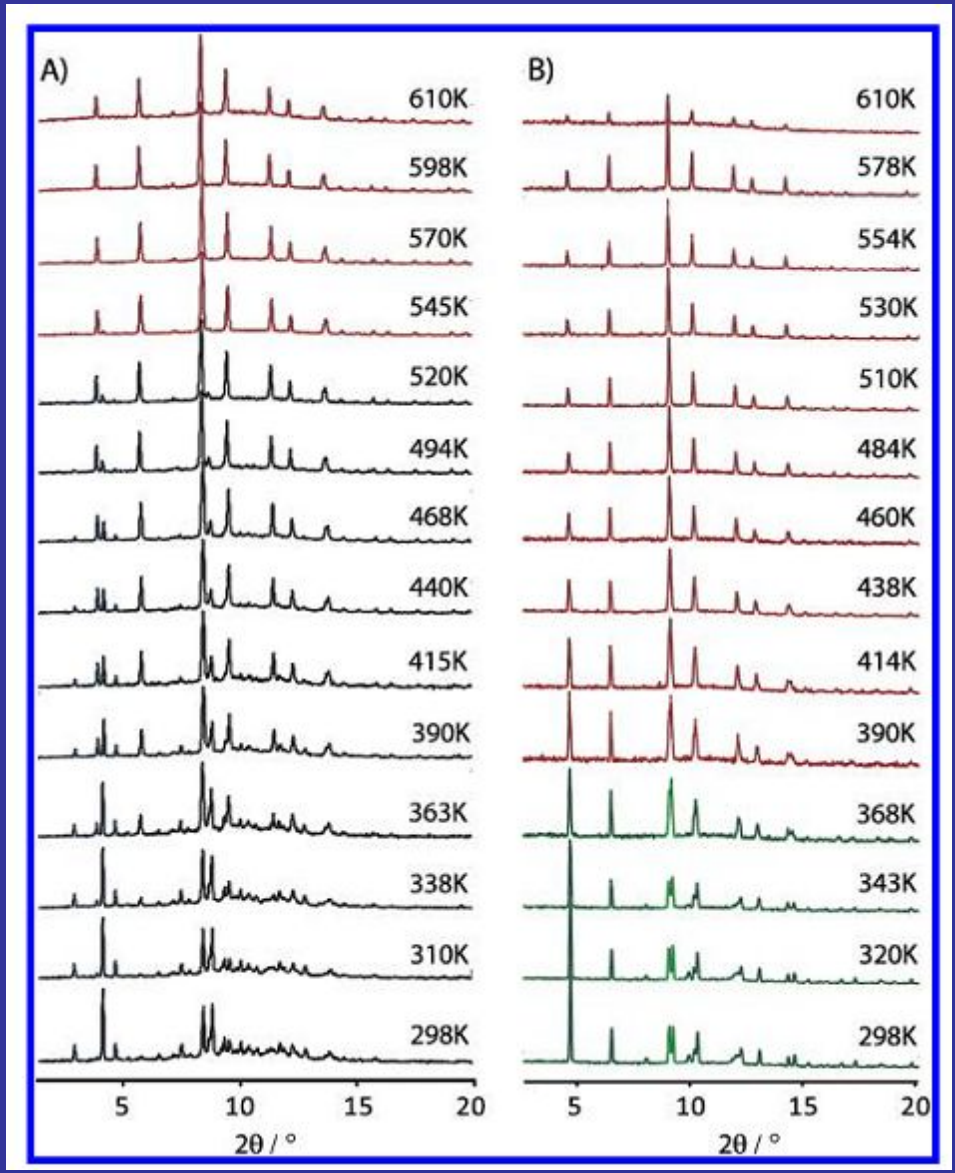




Time resolved XRD
About 2'/ pattern

A) Close packed TPP (monoclinic, black)
B) porous TPP (hexagonal, green)

Inclusion of the block copolymer in the hexagonal holes (red)



Time resolved diffraction patterns

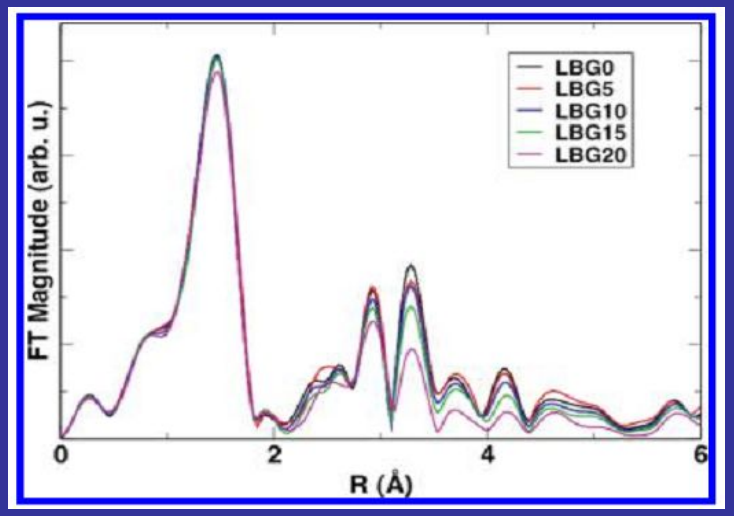
298 J. Phys. Chem. C 2011, 115, 298–304

Crystal Structure and Local Dynamics in Tetrahedral Proton-Conducting $La_{1-x}Ba_{1+x}GaO_4$

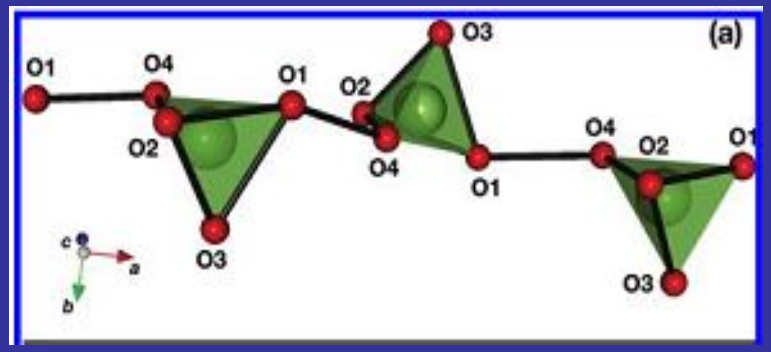
Francesco Giannici,*,† Diego Messana,† Alessandro Longo,‡ and Antonino Martorana†

Dipartimento di Chimica Inorganica e Analitica "Stanislao Cannizzaro", Università degli Studi di Palermo, Viale delle Scienze, I-90128 Palermo, Italy, and Istituto per lo Studio dei Materiali Nanostrutturati, Consiglio Nazionale delle Ricerche, Via Ugo La Malfa 153, I-90146 Palermo, Italy

Origin of the H conduction
Combined XAS, XRD, IR study



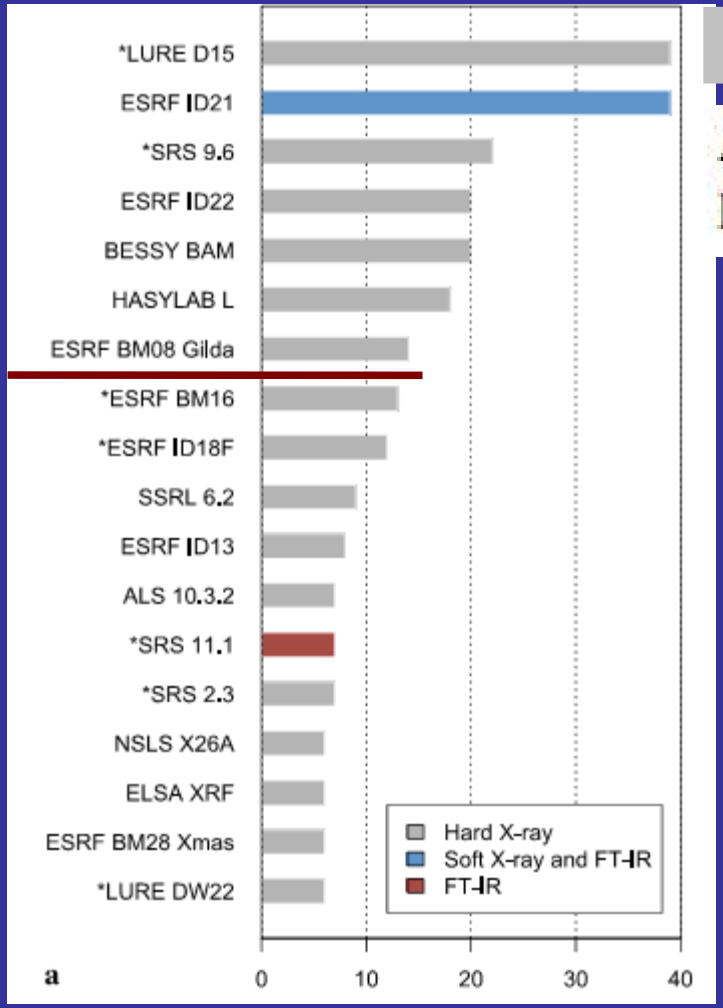
Ga-K edge XAS shows the rigidity of the GaO4 units



- Proposed structure for the GaO4 chains
- NO corner sharing tetrhedra
- O1-H●●●O4 bonds
- Stiffness of GaO4: no intra Tetrahedral H diffusion

Cultural Heritage

GILDA in the international landscape



L. Bertrand & al.

Appl Phys A (2012) 106:377–396
DOI 10.1007/s00339-011-6686-4

GILDA represents a considerable instrument for the italian Cultural Heritage community

Thanks to Marine Cotte

Cite this: *J. Anal. At. Spectrom.*, 2011, **26**, 2500

www.rsc.org/jaas

PAPER

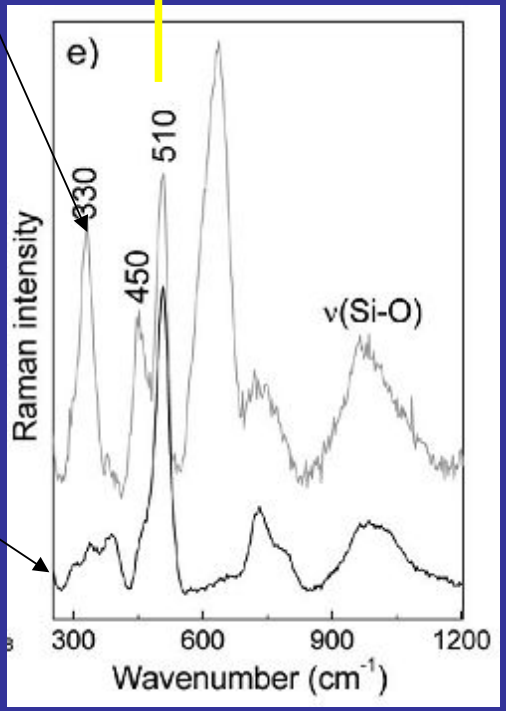
Modified Naples yellow in Renaissance majolica: study of Pb–Sb–Zn and Pb–Sb–Fe ternary pyroantimonates by X-ray absorption spectroscopy†

Laura Cartechini,*[a] Francesca Rosi,[a] Costanza Miliani,[a] Francesco D'Acapito,[b] Brunetto Giovanni Brunetti[c] and Antonio Sgamellotti[c]

Orange

Yellow

SbO_6 Symm. Stretching

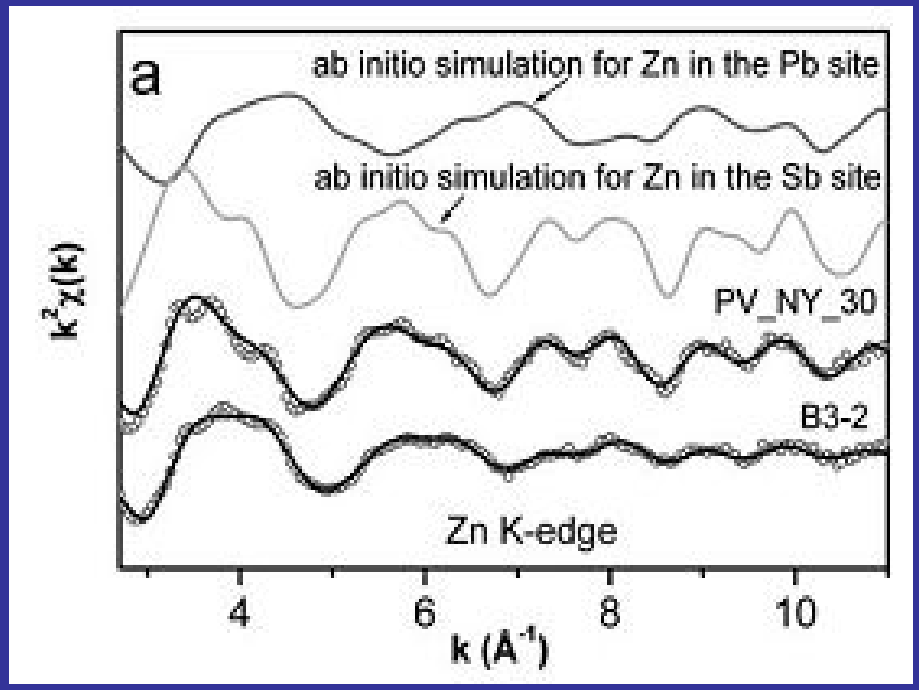


F. Rosi et al. J. Raman Spectrosc. ***42*** *(2011) 407.*
C. Miliani et al. Acc. Chem.Res. ***43*** *(2010) 728*

- Example on *Putto con trofei by* Mastro Giorgio Andreoli (VAM, London), portable RAMAN spectrometer (MOLAB project, http://www.eu-artech.org/)

Example in ceramics

Zn was found in Naples Yellow ceramics of Umbrian production (Muser Civici di Pesaro)



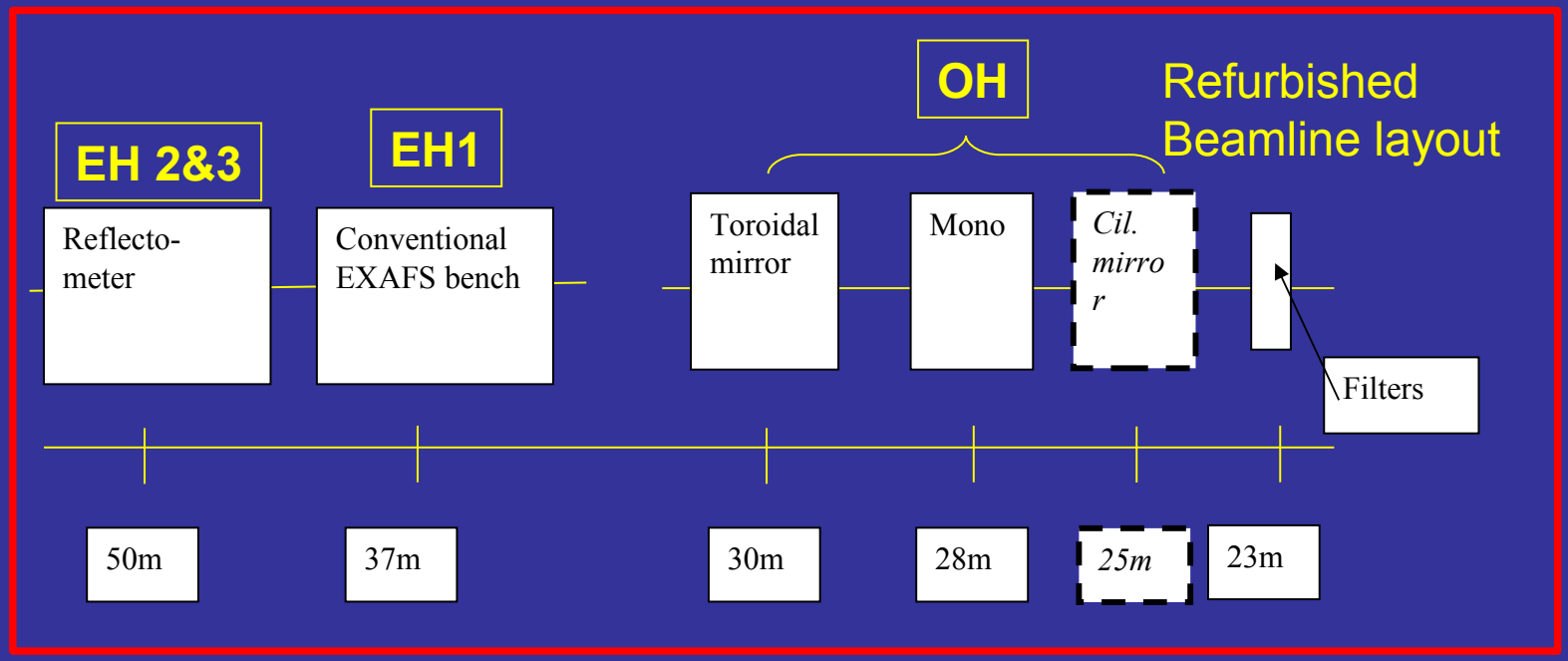
XAS + ab initio structural modeling permitted to demonstrate that Zn occupies a Sb site

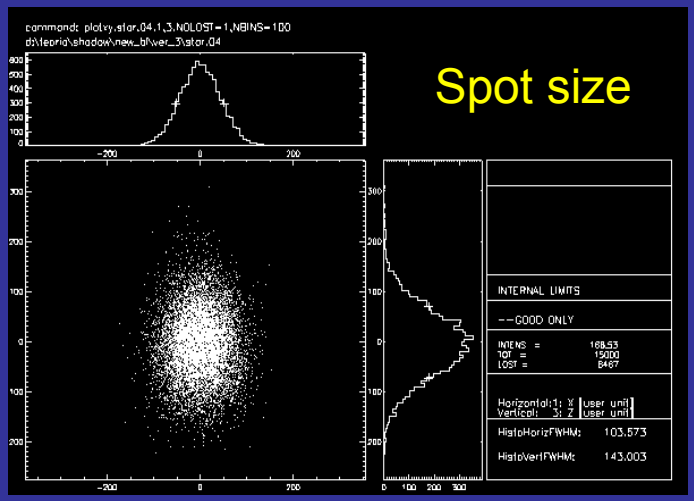
Perspectives

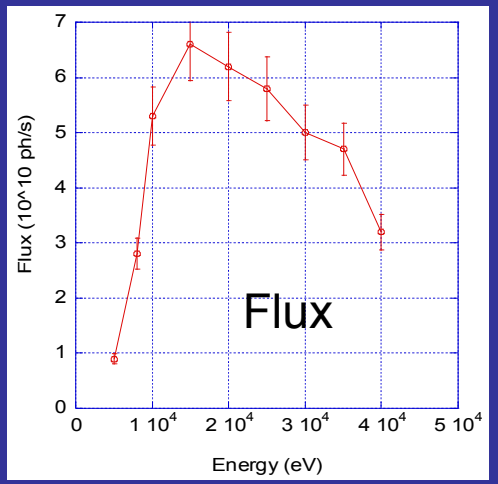
Short term

- Renewal of some hardware
- Improve high throughput capability
- Automation / remotization
- Increase time-resolved capability

Long term


OH
Refurbished
Beamline layout
EH 2&3
EH1
Reflecto-
meter
Conventional
EXAFS bench
Toroidal
mirror
Mono
Cil.
mirro
r
Filters
50m
37m
30m
28m
25m
23m


Spot size
INTERNAL LIMITS
--GOOD ONLY


Flux
Flux (10^10 ph/s)
Energy (eV)

FUTURE PERSPECTIVES FOR GILDA, THE ITALIAN CRG BEAMLINE AT ESRF. TECHNICAL AND SCIENTIFIC ASPECTS.

PROCEEDINGS OF THE GILDA MEETING, PALERMO DEC 3-4 2009.

ABSTRACT. This document reports the results of the Meeting hold in Palermo on Dec 3-4 2009 about the future of GILDA, the Italian CRG beamline at the ESRF. The history of the project as well as the limits of the present instrument and the scientific case for the refurbished instrument are presented in the first part of the document. In the second part the conceptual basis for the new design and the technical details are presented. The final section collects the proposals of experimental activities presented by the participants to the meeting.

Chairmen: F. d'Acapito (CNR-IOM-OGG), A. Longo (CNR-ISMN)
Co-chairmen: S. Mobilio (Univ. Roma TRE)

Scientific committee:
A. Balerna(INFN-LNF), C. M. Bertoni(Univ. Modena e Reggio Emilia), F. Boscherini (Univ. Bologna), D. Fiorani (CNR-ISM), G. Deganello (Univ. Palermo and CNR-ISMN), C. Mariani (Univ. Roma La Sapienza), A. Martorana (UNiv. Palermo), A. Morgante (CNR-IOM-TASC and Univ. Trieste), F. Priolo (CNR-IMM-MATIS and Univ. Catania), S. Quartieri, (Univ. Messina), F. Rocca (CNR-IFN and Univ. Trento), G. Rossi, (CNR-IOM-TASC and Univ. Modena e Reggio Emilia), P.L. San Biagio (CNR-IBF), A. Sgamellotti (CNR-ISTM and Univ. Perugia)

Project discussed with ESRF and the Italian User community

Well received

Funding needed

Conclusion

GILDA is a major infrastructure for the italian scientific community

Inserted in a unique scientific environment

Privileged place for student formation and insertion in international resarch

Highly appreciated by the Review Committees

High impact in the overall italian activity at ESRF

Performs experiments in a wide range of scientific fields

High production and reliability

Thanks to…

Technicians, students and scientists, who have contributed to the success of GILDA:

S. COLONNA[2], S. PASCARELLI[2], G. ANTONIOLI[3], A. BALERNA[4], A. BAZZINI[3], F. BOSCHERINI[4], F. CAMPOLUNGO[4], G. CHINI[5], G. DALBA[5], I. DAVOLI[6], P. FORNASINI[5], R. GRAZIOLA[4], G. LICHERI[7], C. MENEGHINI[2], F. ROCCA[8], L. SANGIORGIO[4], V. SCIARRA[4], V. TULLIO[4] AND S. MOBILIO[9]

F. d'Anca, F. Bardelli, C. Battocchio, F. Benzi, S. Cammelli, G. Ciatto, T. Costanzo, N. Daldosso, M.C. Dalconi, J. Frascaroli, P. Ghigna, F. la Manna, C. Maurizio, H. Pais, S. Pin, A. Rizzo, M. Rovezzi, P.L. Solari, S. Thorpe, A. Trapananti.