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Book of abstracts



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Programme

	Monday, September 9, 2019			
12:30	14:30	Registration		
14:30	15:15	Welcome & Introduction C. Pettinari (Unicam), D. Vitali (Unicam), A. Trapananti (Unicam), A. Di Cicco (Unicam/SILS), C. Spinella (CNR), S. Gross (ESUO), A. Marcelli (MAECI) Room: Aula 3		
15:15	16:00	Plenary Lecture 1 Diamonds: a deep journey into the Earth F. Nestola (University of Padova) Room: Aula 3		
16:00	16:30	Coffee Break		
16:30	18:30	 Large Scale Facilities updates 16:30 S. Lizzit (ELETTRA) Current status and future perspectives of Elettra and FERMI 17:00 P. Raimondi (ESRF) Twenty six years of operation of the ESRF Synchrotron and the EBS Project 17:30 S. Pascarelli (European XFEL) The European XFEL) The European XFEL: start of user operation and first results 18:00 R. Pompili (LNF-INFN) From SPARC_LAB to EuPRAXIA@SPARC_LAB 		
18:30	19:30	 Tribute to Carlo Lamberti 18:30 Ricordo di Carlo (P. D'Angelo and other colleagues) 18:50 L. Mino (University of Torino) Direct writing of conductive channels in TiO₂ single crystals by a synchrotron X-ray nanobeam 19:10 A. Martini (University of Torino) Retrieving quantitative structural information from XANES spectra by means of Multivariate and Machine Learning Approaches Room: Aula 3 		
19:30		Welcome Party		

	Tuesday, September 10, 2019					
09:00	09:45	Plenary Lecture 2 Ultra-modern synchrotron-based microscopes for the study of ancient materials: a review of applications to Roman/Italian artefacts and/or by Italian researchers M. Cotte (ESRF) Room: Aula 3				
09:45	10:00	Commercial presentation Breakthrough Lab X-ray Techniques approaching Synchrotron Beamline Performances S. Paziani (Quantum Design Europe) Room: Aula 3				
10:00	10:30	Coffee Break				
10:30	13:10	 MS2 - Photon based multi-dimensional (2D/3D/4D) imaging from VUV to X-rays Chairpersons: C. Giannini/C. Masciovecchia Room: Aula 2 MS3 - Synchrotron based characterization of sufaces and interfaces Chairpersons: G. Aquilanti/S. Colonna Room: Aula 3 In30 KN1: I. Robinson (University College London) AD Bragg Coherent Diffraction Imaging of Nanocrystals using XFELS O O1: C. Callegari (Elettra Sincrotrone Trieste) Diffraction imaging of helium nanodroplets with the FERMI Free Electron Laser O Q2: F. Capotondi (Elettra Sincrotrone Trieste) Study fast-demagnetization processes using FERMI seeded-FEL O 3: M. Zambrano (University of Camerino) The use of synchrotron-based X-ray microtomography for the pore network quantitative and computational fluid dynamics experiments on porous carbonate rocks O 4: M. Romano (Ludwig Maximilian University) High resolution X-ray Phase Contrast Imaging for studying the effects of novel radiotherapies O 5: A. Moliterni (IC-CNR) Single-crystal synchrotron X-ray diffraction study of new anthracene derivatives compounds tody of new anthracene derivatives compounds O 6: G. Campi (C - CNR) Complex nanoscale geometry in functional materials as seen by synchrotron x-ray micron beam techniques D 05: G. Gotter (IOM-CNR) Unexpected electron corleation (Coulomb and exchange) at the nanoscale probed by Auger Photo-Electron Coincidence Spectroscopy: size and bias effects 				
13:10	15:00	Lunch & Poster Session				

		MS1 - Multi-techniques approach for in-situ/in	Open S	Session 1	
		operando studies Chairpersons: R. Arletti/S. Gros Room: Aula	s 2	Chairperson: P. D'Angelo Room: Aula 3	
		15:00 KN1: T. L. Sheppard (KIT) Harnessing X-ray (Spectro)microscopy for Chemical Imaging of Heterogeneous Catalysts	15:00	O1: G. Aquilanti (Elettra Sincrotrone Trieste) X-ray fluorescence beamline at Elettra Sincrotrone Trieste: a versatile tool for structural and chemical investigations	
		15:30 O1: M. Giorgetti (University of Bologna) Dynamic Processes in Metal Hexacyanoferrate- based Batteries Revealed by Operando XAS and XRD	15:20	O2: E. Principi (Elettra Sincrotrone Trieste) FEL time-resolved methods for monitoring ultrafast structural and electronic changes in condensed matter	
15:00	16:40	15:50 O2: D. Lizzit (Elettra Sincrotrone Trieste) On the hydrogenation of the Graphene/Ni(111) system	15:40	O3: L. Paolasini (ESRF) Mixed Spin-Quadrupole-Phonon modes in UO ₂ Studied by Inelastic X-ray Scattering	
		16:10 O3: L. Monico (ISTM - CNR) Probing the chemistry of cultural heritag materials via different 2D XANES-base approaches: the alteration processes of pigment and carbonatation of calcium-based consolidant into limestone matrix	e 16:00 1 5 5	O4: A. Verna (University of Roma Tre) Magnetic proximity effect in Co/Pt multilayer investigated through X-ray resonant magnetic reflectivity	
			16:20	O5: P. Dolcet (Karlsruhe Institute of Technology)	
				Increasing the performance of Pd/Al_2O_3 and Pd/CeO_2 catalysts for total methane oxidation by pre-reduction	
16:40	17:00	Coff	e Break		
		17:00 O4: F. Tajoli (University of Padova) Effect of space confinement on crystallization of molybdenum oxide synthetized by inverse miniemulsion –an in-situ SAXS/WAXS study	17:00	O6: R. Cimino (LNF - INFN) Synchrotron Radiation studies of relevance to Accelerator R&D	
17:00	18:00	17:20 O5: G. Confalonieri (University of Modena and Reggio Emilia) Pressure and zeolite Framework Typ Cooperation Effect in the Differential Absorptio of Ethanol and Water from the Azeotrop Solution: the case of Si-Chabazite	17:20	O7: F. Offi (University of Roma Tre) Quantum size and surface effects on the electronic structure of Yb thin films	
		17:40 O6: G. Cruciani (University of Ferrara) Assessing by in situ synchrotron powder diffraction the effect of enhanced ferroelastic domain switching in zeolite ZSM-5 in order to tailor the secondary induced mesoporosity	17:40	O8: R. Flammini (ISM-CNR) Evidence of quantum well states at the Ag/β- Si ₃ N ₄ (0001)/Si(111) interface	
18.00	19.15	SILS Morr	ers Asser	nbly	
10.00	19.19	Room: Aula2			
20:00		Social Dinner			
20:00				Ristorante Pappafò Via Montagnano 98, Camerino	

99:00 99:45 Plenary Lecture 3 High resolution Resonant Inelastic X-ray Scattering for the study of correlated material G. Ghiringhelli (Polytechnic University of Milano) SILS Awards and Prizes Best PhD thesis Awards SILS young researcher Award SILS outstanding scientist Award Room: Aulu Room: Aulu Room: Aulu 10:30 11:00 Coffee Break Room: Aulu 10:30 11:00 Coffee Break Room: Aulu 10:30 11:00 Coffee Break Room: Aulu 10:30 11:00 KS4 - Advanced Radiation Sources: State-of- the-art and future applications Chairpersons: E. Chiadroni, F. Stellato Room: Aula 2 Young Investigators session 11:00 KN1: L. Giannessi (ELETTRA Sincrotrone Trieste) Laser in the extreme ultraviolet and soft X-ray spectral regions 11:00 KN1: F. Coppari (Lawrence Livermore National Laboratory) 11:30 O1: S. Di Mitri (Elettra Sincrotrone Trieste) Laser-Slicing at a Diffraction Limited Storage Ring 11:30 Recipient of the best PhD thesis Award SILS 2019 Best PhD thesis award talk 11:20 O2: G. Rossi (University of Milano) MariX, an advancedMHz-class repetition rate X-ray source for linear regime time-resolved spectroscopy and photon scattering 11:42 O1: E. Giangrisostomi (Helmholtz Zentrum Berlin) Directional sub-fs charge transfer dynamics i 17-TaS2 11:00 13:30 12:30 O4: S. Lupi (University of R			Wednesday, September	- 11, 2019	
09:45 10:30 SILS Awards and Prizes Best PhD thesis Awards SILS young researcher Award SILS outstanding scientist Award Room: Ault Room: Ault Roo	09:00	09:45	Plenary Lecture 3 High resolution Resonant Inelastic X-ray Scattering for G. Ghiringhelli (Polytechnic University of Milano)	the study of correlated material	
10:30 11:00 Coffee Break MS4 - Advanced Radiation Sources: State-of- the-art and future applications Chairpersons: E. Chiadroni, F.Stellato Room: Aula 2 Young Investigators session 11:00 KN1: L. Giannessi (ELETTRA Sincrotrone Trieste) FERMI: the first externally seeded Free Electron Laser in the extreme ultraviolet and soft X-ray spectral regions 11:00 KN1: F. Coppari (Lawrence Livermore National Laboratory) 11:30 O1: S. Di Mitri (Elettra Sincrotrone Trieste) Laser-Slicing at a Diffraction Limited Storage Ring 11:30 Recipient of the best PhD thesis Award SILS 2019 Best PhD thesis award talk 11:50 O2: G. Rossi (University of Milano) MariX, an advancedMHz-class repetition rate X-ray source for linear regime time-resolved spectroscopy and photon scattering 11:42 O1: E. Giangrisostomi (Helmholtz Zentrum Berlin) Directional sub-fs charge transfer dynamics of 11:42 11:00 13:30 12:30 O4: S. Lupi (University of Rome "La Sapienza") High-Intensity Terahertz and Mid-Infrard Radiation: Production and Opportunities in Surface x-ray diffraction investigation of to	09:45	10:30	SILS Awards and Prizes Best PhD thesis Awards SILS young researcher Award SILS outstanding scientist Award	Room: Aula 3 Room: Aula 3	
MS4 - Advanced Radiation Sources: State-of- the-art and future applications Chairpersons: E. Chiadroni, F.Stellato Room: Aula 2 Young Investigators session 11:00 KN1: L. Giannessi (ELETTRA Sincrotrone Trieste) FERMI: the first externally seeded Free Electron Laser in the extreme ultraviolet and soft X-ray spectral regions 11:00 KN1: F. Coppari (Lawrence Livermore National Laboratory) A new phase transition in laser-shu compressed gold from X-ray diffraction at to Dynamic Compression Sector beamline 11:30 O1: S. Di Mitri (Elettra Sincrotrone Trieste) Laser-Slicing at a Diffraction Limited Storage Ring 11:30 Recipient of the best PhD thesis Award SILS 2019 Best PhD thesis award talk 11:50 O2: G. Rossi (University of Milano) MariX, an advancedMHz-class repetition rate X-ray source for linear regime time-resolved spectroscopy and photon scattering 11:42 O1: E. Giangrisostomi (Helmholtz Zentrum Berlin) Directional sub-fs charge transfer dynamics of 11:742 11:00 13:30 12:30 O4: S. Lupi (University of Rome "La Sapienza") High-Intensity Terohertz and Mid-Infrared Radiation: Production and Opportunities in 12:06 O3: F. Zarotti (University of Rome Tor Vergata) Surface x-ray diffraction investigation of to	10:30	11:00	Coffee Break		
 Condensed Matter Research 12:50 O5: L. Gelisio (DESY) Structural evolution of Platinum nanostructured thin films driven by ultrashort IR radiation 13:10 O6: M. Coreno (ISM-CNR) Shedding light on low density matter with novel XUV light sources 12:30 O5: F. Tavani (University of Rome "La Sapienza") Investigating chemical reactions in temillisecond time scale through coupled X-F Absorption and UV-Vis spectroscopies 12:42 O6: I. Schiesaro (University of Rome Tre) Copper Coordination Compounds Conjugat to Gold Nanoparticles as InnovativeAntican Drugs: Structural Investigation Carried Out 	11:00	13:30	 MS4 - Advanced Radiation Sources: State-of- the-art and future applications. Chairpersons: E. Chiadroni, F.Stellato Room: Aula 2 11:00 KN1: L. Giannessi (ELETTRA Sincrotrone Trieste) FERMI: the first externally seeded Free Electron Laser in the extreme ultraviolet and soft X-ray spectral regions 11:30 O1: S. Di Mitri (Elettra Sincrotrone Trieste) Laser-Slicing at a Diffraction Limited Storage Ring 11:50 O2: G. Rossi (University of Milano) MariX, an advancedMHz-class repetition rate X-ray source for linear regime time-resolved spectroscopy and photon scattering 12:10 O3: A. De Vita (IOM-CNR) A novel high repetition rate HHG source for the study of time-resolved electronic and magnetic structure of strongly correlated systems 12:30 O4: S. Lupi (University of Rome "La Sapienza") High-Intensity Terahertz and Mid-Infrared Radiation: Production and Opportunities in Condensed Matter Research 12:50 O5: L. Gelisio (DESY) Structural evolution of Platinum nanostructured thin films driven by ultrashort IR radiation 13:10 O6: M. Coreno (ISM-CNR) Shedding light on low density matter with novel XUV light sources 	 Young Investigators session Room: Aula 3 11:00 KN1: F. Coppari (Lawrence Livermore National Laboratory) A new phase transition in laser-shock compressed gold from X-ray diffraction at the Dynamic Compression Sector beamline 11:30 Recipient of the best PhD thesis Award SILS 2019 Best PhD thesis award talk 11:42 O1: E. Giangrisostomi (Helmholtz Zentrum Berlin) Directional sub-fs charge transfer dynamics in 1T-TaS₂ 11:54 O2: J. S. Pelli Cresi (ISM-CNR) Structural modifications in cerium oxide ultrathin films induced by reduction 12:06 O3: F. Zarotti (University of Rome Tor Vergata) Surface x-ray diffraction investigation of the interface structure of Yttrium doped Barium Zirconate proton conductor grown on different substrates 12:18 O4: M. Bogar (CERIC-ERIC) In Situ GISAXS Investigation of PtNi Alloy Under Operational Conditions of PEM Fuel Cells 12:30 O5: F. Tavani (University of Rome "La Sapienza") Investigating chemical reactions in the millisecond time scale through coupled X-Ray Absorption and UV-Vis spectroscopies 12:42 O6: I. Schiesaro (University of Rome Tre) Copper Coordination Compounds Conjugated to Gold Nanoparticles as InnovativeAnticancer Drugs: Structural Investigation Carried Out by Synchrotron Badiation-Induced Techniaus 	

			 12:54 O7: G. Fazio (University of Rome "La Sapienza") Structural investigation of HgCl₂ solvation structure using X-Ray Absorption Spectroscopy 13:06 O8: S. Pollastri (CERIC-ERIC) In-situ time resolved XAS investigation of Mg in magnesium-potassium phosphate cements 13:18 O9: F. Galdenzi (University of Rome Tre) Iron rich amphiboles: a study on correlated structural and electrical properties 		
13:30	15:00	Lunch			
15:00	17:30	 Open Session 2 <i>Room: Aula 2</i> 15:00 O1: M. A. Muñoz-Marquez (CIC EnergiGUNE) Study of the reaction mechanisms of dry room gases on metallic lithium anodes for Li-ion batteries using in-situ ambient pressure X-ray photoelectron spectroscopy 15:20 O2: D. Oliveira de Souza (Elettra Sincrotrone Trieste) Experimental Aspects and Analysis Strategies for in Operando XAS experiments of catalysts in Electrochemistry 15:40 O3: A. Puri (IOM-CNR) XAFS comparative study of the crystal structure formation and evolution in Ln₂M₂O₇ (Ln = Gd, Tb, Dy; M = Ti, Zr) 16:00 O4: D. Medas (University of Cagliari) Zinc chemical speciation in bivalve shells from a polluted site 16:20 O5: A. Guarnaccio (ISM - CNR) From thiophene building blocks to conjugated molecular systems for OLEDs: an investigation by synchrotron spectroscopies 16:40 O6: F. Vita (Marche Polytechnic University) The Unconventional Nature of the Nematic Phase of Bent-Core Liquid Crystals Revealed by X-ray Diffraction 	 Satellite workshop "Coherence of UV-SoftX beams, a contribution to its exploitation" Chairpersons: S. Nannarone G. Stefani Room: Aula 3 15:00 O1: L. Avaldi (ISM - CNR) Examples of coherence in atomic and molecular photoionization by a single photon (synchrotron radiation) and few photons (FEL) 15:25 O2: S. Lupi (University of Rome "La Sapienza") Terahertz and Infrared Synchrotron Radiation: Coherence helps its use? 15:50 O3: G. Margaritondo (Ecole Polytechnique Federale de Lausanne) Microtomography with Coherent Synchrotron Radiation: Mapping the Human Brain 16:15 O4: C. R. Natoli (LNF-INFN) Some odd consequences of self-coherence in the photo-diffraction and photo-absorption processes 16:40 O5: G. Rossi (University of Milano) Measuring linear and nonlinear response by the photoelectric effect: first order diffraction and higher-order in 3D and 2D systems 17:05 O6: S. Turchini (ISM - CNR) Opportunities for spatial coherent spectroscopies in the VUV-X ray energy range 		
17:30	17:45	Closing Farewell	ceremony and coffee		

List of Posters

P1: A. Balerna "Structural characterization of hybrid Au-CuO Nanoparticles and their role in Selective Benzyl Alcohol Oxidation"

P2: M. Franca "Electronic and magnetic properties of quaternary spinel ferrites prepared by low-temperature hydrothermal synthesis: a combined XAS-XMCD investigation"

P3: F. Tajoli "Following crystallization of ZnS nanostructures in confined space by in-situ and timeresolved SAXS"

P4: S. J. Rezvani " Structure rearrangements induced by lithium insertion in metal alloying oxide spinel structure studied by x-ray absorption near-edge spectroscopy"

P5: S. J. Rezvani "Structurally induced effects on electronic properties of the semiconducting one dimensional systems"

P6: R. Parmar "Structural evolution of Lithium Manganate cathodes during charge/discharge cycles"

P7: A. Minelli " Charge density wave and framework instabilities in monophosphate tungsten bronzes"

P8: Y. Mijiti "New internally heated diamond anvil cell for fast heating and cooling rates at high pressure"

P9: Y. Mijiti "Collapse of itinerant ferromagnetism in CoS₂ under pressure: An x-ray absorption spectroscopy study"

P10: F. C. Adamo "*X-ray probing of surface anchoring in films of bent-core liquid crystals*"

P11: G. Confalonieri " *High Pressure Intrusion of Electrolyte Aqueous Solution into Si-LTA Zeolite*"

P12: L. Gigli " Structural characterization of Ga-Ferrierite, combining synchrotron high pressure XRPD and XAS experiments"

P13: R. Arletti "High pressure behavior of the hybrid material AIPO₄-5+azobenzene: an in situ synchrotron X-ray diffraction study"

P14: F. Arzilli "A new vision of kinetic processes in geosciences: 3D and in situ 4D X-ray microtomography"

P15: F. Arzilli "The evidence of mixing between basalt and rhyolite unraveled by microanalysis and X-ray microtomography"

P16: A. Puri "Earth and Environmental Sciences at LISA"

P17: A. Witkowska "Structural investigations of niobium-doped bioactive calcium-phosphate glass-ceramics by means of spectroscopic studies"

P18: P. Andreozzi "Mechanistic Study of the Nucleation and Conformational Changes of Polyamines in Presence of Phosphate Ions"

P19: A. Terzi "Sub and supramolecular investigation of the impact of tissue engineering's protocols on equine type-I collagen structural features"

P20: G. Biella "Brain and brain vessel X-ray synchrotron microbeams and microtomography for Chronic Pain studies and treatments"

P21: A. Di Cicco "*Revisiting the probing depths of soft x-ray absorption techniques by Constant Initial State photoemission experiments*"

P22: F. Stellato "A Coherent Imaging XUV-FEL users end-station for the EuPRAXIA@SPARC_LAB Free Electron Laser"

P23: F. Villa " *A photon beamline for the water window FEL at EuPRAXIA@SPARC_LAB*"

P24: S. Di Mitri "Generation of Coherent Sub-Picosecond THz Transition Radiation in Parasitic Mode to a Free Electron Laser"

P25: S. Di Mitri "Simple and Robust Free-Electron Laser Doubler for Full Control of Two-Pulse Twocolor FEL operation"

P26: P. Carrara "A novel beamline for advanced photoelectron spectroscopy with narrowband extreme ultraviolet high harmonics at variable high repetition rate"

P27: A. Puri "Developing new beamline instrumentation at LISA"

P28: M. Faiferri "The design of research infrastructures"

P29: G. Giuli "V K-edge XANES spectra of V model compounds and V-bearing phosphate glasses: a Full Multiple Scattering study"

Summary

1.	Plenary Lectures	2
2.	Large Scale Facility updates	6
3.	Tribute to Carlo Lamberti	11
4.	Commercial presentation	14
5.	MS1-Multi-techniques approach for in-situ/in operando studies	16
6.	MS2- Photon based multi-dimensional (2D/3D/4D) imaging	
	from VUV to X-rays	24
7.	MS3- Synchrotron based characterization of surfaces and interfaces	33
8.	MS4- Advanced Radiation Sources: State-of-the-art and future applications	41
9.	Open session 1	50
10	. Open session 2	59
11	. Young Investigators session	66
12	. Satellite workshop "Coherence of UV-SoftX beams, a contribution to	
	its exploitation"	77
13	. Poster session	. 84

Plenary Lectures

- PL1 -

Diamonds: a deep journey into the Earth

Fabrizio Nestola

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Diamonds and their mineral inclusions represent the only direct evidences that we have from the deep Earth between 120/130 km down to about 1000 km depth. If this is combined with the age of these precious stones, ages ranging between 3.6 billion years and 100 milion years ago, diamonds can really provide a "picture of our planet of every its evolution step with time". However, for a geologist, inclusions in diamonds are likely even more precious than diamond themselves: such direct fragments from the deep Earth are opening new and totally unexpected scenarios about how the interior of Earth works. However, very often, in-house experimental investigations are not able to study such inclusions and the synchrotron radiation in the last 10 years become one of the most useful technique to retrieve all crucial information from the diamond-inclusion systems. In 2014, we identified a micrometric inclusion of the mineral ringwoodite [(Mg,Fe)₂SiO₄] within a Brazilian diamond [1]. This was possible combining X-ray diffraction, micro-Raman spectroscopy and micro-Xray fluorescence (µXRF) using a synchrotron radiation (DORIS-III at HASYLAB, DESY, Germany, beamline L). Not only the presence of ringwoodite demonstrated that the diamond host crystallized at depths between 525 and 660 km but its high water content (1.4% H₂O) indicated that the transizion zone is one of the most hydrous shell of our Planet. Again thanks to synchrotron X-ray micro-tomography [2] (Swiss Light Source, Paul Scherrer Institut, TOMCAT beamline Switzerland), we were able to retrieve the depth of formation of the mineral ferropericlase [(Mg,Fe)O], the most abundant mineral in super-deep diamonds (those extremely rare diamonds that form at great depths down to 1000 km depth) recontructing high-resolution 3D maps and allowing us to apply for the first time an elasto-plasto model for geobarometry approaches. Thanks to such approach, it was possible to determine a minimum depth of formation of 450-500 km for the diamond-ferropericlase pair. On the same ferropericlase inclusion still trapped in its diamond host, we applied Synchrotron Mössbauer Source (SMS) [3] (European Synchrotron Radiation Facility, France, beamline ID18) in order to determine the Fe³⁺/Fe_{tot} distribution over the volume of the inclusion. This represents the first direct measurement of Fe³⁺ on an inclusion formed at 450-500 km depth and still kept within its diamond host providing in this way fundamental input on the oxidation state of ambient mantle at great depths.



Figure 1. Three-dimensional confocal μ XRF view of two-phase ringwoodite - breyite still kept within their diamond host (in blue).

A further application of synchrotron radiation was the use of synchrotron micro Fourier-Transform InfraRed spectroscopy (at Brookhaven National Laboratory, USA, beamline U2A) on a 100 μ m sized single crystal of ferropericlase [4], which allowed to map the inclusion over its entire area with an instrumental spatial resolution of 10 × 10 μ m. The analysis revealed the presence of OH⁻ homogenously distributed over the inclusion likely due to nanoparticles of brucite Mg(OH)₂ to indicate that the entrapment of ferropericlase by diamond at great depth could be occurred with the simultaneous entrapment of fluids.

Synchrotron single-crystal X-ray diffraction [5] (Diamond Light Source Ltd, UK, beamline I15) was also used to collect high-quality structural data on clinopyroxenes [\sim (Ca,Na)(Mg,Al)Si₂O₆] of relatively limited crystal size still kept within their diamond hosts. Such analysis allowed to distinguish different clinopyroxenes indicative of specific environments of formation, which is of crucial importance for diamond exploration.

[1] D.G. Pearson, F.E. Brenker, et al. Nature 2014, 507, 221.

[2] C. Anzolini, F. Nestola, et al. Geology 2019, 47, 219.

[3] F. Nestola, V. Cerantola, et al. Lithos 2016, 265, 328.

[4] M. Palot, S.D. Jacobsen, et al. *Lithos* **2016**, 265, 237.

[5] F. Nestola, M. Alvaro, et al. Lithos 2016, 265, 334.

- PL2 –

Ultra-modern synchrotron-based microscopes for the study of ancient materials: a review of applications to Roman/Italian artefacts and/ or by Italian researchers

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Cultural heritage has represented an important research activity at the European Synchrotron Radiation Facility (ESRF) for more than 15 years. At ID21, the spectro-microscopy beamline, this field represents about one third of the scientific activities (while main other fields are environmental science, life science and medicine). The ID21 X-ray and infrared microscopes have been regularly used to study various ancient and artistic materials, such as fragments from paintings, glasses, ceramics, wood, papyrus, photographs... [1] μ XRF, μ XRD, μ XANES and μ FTIR can be combined to obtain elemental maps, phase maps, speciation maps and molecular maps. These complementary pieces of information can be used to reveal manufacturing processes or to understand degradation phenomena. For what concerns Italian artefacts, the ID21 instruments have been used to study cinnabar degradation in Pompeian paintings [2], to reveal ink composition in papyrus from Herculaneum [3-4], to assess the origin of the colors and opacity in glasses [5-6], but also to study more modern materials such as 50's plastic design objects [7]. Besides, some Italian user groups are also very active in analyzing major masterpieces abroad. As an example, the SMAArt Centre and Department of Chemistry, in Perugia, is expert in the development and application of portable instruments for the *in-situ* study of artworks, and travel all over Europe to perform non-invasive analyses of artworks. But to go in more details into material composition and degradation, they may combine portable instruments with synchrotron-based micro-analyses performed on micro-fragments. They notably develop a strong research project about pigment degradation in 19th C. paintings by van Gogh or Munch as well [8]. Some of these examples will be presented.

The ESRF is currently benefiting from a major upgrade, with the coming implementation of an "extremely brilliant source" (EBS). This upgrade will significantly increase the brilliance and coherence of the X-ray beam. In this context, the ID21 instruments are being deeply refurbished. The modification of X-ray optics is on-going with the objectives to extend the energy range (to ~2-11keV) and to obtain a smaller (~100nm) and more stable beam. The X-ray microscopes will be completely re-designed to make their use more efficient and reduce set-up time. Software developments are also planned to improve data acquisition, data processing, data analysis and data archiving. Plans and schedule will be presented.



Figure 1. Some examples of artistic materials studied at ID21, by Italian users (eg van Gogh sunflowers [8]) or on Italian artefacts (plastic design objects [7], ink in Herculaneum papyrus [1, 3, 4], Pompein mural painting [2] and Roman mosaic tesserae from Aquilea [5]).

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High resolution Resonant Inelastic X-ray Scattering for the study of correlated materials

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Resonant inelastic soft x-ray scattering huge potential is quickly becoming reality. RIXS is element and site selective, like x-ray absorption spectroscopy. It is momentum resolved, like x-ray diffraction. And it probes several kinds of excitations at a time, from charge transfer and electron-hole pair generation, to orbital (dd or ff) excitations, to spin waves and lattice modes, unlike any other energy loss spectroscopy. Moreover, the elastic component of the spectra carries information on commensurate and incommensurate orders, such as charge density waves (CDW) and orbital order. The ERIXS endstation at the ID32 beam line of the ESRF is the founder of a new generation of RIXS instruments capable of exploiting all the strongpoints of this technique, thanks to the very high resolving power (30,000 at 1 keV), the diffractometer-like manipulator and the full control of photon polarization provided by the combination of the APPLE II source and the polarimeter on the analyzer. Similar facilities have started operations at DLS, NSLS II, MAX IV, TPS, to the greatest benefit of beamtime availability worldwide

I will review some of the results obtained in the first years of operations of ID32, with a special focus on cuprate superconductors studied at the Cu L_3 edge. High resolution RIXS has been used to determine the relation between crystal structure and the extent of hopping integrals in parent compounds, revealing why apical oxygens are detrimental to superconductivity [1]. Ultra-high resolution RIXS has provided a direct measurement of the momentum-dependent electron phonon coupling in undoped and superconducting samples, and has revealed new collective modes related to charge density waves (CDW) in underdoped Bi2212 [2,3]. Polarization analysis has definitively demonstrated the spin-flip character of the mid-IR spectral region in superconducting compounds. And the quasi-elastic part of RIXS spectra has brought new evidence of the universality of charge ordering phenomena in cuprates, including striped cuprates [3] and single layer Bi2201 [4]; in particular, by RIXS the charge order can be observed and carefully studied also outside the pseudogap region of the phase diagram, with significant progress in the understanding of its role in high Tc superconductors [5].

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Large scale facility updates

- LSF1 -

Current status and future perspectives of Elettra and FERMI

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Elettra is the third generation synchrotron radiation facility located in Trieste. It is serving the national and international scientific and industrial community since 1993. The 27 beamlines open to external users allow to conduct research in diverse fields, from materials to life sciences. The storage ring operates in top-up mode that affords constant photon beam intensity with improved stability and up-time exceeding 97%. Some 1000 research proposals from external users are submitted and assessed by the international peer-review panel every year but only half of them can be allocated because of the significant over subscription for most of the beamlines. Important upgrades of the beamlines have been performed during the years to guarantee state of the art performance and to satisfy the users'needs. A mayor upgrade plan of the Elettra storage ring and beamlines, has recently been funded. From the machine side, the project aims at asubstantial reduction of the emittance of the electron beam leading to a strong increase on brightness and coherence above 1 KeV. This will be obtained by replacing the current ring with the new Elettra 2.0 multi-bendachromat lattice. New beamlines will be constructed, that will take advantage of the improved performances of the ring, such as micro-XRD, micro-XRF, High Brilliance SAXS on in-vacuum undulators, Coherent Diffraction Imaging in the soft to tender X-ray region, and beamlines on super-bending magnets for hard X-ray imaging for materials and life/medical sciences. Most of the existing beamlines will be further upgraded to match the new parameters of Elettra 2.0.FERMI, the free electron laser (FEL) facility next to the Elettra storage ring, maintains its leadership worldwide as the only seeded FEL providing fully coherent ultrashort (10-100 femtosecond) pulses in the ultraviolet and soft X-ray range with full polarization control. In order to provide the most advantageous conditions for cutting edge science, and to cope with user needs, FERMI, that has officially entered into operation for users in January 2019, has been continuously improving on both accelerator and instrumentation side. Concerning the accelerator the last year has seen the implementation of a novel scheme, based on the so-called echoenabled harmonic generation (EEHG) principle, for the production of highly coherent pulses in an extended spectral range and with enhanced capabilities in tuning spectro-temporal properties. The portfolio of experimental end stations has increased thanks to the opening to the user community of the MagneDyn beamline. Moreover the recent implementation of new instruments such as wide energy range spectrometers oroptical parametric amplifiers, improved the capabilities of the FERMI end-stations. Selected examples will be presented to highlight the capabilities of the Elettra and FERMI beamlines as well as future upgrades will be discussed.

- LSF2 -

Twenty six years of operation of the ESRF Synchrotron and the EBS Project

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The ESRF – the European Synchrotron Radiation Facility – is a user facility in Grenoble, France, and the source of the most intense high-energy (6 GeV) X-rays in the world. It was the very first 'third-generation' synchrotron to be built and its light provides opportunities for scientists all over the world in the exploration of materials and living matter ranging from the chemistry and physics of materials to archaeology and cultural heritage, together with structural biology and medical applications, the sciences of the environment and the sciences of information and nanotechnologies. As of 2019, the former storage ring has been removed and a first-of-a-kind new lattice, based on an innovative arrangement of magnets that will dramatically reduce the horizontal equilibrium emittance, has been installed in its place. This 'fourth-generation' synchrotron will produce an X-ray beam 100 times more brilliant and coherent than the ESRF source today, allowing imaging down from the micrometre to the nanometre scale and – in parallel with upgraded beamlines, instrumentation and data infrastructure – providing previously unimaginable opportunities for applications as varied as nanoscopy, science at extreme conditions and structural biology. The ESRF – Extremely Brilliant Source (EBS) project was launched in 2015 and its current status will be presented, alongside the expected performance of the accelerator, the technical challenges confronted and its future potential fields of applications. A summary of the twenty six years of operation of the former ESRF Synchrotron will also be presented.

- LSF3 -

The European XFEL: start of user operation and first results

Sakura Pascarelli

European XFEL

After many years of construction, user operation at the European XFEL has finally begun. In the fall of 2017, two hard Xray instruments FXE (devoted to studying extremely fast processes) and SPB/SFX (for investigating biomolecules and biological samples) opened to external users. Before the end of 2018, the two soft X- ray instruments SQS (Small Quantum Systems) and SCS (Spectroscopy and Coherent Scattering) followed. Finally, two additional hard X-ray instruments have welcomed first user groups: HED for studying matter under extreme pressures and temperatures, and MID for investigating nanostructures or irregularly ordered materials such as glass, liquids and biological substances. In this presentation I will first briefly introduce the present performance of the facility in terms of electron and photon beam characteristics and operation modes. I will then report first results from early user experiments, and comment on some important challenges ahead.

- LSF4 -

From SPARC_LAB to EuPRAXIA@SPARC_LAB

Riccardo Pompili

INFN

On the wake of the results obtained so far at the SPARC_LAB test-facility in Frascati (Italy), it has been recently submitted our proposal to develop a new facility driven by a plasma accelerator module for extended and user-oriented applications. We are currently investigating the final design of such a new multi-disciplinary user-facility, equipped with a soft X-ray Free Electron Laser (FEL) operating with energies larger than 1 GeV. This design study is performed in synergy with the EuPRAXIA design study. Here the latest layout and beam parameters are presented.

Tribute to Carlo Lamberti

- TCL1 -

Direct writing of conductive channels in TiO₂ single crystals by a synchrotron X-ray nanobeam

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It is well known that intense synchrotron beams can alter the state of materials, but this effect is generally considered undesired radiation damage. However, intriguing phenomena, which enable to modify materials in a controlled way, have been recently reported [1, 2, 3]. We have investigated the effect of irradiating selected areas of TiO_2 rutile single crystals by a 56 \times 57 nm² synchrotron X-ray nanobeam at 17.4 keV (see Figure 1A) [4]. Besides a transient increase of conductivity due to a photovoltaic-like process, we have measured a non-volatile localized change of resistance by about 4 orders of magnitude after X-ray exposure when an irradiation line is realized with a photon flux in the order of 10¹⁰ photons per second (see Figure 1B). The non-volatile increase of conductivity can be modulated by varying the beam intensity and the exposure time. This effect can be ascribed to the local generation of oxygen vacancies by the X-ray nanoprobe, which are subsequently ordered by the electric field applied during the acquisition of the I-V curves. Conductive AFM measurements show that the conductive channels induced by the X-rays are sub-superficial. Our results demonstrate that intense synchrotron beams can create oxygen vacancies in materials with tightly bound oxygen atoms, highlighting that X-ray nano-probes could become an effective tool for nano-fabrication of oxides, able to locally increase or decrease the material resistivity [4, 5, 6]. For instance, since the localized presence and migration of oxygen vacancies is an essential requisite for redox-based memristive devices, the possibility to locally induce oxygen vacancies in a prototype oxide like TiO₂ could represent a novel tool for the rational design and production of oxide-based memristive devices, replacing the problematic electroforming step.



Figure 1. A. Scheme of the Au contacts deposited on the TiO₂ single crystal for electrical characterization during X-ray irradiation. **B.** I-V curves of the TiO₂ single crystal acquired after each irradiation line between two Au electrodes at increasing X-ray photon fluxes. In the inset a magnification of the I-V curves for the irradiation at low photon fluxes is reported.

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Retrieving quantitative structural information from XANES spectra by means of Multivariate and Machine Learning Approaches

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X-ray absorption near-edge spectroscopy (XANES) is becoming an extremely popular tool for material science thanks to the development of new synchrotron radiation light sources. However, in contrast to X-ray diffraction, a quantitative analysis of XANES spectra is rarely performed in the research papers. The reason must be found in the larger amount of time required for calculation of a single spectrum if compared to a diffractogram simulation. For such time-consuming calculations, in the space of several structural parameters, we developed a new approach based on different multidimensional interpolation methods realised by machine learning algorithms (ML) [1,2]. The analytical work is organised in two steps. First, a series of experimental spectra are analysed statistically by means of principal component analysis (PCA). Herein, a new method based on the usage of a transformation matrix is applied to identify the "pure" (having a chemical/physical meaning) spectra and their related concentration values. Second, the extracted pure spectral profile/s is/are fitted by interpolated theoretical spectra exploiting a defined set of geometrical parameters that can be obtained using different sampling methods (e.g. grid, random or IHS). This technique, usually goes under the name of "indirect" method [3] of fitting and implies that each point of a general XANES spectrum is considered as a function of a determined set of structural parameters **P** (i.e. $\mu(E, P)$). On this basis, ML algorithms demonstrated to be a proper working tool to generate interpolated spectra, especially thanks to their ability to provide a good approximation in the whole region of variation of the structural parameters. Finally, the optimization procedure requires to find the geometric parameters whose the calculated spectrum fits best the experimental one in terms of L_2 norm, which is defined as the integral over the square of the difference between the theoretical and the experimental spectrum. The final output is then characterised by the XANES best-fit spectrum associated to its related set of structural parameters. A schematic representation of the entire process is shown in Figure 1.



Figure 1: Block diagram of the technique. The input data can be represented by a single spectrum or by a series of experimental XANES data acquired during the variation of a physical/chemical parameter (e.g. time, temperature, pH ...). In this last case the entire experimental dataset can be processed by PCA approach and the related pure spectra and concentration profiles can be retrieved by means of an appropriate transformation matrix. ML algorithms are trained on a set of XANES calculated starting from a set of points (chosen using different approaches such us: grid, random sampling or IHS) in a user-defined parameters space. Herein, they the ML application provides a good and fast approximation of a XANES spectrum in the whole continuous region of variation of the structural parameters. The optimization routine takes place minimizing the L_2 norm between the experimental spectrum and the interpolated one. The final output is then represented by the XANES best fit and its related set of geometrical parameters.

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Commercial Presentation

Breakthrough Lab X-ray Techniques approaching Synchrotron Beamline Performances

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Quantum Design Europe

Synchrotron beamline X-ray techniques have several inherent advantages over their laboratory equivalent in terms of their massively higher source brillance, energy coherence, tuneability and sub-micron resolution capabilities. Synchrotron x-ray techniques such as microXRF (X-ray fluorescence), XAS (X-ray Absorption Spectroscopy with XANES & EXAFS) and nano XRM (X-ray Microscopy) are becoming increasingly central to advanced research in alternative energy, catalysts, medicine, semiconductor materials to geology. This has led to oversubscription and immense competition in acquiring beamtime. In spite of the growth of these techniques at synchrotron facilities, efforts toward developing higher sensitivity and smaller X-ray spot size laboratory X-ray capabilities have progressed relatively slowly due to bottlenecks in X-ray optics and low brightness laboratory X-ray sources. Sigray developed a breakthrough laboratory microfocus X-ray source with user selectable or tunable energy which has significantly higher brightness/flux than conventional micro focus &/or rotating anode sources. Coupling this patented source with their novel double-paraboloidal X-ray mirror lenses, they are introducing a suite of laboratory X-ray instrumentation with performances close to their synchrotron equivalent. These include microXRF, XAS, and nano-XRM.

MS1

Multi-techniques approach for in-situ/in operando studies

- MS1·KN1-

Harnessing X-ray (Spectro)microscopy for Chemical Imaging of Heterogeneous Catalysts

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Heterogeneous catalysis is ubiquitous in chemical industry, with an estimated 90 % of all chemical processes involving use of a catalyst at some stage [1]. These materials typically possess a complex hierarchical structure often spanning multiple length scales and containing various physical components, such as active metal nanoparticles (e.g. 1 to 10 nm), porous supports (nm- μ m scale), macroscopic structure such as crystalline phases, pellets or monoliths (μ m-mm scale). Furthermore, catalysts are functional materials, the performance of which is integrally related to their structure. Therefore to improve efficiency, sustainability and versatility for their numerous applications, it is optimal to develop an understanding of catalysts: (i) across multiple length scales covering all structural features of interest; (ii) in a spatially-resolved manner, avoiding the use of bulk or averaging analytical methods; (iii) under reaction conditions using '*in situ*' or '*operando*' analysis, allowing derivation of structure-activity relationships [2-3]. Structure-activity relationships in particular are a cornerstone of modern catalysis research, while the collection of spatially-resolved data avoids generalization and over-simplification of the structure observations made.

It is not surprising that the high flux, tunable energy and flexible experimental potential of synchrotron light sources play a crucial role in catalysis research, through the application of both X-ray spectroscopy and microscopy techniques. Modern hard X-ray microprobes and nanoprobes at third and upcoming fourth generation synchrotron light sources offer excellent opportunities for catalyst characterization [4], specifically through the development of so-called 'chemical imaging' methodologies - extracting chemically relevant information through the combination of highly focused X-rays with absorption, phase, fluorescence, diffraction or spectroscopic measurements, for example [5]. In many cases, the application of hard X-ray microscopy for chemical imaging is currently unexplored, despite the wealth of information which may be obtained.

This contribution will highlight several recent experiments in the field of exhaust gas catalysis, energy conversion, and nanostructured materials [6,7,8]. The specific focus will be on deriving chemically relevant data through hard X-ray microscopy on the μ m and nm scale, such as metal oxidation state, crystalline structure, deactivation effects (e.g. sintering, structure collapse) and analysis of porosity. In most cases this data is acquired through tomographic imaging, meaning that the results are 3-dimensional renderings, offering numerous advantages in comparison to conventional bulk measurement. The design of reaction environments for *in situ* and *operando* chemical imaging in 2D and 3D will be demonstrated, along with case studies performed at the ESRF (Grenoble, France) and PSI (Villigen, Switzerland). A perspective on the imminent arrival of diffraction limited light sources and the implications for the field of X-ray microscopy in catalysis research will also be discussed.

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- MS1·O1 -

Dynamic Processes in Metal Hexacyanoferrate-based Batteries Revealed by *Operando* XAS and XRD

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Dynamic processes occurring in batteries are generally studied by ex situ modality. However, those processes that rule out electrochemical energy storage in batteries can be studied under operating conditions. *Operando* experiments provide a realistic representation of the reaction behavior occurring at electrodes. The typical drawbacks of ex situ experiments due to sample transfer, such as the alteration of air or moisture-sensitive species, are avoided, and so are the relaxation reactions that may occur when the electric circuit is opened. *Operando* data collection allows to check the structural and electronic reversibility of a battery system, while at least one full cycle is performed. For all these reasons, ex situ studies of electrode materials are now complemented by *operando* measurements using complementary tools such as X-ray diffraction (XRD) and/or spectroscopic techniques such as X-ray absorption spectroscopy (XAS).

X-ray absorption spectroscopy is a synchrotron radiation based technique that is able to provide information on local structure and electronic properties in a chemically selective manner. *Operando* synchrotron radiation powder diffraction experiments allow monitoring changes in the crystalline phase and the periodic structure of a material during the intercalation/release process.

The potentiality of the joint XAS-PXRD approach in the newly proposed Prussian Blue-like cathodes materials (also called metal hexacyanoferrates) for Li and Na batteries is here underlined [1, 2, 3]. Metal hexacyanoferrates represent a new class of active material electrodes for batteries. Structurally speaking they are formed by three-dimensional bimetallic cyanides lattice, enabling to host a wide variety of ions due to the large interstices and channels. The rigid and open framework that characterizes Prussian Blue analogues allows facile and reversible ion-exchange, permitting their use not only in lithium- and sodium-ion batteries but also on polyvalent ions. The intercalation and de-intercalation processes are accompanied by a structural modification as well as in the oxidation state of metals constituting the framework. The presence of two transition metals in the compound also enable multiple edge EXAFS investigation, accompanied with strong multiple scattering effects [4, 5].

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- MS1·O2 -

On the hydrogenation of the Graphene/Ni(111) system

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Due to the high surface-to-weight ratio of graphene, there has always been a big interest in the possibility to use it as support for hydrogen storage.

However, given the difficulties in hydrogenating free standing graphene, solutions based on Gr supported on metals are actively investigated. In particular, hydrogenation of epitaxial graphene supported on transition metal crystals has been studied in several cases. In these systems the substrate induces periodic corrugations of the Gr layer (moiré superstructure) thus modulating the H adsorption.

In this framework, Gr on Ni(111) appears of great interest since the Gr and Ni(111) lattices are commensurate and in principle there are no limitations due to the moiré pattern. Moreover, hydrogenation might be favored by the peculiar reactivity of Gr/Ni(111). These reasons motivated a re-investigation of the interaction on this system with hydrogen.

In this study [1] we have deeply investigated the Gr/Ni(111) system when exposed to atomic hydrogen at room temperature. We used fast x-ray photoelectron spectroscopy (XPS) to follow the hydrogenation in real time combined with high resolution core level spectroscopy and near edge x-ray adsorption fine structure spectroscopy (NEXAFS), as well as STM measurements, to determine the configuration of the hydrogenated interface.

We found that hydrogenation proceeds through a dual path that first includes hydrogen chemisorption on top of Gr followed by a slow but continuous intercalation below Gr.

Hydrogen chemisorption initiates as soon as the sample is exposed to the atomic hydrogen flux and saturates quite rapidly when ~25% of the Gr surface is hydrogenated. The formation of C-H bonds reflects in new C1s components that we assigned through DFT calculations to C atoms directly bonded to H and to their first neighbors. In parallel, with a much lower rate, H atoms intercalate below Gr and bind to Ni surface sites.

Temperature programmed desorption (TPD) measurements showed that the intercalated H atoms desorb abruptly below 400 K whereas chemisorbed H is released around 600K. This demonstrates that besides offering a storage volume for the intercalated H, Gr stabilizes it above room temperature rising by a few tens of kelvins the H_2 release temperature with respect to the bare Ni(111) surface.



Figure 1. (left panel) C1s core level spectra of Gr/Ni(111) surface exposed to low (top) and high (bottom) H doses corresponding to chemisorbed and intercalated phases, respectively; (middle) NEXAFS and (right) valence band spectra measured at different hydrogenation stages.

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- MS1·O3 -

Probing the chemistry of cultural heritage materials *via* different 2D XANES-based approaches: the alteration processes of pigments and carbonatation of calcium-based consolidants into limestone matrix

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In the cultural heritage field, chemical investigations are usually complicated by the fact that materials show multilayered and heterogeneous networks composed of organic and inorganic components with amorphous and/or crystalline structures that evolve with time. In this context, the use of synchrotron radiation (SR)-based X-ray micro-spectroscopic methods, including μ -XRF, μ -XANES and μ -XRD, has increased within the last few decades due to their capabilities to provide highly specific elemental and molecular speciation information with spatial resolution down to the (sub)micrometer-scale. [1-3]

Nowadays, technological research perspectives are driven by the need for time acquisition reduction in order not only to render the 2D/3D mapping of large areas more feasible but also to overcome possible damages of samples induced by the exposure to SR X-ray sources.

In general, three 2D XANES-based approaches can be used for obtaining chemical speciation information:

1) analysis of one or more regions of interest by acquiring μ -XRF maps at a few different energies around the absorption edge of a specific element in combination with collection of single-point XRF-mode μ -XANES spectra at a limited number of spots;

2) full-spectral XANES imaging in XRF-mode (by employing either traditional ED-XRF or fast X-ray detectors);

3) transmission-mode full-field XANES imaging.

These approaches have found various applications, such as the investigation of the alteration mechanisms of different artists' pigments and the study of the manufacturing processes of ceramics. [4-11]

In this contribution, the advantages and drawbacks of the three above mentioned 2D XANES-based approaches in the context of the degradation processes of pigments (i.e. Prussian blues, chrome yellows and cadmium yellows) and of carbonatation of calcium-based consolidants into limestone matrix will be discussed.

Notably, XANES/ XRF results, in combination with μ -XRD ones, acquired at ESRF-ID21 (Grenoble, FR) and PETRA III-P06 (Hamburg, DE) beamlines from the analysis of artificially aged mock-ups and of paint micro-samples from original artworks [3,12] will be presented.

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- MS1·O4 -

Effect of space confinement on crystallization of molybdenum oxide synthetized by inverse miniemulsion – an *in-situ* SAXS/WAXS study

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Molybdenum oxides are of significant importance for applications such as sensing and catalysis [1]; among them, the most common oxide of molybdenum is molybdenum(VI) oxide, MoO₃, which is known to crystallize in a wide variety of polymorphs, both anhydrous and hydrated. In particular, metastable hexagonal h-MoO₃ phase is very interesting due to its one-dimensional behaviour and tunnel structure, exhibiting superior photo-physical and photo-chemical properties in comparison to other MoO₃ structures, such as orthorhombic and monoclinic [2]. Typically, h-MoO₃ is crystallized at high temperature and/or in hydrothermal conditions [2, 3]; on the contrary, we address the synthesis of highly crystalline hexagonal h-MoO₃ at room temperature, by using an inverse (water-in-oil, w/o) miniemulsion (ME) method.

ME are heterophase systems characterized by droplets with a typical size ranging from 30 to 300 nm, dispersed in a continuous phase, which can be exploited as "nanoreactors" for synthetizing inorganic colloids within constrained environment [4]. The physical properties of liquids in nanodroplets can be substantially different from those of the bulk phase and the dynamics of the crystallization and melting process are consequently affected. Indeed, it has been widely reported that the phase diagrams and kinetics of phase transformation processes in confined space can deviate considerably from the respective dependencies and rates as observed in batch.

Confinement effect of ME nanodroplets on the crystallization of $h-MoO_3$ was observed by performing the synthesis of molybdenum oxide both in ME and in batch conditions (simple mixing of the precursors at room temperature). While pure $h-MoO_3$ was crystallized at room temperature in ME, a different unknown phase was obtained in batch conditions, turning to $h-MoO_3$ only after thermal treatment.

The crystallization pathway of h-MoO₃ in ME and in batch conditions was studied *in situ* in a time-resolved fashion (10 s resolution) at SAXS beamline at Elettra synchrotron, with a specifically optimized continuous flow set-up. In particular, the reaction mixtures (inverse ME and the mixing of the precursors in the case of batch synthesis) were produced during measuring by using the ultrasonicator and a remotely controlled syringe pump. The resulting suspensions were funnelled through the continuous flow equipment to a homemade cell mounted in the beamline. The scattering profile of the reaction mixtures was followed as a function of time and Bragg reflections in the SAXS region were observed (Figure 1). The peaks resulting from the ME mixture and the batch one happened to be evidently different, concerning signal intensity evolution, position and width, evidencing how the confined conditions in ME lead to a different crystalline structure of



Figure 2: Bragg peaks of ME sample (left) and batch sample (right), as a function of time.

molybdenum oxide.

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- MS1·O5 -

Pressure and Zeolite Framework Type Cooperation Effect in the Differential Absorption of Ethanol and Water from the Azeotrope Solution: the case of Si-Chabazite

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Pure silica zeolites are able, under pressure, to absorb water molecules despite their hydrophobic nature. The role of pressure has been found to be essential also in the penetration of different aqueous solutions, as mixtures of ethanol and water or of methanol, ethanol and water (m.e.w.) [1, 2]. The absorption of these solutions, however, is strongly driven not only by pressure, but also by the framework type of the zeolites. Indeed, in Si-FER compressed in a water-ethanol solution, the combined effect of pressure and shape constraints induces the formation of organized arrangements of small molecules in the zeolite porosities [1]. Both components penetrate zeolite cavities, but they are segregated in different channels. While the water molecules occupy only ferrierite 6MR channels, the ethanol molecules are located in the 10MR channels. The irreversibility of the process and its coupling with the supramolecular shaping effect can be a more general feature of the high-pressure (HP) behavior of other silica zeolites that can be exploited for future technological applications.

To better understand the zeolite shape-directing action in separating strongly hydrogen-bonded liquid mixtures into their constituents, the influence of different framework geometries should be considered.

In this work, a pure silica chabazite (Si-CHA) was studied by means of *in situ* X-Ray Powder Diffraction (XRPD) during the penetration of an azeotrope ethanol-water solution under HP using a modified Merrill–Basset Diamond Anvil Cell (DAC). The experiment was performed at BL04-MSPD beamline of ALBA synchrotron (Barcelona, Spain). Two-dimensional patterns were recorded on a CCD camera SX165 (Rayonix), with a sample-detector distance of 160 mm, using a fixed wavelength of 0.5340 Å and 50 s collection time. Data were collected from Pamb to 2.66 GPa and upon pressure release at 0.37 GPa.

Data show that both water and ethanol penetrate Si-chabazite at both ambient and HP conditions. However, while at P_{amb} the water : ethanol ratio absorbed inside Si-chabazite is similar to that of the external azeotrope mixture, upon compression we observed a dehydration effect. In fact, at 1.84 GPa, zeolite extraframework content corresponds to a composition much richer in water than the azeotrope. The arrangement of the extraframework molecules, in comparison to Si-FER, does not present any separation between the two species. In this case, indeed, the peculiar chabazite structure, made by cages instead of separate channels, favors the interactions between ethanol and H₂O molecules. At 2.44 GPa the external solution crystallizes, whereas an ideal azeotrope solution proved to crystallize at 4.8 GPa. Since pure ethanol crystallizes at about 1.9 GPa, this is a further proof of the HP-induced dehydration of the ethanol-water azeotrope. The results obtained at this pressure by XRPD were also compared to those obtained by DFT calculations.

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- MS1·O6 -

Assessing by *in situ* synchrotron powder diffraction the effect of enhanced ferroelastic domain switching in zeolite ZSM-5 in order to tailor the secondary induced mesoporosity

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The ZSM-5 zeolite (MFI framework topology) belongs to the pentasil zeolite family and it is characterized by a threedimensional pore system formed by two intersecting sets of tubular channels delimited by 10-membered rings of tetrahedral: the so-called straight channel parallel to the [010] direction and the sinusoidal channel parallel to the [100] direction. Its unique microporous structure coupled with high surface area, mechanical, thermal, biological, and chemical stability has made ZSM-5 one of the most employed synthetic zeolites in catalysis and adsorption processes.

A ferroelastic monoclinic (s.g. $P2_1/n$) to orthorhombic (s.g. Pnma or $Pn2_1a$, or $P2_12_12_1$) phase transition was early recognized in ZSM-5, suggesting that monoclinic crystals consists of an aggregate of monoclinic twin domains which reversibly switch to an orthorhombic single-crystal upon heating [1]. The ferroelastic behavior was more recently investigated, on a high-silica form, using the Landau theory for the rigorous analysis of spontaneous strain variation through the temperature-dependence of the order parameter (the crystallographic beta angle) obtained from Rietveld refinements of in situ synchrotron radiation high-resolution powder diffraction data [2]. The latter study assessed the tricritical character (i.e. borderline between second order and first order) of the $m \leftrightarrow o$ phase transitions are generally less relevant than those associated to truly second order transitions [3]. In a successive study we showed that the adsorption of different organic contaminants in highly siliceous ZSM-5 affects the $m \leftrightarrow o$ transition temperature and its related thermodynamic properties highlighting the strong effect of host-guest interactions on the ferroelastic spontaneous strain [4].

The present work is aimed to assess the effect of ferroelastic domain switching enhanced at the exact critical temperature (T_c) of the $m \leftrightarrow o$ phase transition in order to optimize the post-synthesis procedure used to induce secondary mesoporosity in the as-synthesized ZSM-5 to form the so-called 'hierarchical ZSM-5'. These zeolites are currently attracting much interest in both catalysis and adsorption processes where bulky molecules are involved. For instance, it has been shown that the generation of large mesoporosity (enhancing the diffusion of coke precursors) while keeping the zeolite crystallinity intact (suppressing coke formation by shape-selectivity) is highly desirable for designing a zeolite catalyst with an enhanced catalyst lifetime. On the other hand, much effort has been devoted to tailor the extent and the secondary mesoporosity. Given the reported cooperative interplay between zeolite defect sites and mesoporosity [5], the working hypothesis of the present investigation is that defect species are stabilized by interaction with the twin wall structure so that defects are collected on twin walls by domain wall pinning [6]. Therefore, the so-called 'twin memory effect', which is predicted to occur when ZSM-5 is cyclically heated into its paraphase and then cooled back into the ferrophase, can be developed as a tool to generate and control the hierarchical porous structure of ZSM-5. To achieve this goal ZSM-5 materials with several Si/Al framework ratios have been synthesized and prepared in their protonic form. Those with Si/Al = 25 and 100 were also used to fabricate hierarchical ZSM-5 by treatment with NaOH solutions at different time-length (15, 30, 60 minutes). In situ powder diffraction data have been collected both in laboratory with conventional radiation and at synchrotron radiation sources (ID22 beamline at ESRF), and combined with calorimetric data. Although the dependence among T_c , Si/Al ratio, and the enthalpy change ΔH related to the ferroelastic $m \leftrightarrow o$ phase transition in ZSM-5 compounds has been already outlined, the thermodynamic processes that govern these relationships at both the crystal structure and mesostructure levels have to be still disclosed. The first goal achieved is therefore the most accurate as possible quantitative relationships for the dependence of the $m \leftrightarrow o$ phase transition temperature and thermodynamic parameters upon the Si/Al ratio.

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MS2 Photon based multi-dimensional (2D/3D/4D) imaging - from VUV to X-rays

- MS2·KN1 -

4D Bragg Coherent Diffraction Imaging of Nanocrystals using XFELs

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The Bragg Coherent Diffraction Imaging (BCDI) method will be described. Its greatest strength is to reveal 3D phasecontrast images of the interiors of crystals with image resolution in the 30nm range. It achieves this through the projection of lattice displacements onto the diffraction **Q**-vector, showing up as a phase shift on a very sensitive scale: one lattice constant results in a phase shift of 2π . Using this new channel of information about the detailed structures of crystals, we have found striking patterns of phase nano-domains within otherwise solid-looking crystals up to one micron in dimension. When excited with a laser, the pattern of strains evolves in time to give 4D images recorded using X-ray Free-electron Lasers.

This keynote presentation will describe the BCDI method and illustrate it with our work on Au nanocrystals. The shapes of nanocrystals are strongly influenced by the presence of internal strain, which can be induced by laser excitation and imaged in 4D. The strain patterns in both breathing and shear modes of vibration are imaged [1] and when the laser fluence is increased, the beginning of melting can be observed [2]. XFEL powder diffraction studies have since resolved the characteristics of the melt front at early time [3].



Figure 1. a,b) Coherent Diffraction patterns of a gold nanocrystal c) Peak centre as a function of pump-probe delay d) Images of the strain inside the nanocrystal.

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Diffraction imaging of helium nanodroplets with the FERMI Free Electron Laser

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The FERMI Free Electron Laser (FEL) facility in Trieste (Italy) is unique in the FELs landscape because it has been designed as a seeded source, resulting in superior performances in terms of control and reproducibility of its light pulses. Transverse and temporal coherence are those expected from a true laser, and have been exploited in a series of pioneering experiments. The Low Density Matter (LDM) beamline at FERMI has been serving the atomic, molecular and cluster science community since its opening at the end of 2012. Through the use of interchangeable supersonic jet sources, it offers the possibility of studying atoms, molecules, and clusters.

In this talk I will present the results of Users' experiments performed at the LDM beamline on the coherent imaging of superfluid helium nanodroplets produced in a free-jet supersonic expansion. Although their superfluid nature initially led to consider them as non-rotating uniform spheres, it was later accepted that large droplets can accommodate quantized vortices, which have indeed been imaged in a single-shot femtosecond x-ray experiment at the LCLS [1]. At FERMI, we recorded a large set of wide-angle single-shot scattering images of individual helium nanodroplets [2], which were classified with a neural network approach [3]. The diffraction patterns were matched against a catalog of full three-dimensional droplet shapes, which, surprisingly, were found to agree with the predictions of a theoretical model for *normal liquid* droplets.

The FERMI facility is also capable of generating multi-color FEL pulses [4], and we have used them to perform imaging of electronically excited droplets. The experimental setup and first results will be presented.

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- MS2·O2 –

Study fast-demagnetization processes using FERMI seeded-FEL.

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The high degree of coherence, tunability, multiple polarization and jitter-free pump-probe schemes of laser-seeded EUV-Soft X-ray free electron laser FERMI have enabled a great variety of single or multicolor experiments with full control of pulse intensity and duration. This has opened unprecedented opportunities for (i) investigating ultrafast dynamics with chemical sensitivity by tracking how specific excitations in complex systems, triggered by different stimuli, evolve and/or propagate among different sites and (ii) performing X-ray coherent non-linear experiments to exploit, among other, electronic correlations and charge transfer between different atomic constituents in the sample.

This presentation will overview different class of experiments performed at the DiProI end-station [1] that illustrate the recent research achievements thanks to the unique characteristics of the FERMI-FEL [2]. Particular emphasis will be on novel schemes in magnetic dynamics studies probing different absorptions edges in time coincidence, both in real space by means of time resolved holography [3] or using Fresnel zone plate to stretch the incoming X-ray pulse, keeping an angular encoding of the arrival time [4].



Fig. 1 Sequence of two colors time resolved holographic images taken simultaneously at the Co and Fe edges on a $(Co/Pt)_{ML}$ / TbFe bi-layer structure. The sequence shows that, 0.2 ps after the optical excitation Co-based top-layer is demagnetized, while Fe in the below TbFe magnetic structure takes more time to be excited (0.5 ps) on longer time scale (t>1ps) the maze domain structure on the sample surface is recovered [C. Von Korff Schmising, in preparation (2019)].

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- MS2·O3 -

The use of synchrotron-based X-ray microtomography for the pore network quantitative and computational fluid dynamics experiments on porous carbonate rocks

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The morphology and the texture of the pore media exert a primary control in the fluid migration and storage in rocks. In the case of carbonates, their architecture of the pore network of porous carbonates are highly variable due to primary depositional variability, diagenesis processes and deformation [1,2]. This issue represents an important challenge for the characterization and development plan of this kind of reservoirs in different industries such as, hydrocarbon, ground water and geothermal energy. During the evaluation of reservoirs, one of the most elusive aspects is obtaining relationships between porosity and permeability because permeability depends also on textural and hydraulic properties of the pore network such as pores size distribution, pores shape, and tortuosity [2].

This study assesses the control exerted by the pore network on the storage and migration capacity in porous carbonates by combining synchrotron X-ray computed microtomography (SR micro-CT) and computational fluid dynamics. The studied rock samples are mainly porous grainstones exposed in south and central Italy. Some samples may content deformation structures (i.e. deformation bands, Fig. 1) or may be altered by diagenesis. Previous studies have reported permeability differences and significant variabilities of the in-situ hydrocarbon distribution on the studied rocks [e.g. 3, 4].

The selected rock samples were imaged at the SYRMEP beamline of the Elettra laboratory. The X-ray beam delivered from a bending magnet source has a nearly-parallel geometry and a high spatial coherence [7] allowing to take advantage of phase contrast effects. This beamline is suitable for obtaining 3D images of carbonate rocks and extracting valuable information about pores morphology, connectivity, and permeability at the pore scale [e.g. 5, 8]. In this study, the selected spatial resolution of the images is variable $(1.0-9.0 \ \mu\text{m})$ depending on the grain size distribution of the rock sample. The SR micro-CT experiments and the image processing and analysis were performed following the methodology described by Arzilli et al. [5] and Zambrano et al. [6]. 3D image segmentation was performed by the automatic multiphase k-means clustering algorithm, setting 3 to 4 classes of objects, depending on the sample. The segmentation was performed by using the Pore3D software library developed at Elettra [9]. Then, a 3D bilateral filter was applied to the reconstructed data for smoothing the images and preserving edges. The SR micro-CT images were used for both performing a quantitative pore network analysis of the studied rock samples and performing computational fluid dynamics experiments using the opensource software Palabos [10], which is based in lattice-Boltzmann method (LBM). The methodology [11] consists of imposing a single-phase fluid flow through the segmented 3D images by maintaining a fixed pressure gradient between the inlet and outlet faces of the volume, the rest of the faces were padded. The interface pores-voids was converted to bounceback boundary conditions. It was used a Multiple Relaxation Times approach [12] with a D3Q19 lattice. This method generates viscosity-independent results of permeability. The permeability of the volume was calculated using Darcy's law once steady conditions were reached. To evaluate isotropy, the results of permeability and the pore network properties were calculated in three dimensions.

The results indicate that deformation and diagenetic processes may have and important impact on the pore network properties and therefore on storage (porosity) and migration (permeability) capacity of the studied rocks. Moreover, results indicate that permeability depends on the different evaluated properties (i.e. effective porosity, specific surface area and tortuosity). Permeability is directly related to the effective porosity, and inversely related to the specific surface area and the tortuosity. Documented variation in permeability among the evaluated host rock samples is strictly related to the architecture of the pore network expressed by the evaluated properties. Permeability results are in the same order of magnitude of the previous laboratory and field measurements. However, the method applied in this work is more selective than other traditional methods for assessing the permeability and the textural properties of zones of few millimeters of size.



Figure 1. Sample hosting a Deformation Band (DB): a) Volume rendering of the (i) raw reconstructed SR micro-CT images (voxel size = 9 μm) and (ii) segmented pores space (connected pores in yellow and unconnected pores in red, after Zambrano et al. [6, 11]. Detail of velocity fields from the b) and d) host rock, and c) fault core. In the velocity fields rendering, high velocities in lattice units are

represented by warm colors. The z-axis of the volumes is perpendicular to the DB. Note: For the color version of the figure please refer to the online version of the abstract or contact the main author.

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- MS2·O4 -

High resolution X-ray Phase Contrast Imaging for studying the effects of novel radiotherapies

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X-ray Phase Contrast Computed Tomography (PCI-CT) can be used to non-invasively study soft tissues and to investigate in 3D the morphology of bio-pathologies with high detail and sensitivity. This imaging method allows to study target organs with a multiscale approach. In previous work, our team has imaged rat brains bearing 9L glioblastoma, and has shown that PCI is suitable to discriminate between healthy and cancerous tissue [1]. Moreover, we obtained a proof of concept in our studies, that the technique can be used to analyse the different effects of applied X-ray radiotherapies on a rat animal model. We irradiated in-vivo healthy and brain tumour bearing rats with standard broad X-ray beam (BB), Microbeam and Minibeam Radiation Therapies (i.e. arrays of beamlets with tens or hundreds micrometre width, respectively - MRT [2] and MBRT [3]) by using different levels of delivered dose. We compared the three treatments in terms of radiation-related effects by investigating the treated tissue by means of 3D PCI-CT. Following the first promising results on rat brains, the study was extended to rat lungs, which were irradiated with radiotherapy protocols similar to those used for brains. The choice of focusing also on lung cancer is determined by the high oncological relevance of the case: it remains the most common tumour in men worldwide [4] with an incidence that has been increasing during the last decades. We analysed treated healthy rat lungs in 3D and with spatial resolutions down to sub-micron scale to understand the optimal geometrical configuration and doses to be delivered to spare healthy tissues.

For the first part of the study, 49 rats implanted with 9L glioblastoma, as well as 23 non-implanted rats, were alternatively treated with MRT, MBRT and BB with different beam sizes and peak doses at the European Synchrotron Radiation Facility (France). The selected peak doses were: 200, 400 and 600 Gy for MRT; 180 and 350 Gy for MBRT and 5, 10 and 15 Gy of BB irradiation. Two days after irradiation, rats were imaged using Magnetic Resonance Imaging (MRI) (4.7 T) at the IRMaGe MRI facility of Grenoble, in order to compare tumor sizes at the moment of treatment (or just after) with the sizes measured at the time of the PCI-CT experiment. The sequences used were a T_2 -weighted spin-echo sequence and two T1-weighted spin-echo sequences before and 30s after the injection of Gd contrast agent. As for lungs irradiations, 96 rats were divided into 11 groups depending on the delivered beam and dose: 1) controls; 2-3) BB of 30 and 50 Gy; 4-7) MRT of 50, 100, 300 and 600 Gy as peak doses; 8-11) MBRT 50, 100, 300 and 600 Gy as peak. After the organ extraction and fixation, all the samples were then imaged by X-ray PCI-CT by using a sCMOS PCO.Edge 5.5 camera with different pixel size combination depending on the sample to be imaged. Rat brains were analysed with either a monochromatic beam of 35 keV and a pixel size of 3 μ m or a pink beam and 0.7 μ m as pixel size while rat lungs were imaged with a 22 keV energy X-ray monochromatic beam and pizel sizes of 1.63 and 0.65 μ m.

X-ray PCI-CT allows the recognition and differentiation of brain and lungs anatomical details down to the cellular level and identification of microscopic cancerous cell-clusters far from the main lesion, tissue necrosis, tumour oedema, highdensity calcifications as well as micrometric MRT-transections for brains, while for lungs, radiation induced fibrosis is visible. The latter can be visualized as thickening of alveolar walls, expansion of alveolar spaces and destruction of their normal structures, which are replaced by irregular, abnormal air spaces and large areas of scarring.

X-ray PCI-CT provides a very detailed visualization of anatomical structures. It can reproduce the accuracy of histology in discriminating tissues [1] but extended to the full organ volume and not limited to a 2D slice. The method appears to be well suited for investigating cancer development and radiotherapy effects on both the studied biological targets. In the future, other types of tumours and target organs will be considered and the method will be also tested for image-guidance during radiotherapy.

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Single-crystal synchrotron X-ray diffraction study of new anthracene derivatives compounds

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Anthracene derivatives compounds have recently known an increasing scientific interest thanks to their unique physical properties (*i.e.*, bright luminescence and large charge mobility) [1], making them ideal candidates for applications in new optoelectronic devices.

A structural study of new anthracene derivatives compounds was carried out by single-crystal synchrotron X-ray diffraction to have insights on the structure-property relationships, characterize the crystal packing and the main aromatic interactions, and detect the presence of stacking arrangements (see, for example, Figure 1).

Synchrotron data were collected at room temperature at the Swiss Light Source (SLS), Villigen, Switzerland, at the beamline X06DA-PXIII [2]. Structure solution was carried out by Direct Methods using *SIR2019* [3] and refined by *SHELXL2014/7* [4]. All non-hydrogen atoms were refined anisotropically; the carbon-bound H atoms were placed on geometrically calculated positions and refined using a riding-model approximation.

The main crystallographic results are here presented.



Figure 1. 1,2,3,4-Tetrafluoro-5,8-bis(trimethylsilylethynyl)anthracene: a view of the crystal packing. The parallel-offset π - π interactions [5] are indicated by broken lines between centroids.

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- MS2·O6 -

Complex nanoscale geometry in functional materials as seen by synchrotron x-ray micron beam techniques

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Complex materials can be seen as made of structural units kept together by weak interactions giving rise to different spatio-temporal configurations at nanoscale and mesoscale. The visualization of the fluctuations between these configurations require advanced methodologies based on high precision X ray measurements and statistical tools for data analysis. Examples of complex materials include biomaterials, colloids, complex liquids supramolecular assembly and strongly correlated materials. Here we present recent results on the connections between the nanoscale geometry and the macroscopic properties of complex matter in different fields, ranging from material science to biology.

MS3 Synchrotron based characterization of surfaces and interfaces

- MS3·KN1 -

The enticing interaction of graphene with atoms, molecules, clusters and surfaces

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Even though free-standing graphene has shown unique and exotic properties, the two dimensional carbon network will never be used in its isolated form and any realistic technological application is envisaged only in combination with other materials. For this reason the understanding of the interation of graphene with atoms, molecules, atomic aggregates, surfaces and other 2D materials is of paramount importance. In this talk I will show how high-energy resolution core level photoelectron spectroscopy with synchrotron radiation can provide a variety of information about the physical and chemical properties of different graphene-based interfaces. Since core level binding energy shifts can be calculated with a high level of accuracy using density functional theory, the close comparison between experimental and theoretical results represents a key ingredient to obtain precious information about the interaction of graphene with matter.

MS3·KN2 -

Molecular Orbital Tomography: efficient method to study the adsorption geometry and electronic structure

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Angle-resolved photoelectron spectroscopy (ARPES) is a well-established method to study the band structure of single crystals and, recently, it has been shown that it can also provide an alternative route to probe the charge distribution of individual molecular orbitals [1, 2]. This approach, based on the comparison between ARPES measurements and theoretical calculations, forms the basis of the molecular orbital tomography (MOT).

For an ordered layer of organic molecules deposited on a single crystalline substrate, under specific assumptions about the final state of the photo-emitted electron, the angle resolved photoemission current (*Ii*) can be related to the initial state of the system $(|\psi i(k)|)$, i.e. the molecular orbital, via a simple expression [1]:

$$|\widetilde{\psi}_{i}(\mathbf{k})| \propto rac{\sqrt{I_{i}(heta, \phi)}}{|\mathbf{A} \cdot \mathbf{k}|}$$

Ii can be selectively measured using the photoemission electron microscope operating in k-mode (k-PEEM), and, via a subsequent inverse Fourier transform, the reconstruction of molecular orbital densities in real space can be determined. This innovative tool for the investigation of organic molecular films on metallic substrates is well established at the NanoESCA beamline of Elettra synchrotron. As an example, it will be shown how the combination of MOT and density functional theory (DFT) calculations can be used to study the adsorption behavior and peculiarities in the electronic structure of organic molecules (porphyrins and phthalocyanines) adsorbed on noble metals [2, 3]. We exploited the capability of PEEM to directly image a wide reciprocal space range in one single shot, being able to measure the photoemission intensities related to the molecular orbitals in the valence band. This allows us to characterize the molecule-substrate interaction and describe the charge transfer phenomena between adsorbed molecules and metal surfaces.



Figure 1. Comparison between k-PEEM measured pattern (a) and DFT calculations; (b) of molecular orbitals for NiTPP/Cu(100); c) proposed adsorption model: tilt angle $\phi \sim 140^\circ$, twist angle $\theta \sim 70^\circ$.

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- MS3·O1 -

Comparative study of electronic band structure of Pb(Sn)-based topological insulators

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Topological insulators (TIs) have emerged as a novel quantum state of matter. The Dirac-like surface state (topological surface state: TSS) and the peculiar spin-texture play an essential role in manipulating spin-polarization and spin-current of TI-based devices [1,2]. A fine tailoring of TSS electronic properties has been attempted mainly by doping or intercalation, but with strong modifications of the surface states. One other critical point is that future topological based devices will most likely involve surfaces that are exposed to ambient environment; TIs electronic properties need thus to be robust against contaminants. An innovative approach that allows to design TIs with tunable electronic states, *unaffected* by contaminants exposure, relies on Pb-based ternary chalcogenides. In contrast to the binary compounds, the crystal structure of ternary/quaternary compounds is formed by alternating quintuple- (QL) and septuple-layer (SL) blocks. By means of scanning tunnelling microscopy (STM) and angle-resolved photoemission spectroscopy (ARPES) measurements supported by density functional theory (DFT) on PbBi₄Te₇ and PbBi₆Te₁₀ we proved coexisting TSSs, deriving from different surface terminations, displaying distinct electronic band dispersion, different constant energy contours, and Dirac point energies [3,4]. Recently, we also proved that a tailoring of the TSSs is made possible by the replacement of heavy atoms by lighter isoelectronic ones, as predicted by theory [5,6]. In this context, we will present a systematic electronic band investigation of this novel class of ternary/quaternary TIs, $A^{IV}Bi_4Te_{7-x}Se_x$ (A^{IV} = Sn, Pb; x=0, 1), by means of ARPES measurements and DFT calculations. Finally, we show that the electronic structure of the investigated systems is barely affected by contaminants exposure.

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- MS3·O2 -

Comparing free and adsorbed TPA: electronic structure modification induced by the moleculesurface interaction

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Triphenylamine (TPA) is a well-known electron donor molecule largely used in organic solar cells and LED [1-4]. We have characterized the electronic structure of the TPA molecule in gas phase [5] and when adsorbed at a monolayer coverage on a Au(111) surface. The characterizations have been performed by core and valence Photoelectron Spectroscopy (PES) and Near Edge X-ray Absorption Fine Structure (NEXAFS) spectroscopy. The experimental results have been compared with theoretical calculations which confirmed a weak interaction between the adsorbed TPA and the Au(111), with only a slight change of the twisting angle of the TPA phenyl rings. The estimated adsorption geometry can be used to explain the broadening of the C 1s PES line with respect to the gas-phase results and the expected absence of angle dependence in the C K-edge NEXAFS. However, a significant modification was observed in the N K-edge NEXAFS spectra of TPA/Au(111), showing a new pre-edge intensity feature due to transitions involving out-of-plane orbitals. This pre-edge feature is ascribed to the interaction between the molecules and the surface, having a different character and energy position than the pre-edge intensity observed for free TPA.

This talk presents the results obtained within the well-established Swedish-Italian collaboration between the Department of Physics and Astronomy at Uppsala University (Sweden) and CNR at Elettra, Trieste (Italy)

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- MS3·O3 -

Investigating excimer laser effects on ZnO nanorods properties through a multi-scale approach

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Figure 1. SEM images of ZnO nanorods from [2]

In the search for new materials for biosensing applications, metal oxides play a major role. Among them, Zinc oxide (ZnO) nanostructures represent an appealing choice because of the easy growth processes (e.g. hydrothermal growth), high biocompatibility, wide bandgap (3.4 eV), tuneable resistivity, etc.

Different surface morphologies of ZnO thin films were found to result into huge differences in terms of electrical characteristics of transistors [1]. In the case of ZnO nanorods (ZnO-NRs), the surface morphology is affected by the local heating induced upon excimer laser exposition (Fig.1 from[2]): the irradiation gives rise to the partial melting (Fig.1b), or even to the ablation of the ZnO-NRs (Fig. 1c), depending on the fluence [2]. This shows how by properly tuning of the laser energy density, it is possible to optimise the material properties.

A fine understanding of the specific chemical and physical mechanisms determining the sensing phenomena on the local and on the macroscopic scale is still missing. This information represents the key not only to finely tailor the sensor properties but also to increase the device selectivity and sensitivity.

Accessing the complex interplay between micro- and macroscopic properties requires the use of a versatile, nondestructive probe capable of investigating not only the structural features, but also the electronic and chemical properties of the ZnO-NRs. Synchrotron radiation (SR), thanks to the high penetration depth and tunability, is the perfect tool to perform such multi-scale investigations yielding complementary information on the properties of a system. In this work, SR X-ray Photoemission Spectroscopy (XPS), Ultraviolet Photoemission Spectroscopy (UPS), and X-Ray Diffraction (XRD) were employed to probe the ZnO-NRs local structure, their long-range crystalline order, and their electronic properties. The complex picture emerging from these techniques was combined with evolution of the morphology and electrical response probed by laboratory techniques. The result is a fine description of the laser-irradiation effects in terms of nanorods morphology and homogeneity, crystalline arrangement, chemical state, and surface electronic structure.

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- MS3·O4 -

1D and 2D polymers via on-surface Ullmann coupling: intermediate reaction steps to growth extended ordered structures

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Surface-confined polymerization is a bottom-up strategy to create one- and two-dimensional covalent organic nanostructures with a π -conjugated backbone, which are suitable to be employed in real-life electronic devices, due to their high mechanical resistance and electric charge transport efficiency. This is a promising approach that allows the creation of layers with desired architectures and tunable properties changing the molecules used as precursor. One of the main challenges of such an approach is to obtain nanostructures with long-range order, to boost the conductance performances. Most of the exploited chemical reactions use irreversible coupling and, as a consequence, the resulting structures often suffer from poor order and high defect density [1]. This talk will focus on our results about irreversible processes including intermediate states, which are key aspects to control the order of the final nanostructure. I will report on our studies on surface-confined polymerization by using Ullmann coupling reaction obtained by complementary spectroscopic measurements of electronic states (by photoelectron spectroscopy (fast X-ray photoelectron spectroscopy (fast-XPS), angle-resolved photoelectron spectroscopy (STM) and density functional theory (DFT) calculations. These methodologies have allowed to pinpoint a signature of the polymerization reaction and have added new information on the role played by halogen atoms in the process [1-4].



Figure 1. Example of intermediate state (Transient) in the polymerization process.

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- MS3·O5 -

Unexpected electron correlation (Coulomb and exchange) at the nanoscale probed by Auger Photo-Electron Coincidence Spectroscopy: size and bias effects

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Even though DMFT and DFT-LDA calculations allow to properly predict the itinerant-like electronic properties of transition metals and their oxides, as well as magnetic moments in ferromagnetic (FM) and antiferromagnetic (AFM) systems, the interplay between band structure, magnetism and many-body correlations is still intriguing and debated [1]. In particular, the relevance of the on-site Coulomb interaction in the d orbitals (Hubbard U) as compared to the non-local exchange interaction (J) is far from being clarified in depth even at the experimental level [2]. Furthermore, possible size effects are usually not accounted for by current theories, thus overlooking the role played by the electron-electron interaction in the early stages of growth or synthesis of magnetic thin films and nanostructures.

Core-valence-valence (CVV) Auger decays can potentially provide information about an effective U_{eff} through the distribution of two-hole local density of states 2LDOS, so have the unique capability to probe intimately the electron-electron interaction in the valence band. Unfortunately, for most of the relevant systems, Auger spectra are featureless, thus leading to the astonishing conclusion that the behavior of some of the major magnetic materials, like Fe, is band-like due to a U_{eff} small as compared to the band-width. All of this in sharp disagreement with the magnetic properties of the samples.

In trying to resolve this puzzling contradiction, we resorted on Angle Resolved Auger-PhotoElectron Coincidence Spectroscopy (AR-APECS) which, by accessing to the spin coupling of the two valence hole final state, is capable to unravel the otherwise blurred multiplet structure in Auger spectra, and hence yields a direct measure of Coulomb and exchange interactions for each individual multiplet component [3].

We report on Auger spectra measured by AR-APECS with unprecedented accuracy on FM (Fe, Co and Ni), AFM (CoO and NiO) materials and FM/AFM (Fe/CoO) and FM/diamagnetic (Fe/Ag) interfaces. This novel investigation provides a completely new insight in the role of the electronic correlation in magnetic systems. The major results are summarized in the following:

- U_{eff}, which for the Auger decay is usually referred as to the on-site Coulomb repulsion, is found to fully include the exchange interaction, so extending the exploitation of Auger spectra to magnetic systems and magnetic transitions, and in general to highly correlated systems;
- in the case of Fe a full set of values of U_{eff} has been found concerning all the possible combinations of orbitals involved in the two-hole final state (majority and minority spin, t_{2g} and e_g symmetry)
- unexpected large values of U_{eff} have been measured for FM systems and their values strongly depends on the magnetic state
- a giant size effect has been found on U_{eff} for FM systems in the thin film regime;
- a systematic increase of some of the U_{eff} values has been found at the FM/AFM interfaces, the result leading to the conclusion that the orbital symmetry plays a relevant role in the exchange coupling and in setting up the bias effects;
- in all the investigated cases, features assigned to the band-splitting and the split-off part of the Auger spectrum that is associate with two-holes resonant final states (FM), as well as atomic-like lineshape's displaying multiplet terms with well-defined two hole spin (AFM), disappear when crossing the Curie/Néel point, either by changing the temperature or by changing the thickness, of the magnetic film.
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MS4

Advanced Radiation Sources: state-of-the-art and future applications

- MS4·KN1 -

FERMI: the first externally seeded Free Electron Laser in the extreme ultraviolet and soft X-ray spectral regions

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Presented on behalf of the FERMI team http://www.elettra.eu/lightsources/fermi/fermi-management-page.html

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FERMI is a seeded Free Electron Laser (FEL) user facility at the ELETTRA-Sincrotrone laboratory (Trieste). This 4thgen. light source is based on two FELs operating in the high gain harmonic generation mode. The light from a laser is upconverted in frequency and amplified in the VUV to EUV and soft X-rays spectral range. The FERMI FELs are characterized by a number of desirable properties, such as wavelength stability, low temporal jitter and longitudinal coherence. We provide an overview of the FEL performances, and of the various modes of operation for the generation of multiple color multiple pulses.

FERMI is located at the Elettra laboratory in Trieste (Fig.1) hosting a 3rd generation storage ring and the free electron laser facility. The FEL facility covers the VUV to soft X-ray photon energy range with two FELs, FEL-1 [1] and FEL-2 [2], both based on the High Gain Harmonic Generation seeded mode (HGHG) [3]. The HGHG scheme consists in preparing the electron beam phase space in a first undulator, called modulator, where the interaction with an external laser, the seed, induces a controlled, periodic modulation, in the beam energy distribution.



Figure 1. Aerial view of the ELETTRA Storage ring and the FERMI Free electron laser facility

The beam then traverses a "dispersive section", which converts the energy modulation into a density modulation. The higher order harmonic components of this modulation retain the phase and amplitude properties of the seed. The "density" modulated beam is then injected into a long FEL amplifier where the startup of the amplification process is enhanced by the presence of the modulation. The modulation depth may be tuned by varying the seed intensity or the dispersion, in order to reach saturation and efficient energy extraction at the end of the amplifier.

The HGHG cascade scheme is implemented in FERMI FEL-1 to generate fully coherent radiation pulses in the VUV spectral range [4]. The seed signal, continuously tunable typically in the range 230–260 nm, is obtained from a sequence of nonlinear harmonic generation and mixing conversion processes from an optical parametric amplifier. The radiation resulting from conversion in the FEL up to the 13th harmonic with sub-100fs pulse duration, is routinely delivered to user experiments [5,6].

The amplitude of the energy modulation necessary to initiate the HGHG process grows with the order of the harmonic conversion. The induced energy dispersion has a detrimental effect on the high gain amplification in the final radiator at higher harmonic orders. These high orders can still be reached with a double stage HGHG cascade, where the harmonic conversion is repeated twice. The double conversion is done with the fresh bunch injection technique [7] on the second FEL line at FERMI: FEL-2 [2]. FEL-2 is composed by a first stage, analogous to FEL-1, followed by a delay line, a magnetic chicane slowing down the electron beam with respect to the light pulse generated in the first FEL. The light pulse from the first FEL is therefore shifted to a longitudinal portion of the beam which is unperturbed by the seed in the first FEL. The light from the first FEL functions as a short wavelength seed for the second FEL. This scheme was implemented for the first time on FERMI FEL-2 and was used to demonstrate the seeded FEL coherent emission in the soft-X rays, up to harmonic orders of 65, and larger.

A consistent fraction of the experiments proposed at FERMI, require special setups for the generation of multiple color multiple pulses for pump and probe experiments. This is becoming a standard way of operation for the facility. From FEL-2 for example, two color pulses almost superimposed in time, are naturally available as the emission from the first stage and the second stage. Multiple pulses of different colors can be also generated on FEL-1. An excess of seed can indeed be used for the generation of virtually jitter-free twin pulses delayed in time [8], which can also be separated in frequency by a proper frequency chirp of the input seed [9,10]. A second color may be obtained by simply tuning part of the radiator at one harmonic and part of it at a second, different harmonic. The temporal jitter between the two components was estimated in an experiment of coherent control where the relative phase of two colors (63.0 nm and 31.5 nm) was varied to control the asymmetry of the photoelectron angular distribution of ionized neon with a temporal resolution of 3 as [11]. Temporally separated pulses can also be generated by injecting a double seed with a temporal delay between the two seed pulses. The delay range is bounded by the seed duration and by the duration of the electron bunch current, between 200 and 600–700 fs. The temporal jitter between the two pulses can be sufficiently low to preserve a phase locking between the two pulses [12]. The two seed pulses can be also separated in frequency to generate two distinguishable colors, with the condition that they are both within the gain bandwidth of the FEL amplifier (0.7–0.8%) [13]. A larger frequency separation between the two pulses are separated in frequency by less than the bandwidth of the modulator (3%) and both generate energy, and then density modulation at the entrance of the amplifier. The amplifier is then separated in two parts, one resonant with the modulation resulting from the first seed pulse and the other resonant with the one from the second. The two amplified pulses are separated in frequency so they are amplified separately in these two undulator parts where the amplification occurs on different harmonics of the seed [14].

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- MS4·O1 -

Laser-Slicing at a Diffraction Limited Storage Ring

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The theoretical modeling of laser slicing of electron bunches in a synchrotron light source is discussed as a function of laser and electron beam sizes in a diffraction limited storage ring. The analytical model for emission of short pulses of radiation is benchmarked with simulation results for the Elettra 2.0 6-bend achromatic lattice, in which spatial and spectral separation of the sub-picosecond radiation pulse from a hundreds of picosecond-long background is achieved by virtue of 1:1 imaging of the radiation source. The spectral separation is enhanced when the radiator is a transverse gradient undulator. Laser slicing turns out to be favoured by the diffraction limited optics of Elettra 2.0. In the proposed configuration, laser-slicing allows the simultaneous operation of additional multiple beamlines, without interference to standard multi-bunch operation. Total slicing efficiency as high as 10^{-7} , one order of magnitude larger than the demonstrated state-of-the-art, is promised at the expense of pulse durations as long as 0.4 ps fwhm and average laser power as high as 60 W.



Figure 1. Electron beam longitudinal phase space at successive passes after one laser interaction.

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- MS4·O2 -

MariX, an advancedMHz-class repetition rate X-ray source for linear regime time-resolved spectroscopy and photon scattering

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Fine analysis of quantum materials require to push the limits of experimental resolution in all dimensions, including time to study the recovery path from excited states of matter to ground state, through transient configurations. Linear response and high statistics from 3^{rd} and 4^{th} generation storage rings is ultimately limited to >1-10 ps X-ray pulses. Ultra-short and ultra-brilliant X-FEL sources deliver 10-100 fs pulses at low repetition rates and probe matter in the non-linear regime. The need of a fs-scale pulsed, high repetition rate, X-ray source for time-resolved fine analysis of matter (spectroscopy and photon scattering) allowing to explore the pump-probe methods in the linear response regime is addressed by the conceptual design of a facility called MariX (Multi-disciplinary Advanced Research Infrastructure for the generation and application of X-rays) outperforming all currently operational or planned X-ray sources for the declared scope. MariX is based on the original design of a two-pass two-way superconducting linear electron accelerator, equipped with an arc compressor, to be operated in CW mode (1 MHz).[1-3]

MariX provides FEL emission in the range 0.2–8 keV with 10⁸ photons per pulse ideally suited for photoelectric effect and inelastic X-ray scattering experiments. The accelerator complex includes an early stage that supports an advanced inverse Compton source of very high-flux hard X-rays of energies up to 180 keV that is well adapted for large area radiological imaging, realizing a broad science programme [2] and serving a multidisciplinary user community, covering fundamental science of matter and application to life sciences, including health at preclinical and clinical level.



Figure 1. Marix layout. The injector delivers the beam to the main booster linac (L1) trough a dogleg. The L1 region ends with a high harmonic linac (HHL) then it enters the bubble arc compressor (BAC) used to compress and to perform the beam U-turn. The beam is accelerated again in L1 and is finally tuned in energy in the linac L2 before entering the two undulator chains.

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- MS4·O3 -

A novel high repetition rate HHG source for the study of time-resolved electronic and magnetic structure of strongly correlated systems

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A very useful approach in understanding the interplay between charge, spin and orbital degrees of freedom in strongly correlated systems, as in the case of transition metal oxides, consists in investigating the timescale of the relaxation of the electronic properties after an optical perturbation. However, the prince tool for studying the electronic properties of a material, that is photoemission in all its branches, is difficult to be applied to time-resolved experiment, due to the features of commonly available pulsed sources: infrared or visible light lasers have photon energies too low with respect to the work function of solid samples, whereas Free Electron Lasers (FELs) have too high pulse intensity and too low repetition rate, so that either dramatic space charge effects are produced or a very low electron count rate is achieved.

We present here results from an experimental set-up recently commissioned at NFFA and T-Rex Lab in Trieste, termed SPRINT-lab (Spin Polarized Research Instrument in the Nanoscale and Time domain). The system, based on a High-Harmonic-Generation (HHG) [1], is able to produce high intensity harmonics up to the 27th order of the 2.4 eV fundamental, with tunable repletion rate from single pulse up to 200 KHz. The end station is equipped with a 200 mm-radius hemispherical analyser for angular resolved photoemission and a vectorial Mott detector for the measurement of secondary electron spin polarization in both static and pump-probe method.



Figure 1. Energy-distributed curve of a polycrystalline gold film, acquired with 16.8 eV HHG source. Fit of the Fermi edge is showed in blue dotted line, performed deconvolving the Fermi-Dirac function with T = 40 K from a Gaussian accounting for the instrumental broadening.

We show that space charge effects, which manifest in photoemission spectra as energy shifts and broadening, are readily suppressed by increasing the repetition rate of the driving laser. The final energy resolution of the source has been estimated in the sub-30 meV region (Figure 1), well in agreement with the time width of the photon pulses (300 fs).

With this set-up, an experiment of spin polarization is been planned on a manganite (LaxCa1-xMnO3), which at certain doping level has demonstrated to have an hidden metallic phase accessible by photo-excitation, a result discovered measuring in terahertz conductivity [2] and confirmed by our recent measurements of satellite peaks in core level photoemission.

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- MS4·O4 -

High-Intensity Terahertz and Mid-Infrared Radiation: Production and Opportunities in Condensed Matter Research

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Terahertz (THz) and Mid-Infrared (MIR) radiation, ranging from 0.5 meV to 1 eV, are in resonance with most of the fundamental excitations in condensed matter, allowing to measure, in steady-state linear-response spectroscopy, both their characteristic energy and lifetime. Recently, the developing of new high-intensity, sub-fs pulsed radiation sources emitting in the THz-MIR spectral region, has open a new scenario for condensed matter, allowing not only to excite those excitations but also to modulate and control their behavior in time and frequency.

This is particular important in Quantum Materials, where exotic excitations like Dirac and Weyl electrons, chargephonons, spinons, skyrmions, Higgs and Goldostone modes, with a complex texture of spin, lattice and electronic degrees of freedom, affect their low-energy transport and electrodynamics.

Here, we present some experimental results recently obtained [1,2], discussing also new THz and MIR facilities planned or already existing in Italy.

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- MS4·O5 -

Structural evolution of Platinum nanostructured thin films driven by ultrashort IR radiation.

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By offering pulsed X-rays with a temporal extension of femtoseconds containing up to 10^{12} photons, free electron lasers enable the investigation of the ultrafast structural evolution of non-equilibrium states.

Through the interaction of infrared (IR) radiation with a metal such states can be induced, initially characterized by hot electrons and cold lattice. The excess of kinetic energy of electrons is then partially transferred to the lattice via electron-phonon coupling, and drives the evolution of the lattice within picoseconds.

Investigations exploiting this mechanism – using infrared light as a pump and mostly electrons as a probe – have been performed earlier on Aluminum, showing ultra-fast melting [1], and Gold, demonstrating bond hardening [2] and allowing the identification of the heterogeneous to homogeneous melting transition [3]. While Gold is a widely studied element and possesses an electronic configuration similar to the one of Platinum, theoretical calculations predicted a completely different behavior in terms of electron-phonon coupling and, in turn, of electron-lattice energy exchange [4].

We report here on the investigation of Platinum thin films characterized by a grain size of a few nanometers, recently performed at the Pohang accelerator laboratory free electron laser.

Several IR fluences and sample thicknesses have been explored, with the final goal of understanding how the melting front nucleates, evolves and interacts with grain boundaries.

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- MS4·O6 -

Shedding light on low density matter with novel XUV light sources

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Advances in laser and synchrotron radiation instrumentation have continuously boosted photoionization studies on low density matter. At the Elettra synchrotron radiation laboratory (Trieste, I) for the last 2 decades, the research activity in the field of atomic, molecular and cluster physics has been centred around the Gas Phase Photoemission beamline [1], where thorough studies of isolated system can be carried out by means of photoionization techniques and inner-shell electron photoionization, even with low density targets such as molecular vapours [2] or clusters [3]. But more recently the interest of the physical chemistry-chemical physics community has been attracted by the opportunity of exploring also the temporal dynamics of isolated systems by means of novel state-of-the-art light ultrafast X-ray radiation and vacuum ultraviolet (XUV) sources. For this purpose two new beamlines capable of delivering fs-XUV photon pulses have been commissioned and opened to Users in the framework of the FERMI Free Electron Laser (FEL) facility [4]: the Low Density Matter beamline at FERMI [5] and CITIUS [6], a state-of-the-art laboratory source, based on laser High Harmonic Generation on rare gases.

I will thus outline research opportunities opened in the field of atomic and molecular physics by these novel ultrafast light sources at Elettra, Trieste. In particular I will discuss recent pump-probe experiments, which on one side are used for characterizing our novel VUV light sources [6-9], and on the other side are also paving the way for thorough investigations of electron dynamics in molecular excited states and for femtochemistry application of ultrafast XUV radiation.

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Open Session 1

- OS1·O1 -

X-ray fluorescence beamline at Elettra Sincrotrone Trieste: a versatile tool for structural and chemical investigations

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The X-Ray Fluorescence (XRF) beamline, operated by Elettra Sincrotrone Trieste and the International Atomic Energy Agency, hosts an ultra-high vacuum end-station devoted to X-ray emission and absorption spectrometry [1-2]. A double crystal monochromator allows the X-ray beam energy to be tuned from 3.6 to 14 keV, whereas a motorized sample manipulator coupled with additional motorized stages can move both the sample and the detectors with respect to the beam, setting up several excitation/detection geometries. In addition to the conventional reflection geometry (XRF 45/45), angle-dependent experiments like Total external reflection X-Ray Fluorescence (TXRF), Grazing Incidence/Exit X-Ray Fluorescence (GI/GE-XRF), and X-Ray Reflectometry (XRR) can be performed.

The advanced sample manipulation system can also be exploited to combine different experimental strategies at the same time: for instance, GIXRF and XRR scans can be carried out simultaneously for the investigation of nano-layers; alternatively, X-ray Absorption Near Edge Spectrometry (XANES) carried out in TXRF geometry for the analysis of trace elements speciation.

The information accessible with the abovementioned techniques combines structural and chemical details, being valuable for a wide variety of fields. The majority of the beamtime allocated for external users is employed for the environmental studies, including mostly air or water pollutants in different areas of the world [3-6]. Nevertheless, XRF is well suited for other kinds of science, including medicine [7] and life science, e.g. to study the diseases related to the development of human civilisation [8]. The facility is also used to address issues related to basic physics and material science domains [9], especially through the enrichment of existing databases with newest evaluations of fundamental parameters for the interaction between X-rays and matter [10-12].

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- OS1·O2 -

FEL time-resolved methods for monitoring ultrafast structural and electronic changes in condensed matter

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Condensed matter exposed to intense short (< 100 fs) light pulses exhibits ultrafast phenomena (10-1000 fs) that often lead to the drastic rearrangement of both the electronic and atomic structure. The experimental investigation of those processes is today within reach through innovative time-resolved techniques exploiting the unique properties of the free electron laser sources. We present the experimental methods recently developed at the EIS-TIMEX beamline of the FERMI free electron laser (Trieste, Italy) aimed at monitoring materials driven out of equilibrium and rapidly evolving in the sub-ps time scale after laser excitation. In particular, we describe the ultrafast electron diffraction facility successfully tested in February 2019, designed for operating in combination with an isochoric FEL pump. Experimental and theoretical approaches for time-resolved core hole absorption spectroscopy in the extreme ultraviolet energy range are also discussed, demonstrating the pronounced sensitivity of the used techniques to sub-100 fs changes occuring in the excited electronic structure.

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- OS1·O3 -

Mixed Spin-Quadrupole-Phonon modes in UO₂ Studied by Inelastic X-ray Scattering

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Systems with active orbital degrees of freedom can display collective excitations involving quadrupoles and higherrank multipoles, alone or in combination with dipoles. The identification and modelling of such propagating excitations, more complex than conventional magnetic spin-waves, is important to get quantitative insight on multipolar two-ion interactions, whose nature and form are poorly known. Indeed, whilst the static properties of multipolar-ordered systems provide only space-integrated information on the microscopic interactions between active multipoles, the dynamics of propagating modes depend on their detailed form.

 UO_2 is one of the few systems where these phenomena have been experimentally investigated. This cubic insulator displays a first-order phase transition at 30.8 K to a non-collinear antiferromagnetic (AF) structure with a simultaneous electric-quadrupole ordering of the charge density [1]. Elementary excitations in the lattice originate from two mean-field modes. One of them is purely quadrupolar and leads to quadrupole waves. The other has a magneto-quadrupolar character and gives origin to mixed spin-quadrupole waves where the spin precession is accompanied by charge density oscillations. Strong quadrupolar superexchange and magnetoeleastic couplings with phonons, in addition to spin-spin interactions, result in a mixed character of the excitation modes in extended regions of the Brillouin zone [2]. Such complications have been observed by inelastic neutron scattering focused on the magnetic response of the system [3].

Here, we present the results of inelastic x-ray scattering measurements performed at the ID28 spectrometer at the European Synchrotron Radiation Facility (ESRF) with a resolution of 1.5 meV. Neither the magnetic scattering nor the excitations from higher multipoles can be observed directly with x-rays; the technique is sensitive to only vibrational excitations and others modes that mix with such excitations. This experiment is therefore focused on the vibrational component of the mixed modes, which is difficult to observe with neutrons because low temperature and low momentum transfer imply low intensity.

We observe mixing of the transverse acoustic phonons (TA) with the spin acoustic (SA) mode at low energy of ~ 6 meV, but also a strong mixing of the TA phonon with the quadrupolar optic (QO) around 11 meV and the spin optic (SO) modes, which has been predicted but not observed previously. The QO mode is observed in neutron scattering spectra because it mixes with the spin optic (SO) mode through quadrupolar interactions that in large part have a vibrational origin. It is therefore to expect that the mixed mode at high energy has also a vibrational component, and it is this part that we observe with x-rays.

The temperature dependence of the TA mode shows finite lifetime in the [100] direction well above the AF transition, demonstrating that the low temperature anomalous anisotropic thermal conductivity in UO_2 is mediated by this strong magnon-phonon coupling [4].

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- OS1·O4 -

Magnetic proximity effect in Co/Pt multilayer investigated through X-ray resonant magnetic reflectivity

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Transition metals of the 4d and 5d series close to satisfy the Stoner criterion for ferromagnetism [1] can acquire a permanent magnetic moment when they are interfaced with a ferromagnet [2,3,4]. This proximity-induced magnetism rapidly decays away from the ferromagnet/non-magnetic metal (FM/NM) interface and extends for few monolayers [4,5] but has a significant influence on many properties of these systems. Magnetic proximity effect (MPE) is often linked to a strong perpendicular magnetic anisotropy, as is the case in Co/Pt and Co/Pd bilayers and multilayers, attracting considerable interest for possible applications in various fields, including information storage, sensing and biomedicine [6-9]. Relations between MPE and the Dzyaloshinskii-Moriya interaction are strongly debated [10-12] and possible consequences in the development of more efficient spintronic devices were investigated [13]

Refined information on the distribution in depth of the induced magnetic moment have been obtained in X-ray resonant magnetic reflectivity (XRMR) experiments, a powerful photon-in photon-out technique that can study the magnetic properties of a layered sample with sub-nanometer resolution [12,14,15]. In a recent paper [15] reflectivity measurements on a $Pd_{bottom}/Co/Pd_{top}$ trilayer system demonstrated the presence of a different induced moment between the bottom and top Pd layers. Despite these interesting results, the characterization of the distribution of magnetic moments in real n>1 [Co/NM]_n multilayers with repeated NM/Co/NM interfaces is still lacking.

In the presented work, combined X-ray magnetic circular dichroism (XMCD) and XMRM measurements are used to study the Co and Pt magnetization depth profile of a complete $[Pt/Co]_4/Pt$ multilayer. The main goal of this project is to verify if the induced magnetization in the Pt layers is constant across the 2*n* Pt/Co and Co/Pt interfaces or a dependence along the growth direction is present. A simpler Pt/Co/Pt trilayer was also characterized as a control sample and for comparison with the existing literature. Both samples were grown by sputtering on a thermally oxidized Si substrate with a Ta buffer layer. In-plane and out-of-plane magnetic hysteresis loops were acquired with a vibrating-sample magnetometer. XMCD and XMRM scans were carried out across the Co L_{2,3} and the Pt M₃ edge in order to study the magnetic properties of both the elements. The chemical and magnetic depth profiles of the investigated samples obtained from the fitting of the XRMR curves will be presented and discussed.

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- OS1·O5 -

Increasing the performance of Pd/Al₂O₃ and Pd/CeO₂ catalysts for total methane oxidation by pre-reduction

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Pd-based catalysts, commonly supported on materials like alumina or ceria, are still the most efficient catalysts to oxidize the strong greenhouse gas methane^[1,2] in the low temperature regime typical for lean burn gas engines (approx. 400° C – 450° C). On the other hand, long-term applications still remain a challenge, since in the presence of water vapor^[3,4] or sulfur^[5] a strong deactivation is observed. The active phase is assumed to be PdO and it is claimed that methane oxidation on PdO follows a Mars-van-Krevelen mechanism. Water formed during both the combustion of methane in the engine and the catalytic after-treatment reaction is believed to induce the formation of inactive Pd(OH)_x species on the catalyst's surface. A pre-treatment (i.e., pre-reduction) of Pd-based catalysts was shown to have a positive effect on catalytic activity and stability^[6]. However, neither the origin of the deactivation nor the exact effect of the pre-treatment have been completely elucidated yet.

To understand the activity increase observed after reduction prior to the activity tests, we used *operando* X-ray absorption spectroscopy (XAS) to follow the variations of oxidation state during dynamic operation. Both Pd/Al_2O_3 and Pd/CeO_2 were investigated, in order to evaluate the impact of the different oxygen mobility of the supports.

Pre-reduction of Pd/Al₂O₃ and Pd/CeO₂ catalysts shifted the light-off curve towards lower temperatures^[7]. This effect was also observed under model or simulated exhaust gas mixtures. *Operando* XAS revealed a completely reduced catalyst after the pre-treatment. In reaction mixture, with increasing temperature, continuous oxidation occurs, starting with surface oxidation and finally resulting in bulk PdO above 350°C, irrespective of the catalyst formulation. Although also phenomena such as particle morphology variations or surface roughening can contribute to performance enhancement, our *operando* XAS investigations uncovered that the freshly formed PdO phase, less deactivated by water, is the main reason for the increase of methane oxidation activity at low temperatures.



- Figure 1. a) Activity data of a Pd/Al₂O₃ catalyst without (black lines) or with (red lines) pre-reduction; Dry and wet conditions are compared (solid and dashed lines respectively);b) Oxidation state evolution as obtained from XANES of the same catalyst during light-off after pre-reduction and corresponding activity data; c) Possible evolution of the structure of a Pd nanoparticle during re-oxidation (simplified scheme)
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- OS1·O6 -

Synchrotron Radiation studies of relevance to Accelerator R&D

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In recent and future high performance energy colliders, the knowledge of many physical properties of the materials walls to be used is an essential prerequisite. Among others, it is necessary to study materials behavior after exposure to the synchrotron radiation (SR) produced by the circulating particles. SR interacts with the machine vacuum walls and may induce gas desorption, photoelectrons, heat load, vacuum and beam instability. Moreover, such interaction may chemically modify the surface and its behavior, affecting stability of the machine during its operation. Actually, photon Reflectivity (R), Photo Yield (PY i.e. the number of photoelectrons produced per incident photon) Photo Stimulated Desorption (PSD) and their geometrical distribution, are essential ingredients to simulation codes. Moreover, such parameters must be studied not only on realistic "technical materials", but also in conditions as close as possible to the operative ones. This implies that a significant effort is needed to go also at the very grazing angle of incidence (as low as 0.08°) at which such interaction occurs in real machines while, eventually, keeping the studied surfaces at their very low operating temperatures (from 10 - 60 K).

Here I will introduce the problem and present some results of a still ongoing experimental campaign carried out at various Synchrotron Radiation Centers (BESSY2, Soleil and DAFNE-L) and at LNF. I will also briefly report on the added value

some of these results have in seemingly different research field going from optics to astrochemistry.

Quantum size and surface effects on the electronic structure of Yb thin films

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Yb thin films supported on metal surfaces can be considered model systems for understanding surface and interface phenomena that involve rare earths elements embedded in multilayer structures that may be exploited in spintronics. The interplay of electron confinement and divalent/trivalent configuration of Yb can result in complex electronic and magnetic structures, not easily predictable and still not properly understood. Hard X-ray photoemission spectroscopy suggests Yb as a purely divalent element, with fully occupied 4f states and a Fermi level (E_F) of 6s character [1]. However, the situation is somehow more complicated since the 5dcontribution in the Yb valence band [2]. Photoemission spectroscopy (PES) experiments have identified a sharp structure close to $E_{\rm F}$ interpreted either to *d*-like surface state [3] or to the tail of a very sharp 5d empty band located close to $E_{\rm F}$ [4]. At present, electron confinement effects on Yb films have been revealed only with low-temperature scanning tunnelling spectroscopy (STS) that detected quantum-well states (QWS) above $E_{\rm F}$ on Yb(111) films deposited on W(110) [5]. On a wellordered mono-crystalline Yb(111) film grown on Mo(110) we performed a detailed angular resolved PES (ARPES) study of the valence band. We unveiled electron confinement effects involving electronic states at deep binding energy as well as close to $E_{\rm F}$. QWS dispersing along the $\Box K$ and $\Box M$ high symmetry directions, in these two different energy regions of the valence band, are shown in Fig. 1. We are able to reproduce our data with density functional theory (DFT) calculations, explaining the origin of the QWS and the nature of the prominent peak observed at the $E_{\rm F}$, elucidating the details of the electronic structure of the Yb single crystalline surface.

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Fig. 1: Experimental electronic structure of 29 ML of Yb film on Mo(110) measured with ARPES at hv = 34 eV. (a) 2D intensity maps, along the KГM; (b) second derivative of the image (a); (c) zoom of (b) in the region around $E_{\rm F}$ and Γ .

- OS1·O8 -

Evidence of quantum well states at the Ag/β -Si₃N₄(0001)/Si(111) interface

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Interface states induced by metal silicides (MIGS) degrade the electronic properties of a metal/silicon interface. Nowadays, as the realization of applications linked to spintronics have become likely to occur soon, higher standards are desired for an ideal metal/silicon interface, to match the electronic industry needs. Usually, the interfaces of electronic devices are not abrupt, the buffer layer being always amorphous and source of defects [1]. As an exception, it is known that epitaxial $Si_3N_4(0001)$ films can be formed by thermal nitridation of Si(111) substrates at high temperature, the 2x2 cell of the Si(111) surface being only 1.2% larger than the unit cell of the β -phase of the $Si_3N_4(0001)$ [2]. A peculiarity of this system is that thermal nitridation of Si(111) always produces ultrathin and crystalline films (about 1 nm thick), as the nitridation process is self-limited. As a consequence, the β -Si₃N₄(0001) acts as an ultrathin passivation layer, suppressing the metal-Si reaction [3-5].

Metal adsorbates (Co, Au, Fe for instance) generally follow a Volmer-Weber growth mode [3-5]. However, for an ideal metal/silicon interface with no gap states to be used in electronic devices, a layer-by-layer growth mode is required. This is why we employed another strategy based on the well-known two-step growth: in the first step the sample is kept at the liquid nitrogen temperature during growth and, in the second step, the sample is left recovering room temperature. Preliminary angle resolved photoelectron spectroscopy (ARPES) measurements performed at the VUV beamline (Elettra Trieste) show the presence of quantum well states, signature of the silver epitaxial growth.

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Open Session 2

- OS2·O1 -

Study of the reaction mechanisms of dry room gases on metallic lithium anodes for Li-ion batteries using in-situ ambient pressure X-ray photoelectron spectroscopy

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Metallic lithium, which is a negative electrode for Li-ion batteries with one of the highest specific capacities and lowest voltage, has not reached yet the commercial stage in rechargeable batteries because of safety issues related to instabilities arising on the Li surface during electrochemical cycling [1]. When metallic lithium is in contact with the battery electrolyte, a surface layer called SEI (Solid Electrolyte Interface) is formed owing to the electrochemical instability of the electrolyte at low voltages. In a conventional Li-ion battery with graphite-based anode, the SEI layer is a passivation interface that will help to stabilize the battery in exchange of some irreversible capacity loss. However, when considering Li metal anodes, although some interesting approaches with special salts have been reported [2], the conventional SEI is unable to maintain a uniform plating and stripping of Li during battery operation [3].

In order to find a suitable solution for the stabilization of the lithium surface, it is essential to have a full understanding of the nature and characteristics of its high reactivity. For this purpose, one of the preliminary steps is to analyze the effects that atmospheric gases present in the dry room environment where Li-ion batteries are processed, have on the surface of Li metal. Ambient Pressure X-Ray Photoelectron Spectroscopy (APXPS) is an ideal tool to explore this phenomenon. Our recent studies done in the APXPS from beamline 9.3.2 at the Advanced Light Source, Lawrence Berkeley National Laboratory (California, United States) provide key insight in the reaction mechanism behind the formation of lithium carbonate, one of the main components of conventional SEI layers, when this metal is exposed to CO_2 gas, as can be seen in Figure 1.



Figure 1. Kinetic studies of $Li + CO_2$ gas reaction shows two regimens in the growth of the layer, a reaction controlled regime and a diffusion controlled regime, in good agreement with recent studies [4].

The various gas exposure conditions created different surface final states of metallic lithium, which will affect the composition of the SEI layer that will influence the stability of the interface between metallic lithium anode and electrolyte.

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- OS2·O2 -

Experimental Aspects and Analysis Strategies for *in Operando* XAS experiments of catalysts in Electrochemistry

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The current developing level of new electrochemical batteries requires a fine and detailed understanding of the underlying reaction mechanisms occurring at the catalyst's surface. Particularly, the high theoretical energy density promised by metal-air batteries has boosted large research incentives for the development of more efficient and long-lasting bifunctional gas diffusion electrodes (GDEs). Conventional GDEs are typically made of a two-layered structure: a gas diffusion layer and a catalyst layer. The former must provide both high gas transport rates as well as electrolyte retention capabilities. The latter must exhibit high reactivity and selectivity in reaction products for both the oxygen reduction reaction (ORR, discharge) and the oxygen evolution reaction (OER, charge), and, additionally, it has to demonstrate high stability toward several charge-discharge cycles. Among low-cost alternatives to noble metal electrocatalysts, transition metal oxides and hydroxides based on manganese (α -MnO2) and nickel (Ni/NiO/NiOOH) have recently gained much attention due to their remarkable catalytic activity for ORR and OER, respectively. Several attempts have been made to couple the electrochemical properties of those transition metal oxides [1-3], but a stable and efficient hybrid Mn-Ni oxide catalyst has still to be identified.

Herein, we present an *in operando* X-ray absorption spectroscopy (XAS) based systematic study on the behavior of the catalyst during ORR/OER activities. Fundamental aspects must be taken into account in order to get appropriate data sets for suitable analysis and to obtain proper information necessary for fine and precise understanding of the catalytic mechanism behind the reaction. Firstly, we present aspects of the experimental setup showing, particularly, how the design of the reaction cell can interfere drastically on quality of data collection. Further, for a dynamic system we show criteria used to distinguish a time evolution from ordinary noise. Then, as preliminary results, we show strategies that are critical to detect tiny changes in the XAS spectrum (full of meaning) without which the results are impossible to be correctly interpreted, such as, differential spectra analysis, aka $\Delta \mu$ XANES and $\Delta \mu$ EXAFS. By following so we were able to show, for instance, how edge position fluctuates during charge/discharge of the battery without changing of nearest-neighbors oxygen number and how it can be associated to the small fluctuation of average oxidation state of Mn atoms during the catalytic cycle.

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- 0S2·03 -

XAFS comparative study of the crystal structure formation and evolution in $Ln_2M_2O_7$ (Ln = Gd, Tb, Dy; M = Ti, Zr)

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A great deal of research has been devoted recently to the investigation of $Ln_2M_2O_7$ complex oxides (Ln is a lanthanide and M is a titanium subgroup element), in view of their wide technological applications, such as thermal barrier coatings [1], solid oxide fuel cells [2], neutron absorbing [3] and nuclear waste storage [4] materials. In addition these materials are interesting for their rich physics, indeed they exhibit a variety of fascinating physical phenomena, such as order-disorder phase transitions [5] and geometrically frustrated magnetism [6].

The phase diagrams of the Ln2O3-MO2 systems are quite complicated, exhibiting several types of crystal structures of the oxygen-deficient fluorite-derived A2B2O7 compounds. One of the main factors that determine the resulting crystal structure is the ratio of the cation radii $\text{Ln}^{3+}/\text{M}^{4+}$ (γ). Ln zirconates $\text{Ln}_2\text{Zr}_2\text{O}_7$ (Ln= Gd, Tb, Dy) with $\gamma = 1.45 - 1.48$ may show both pyrochlore and fluorite phase transitions, while the Ln titanates $\text{Ln}_2\text{Ti}_2\text{O}_7$ compounds with $\gamma = 1.70 - 1.74$, are expected to show only the ordered pyrochlore structure.

We have investigated and compared the formation and evolution of crystal and local structure of Ln titanates and zirconates (Ln= Gd, Tb, Dy), prepared by a two stage process of sol-gel and coprecipitation methods, from amorphous to crystalline and from fluorite to pyrochlore phase, using X-ray absorption spectroscopy in combination with x-ray diffraction and Raman spectroscopy. We have found that Ln titanates crystallize directly from the amorphous state to the pyrochlore structure, while the Ln zirconates form the intermediate fluorite phase at first. XAS spectroscopy at Ti K-, Zr K- and Ln L₃- edges revealed to be a powerful technique which allowed us to track the different crystallization pathways of Ln titanates and zirconates as a function of the calcination temperature, at the local absorber sites. In particular the evolution of the Ti K-edge XANES features is a good indicator of the crystalline phase formation from the amorphous state and the splitting of the first Ln-O shell in the FT modulus of Ln L₃-edge EXAFS spectra, clearly observed only for Ln titanates, can be regarded as a fingerprint of the ordered pyrochlore structure formation which is accompanied also by specific changes in the main features of the XANES spectra. For the Ln zirconates these features are less pronounced.

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- OS2·O4 -

Zinc chemical speciation in bivalve shells from a polluted site

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Biomineralization is a biologically mediated process by which available ions are extracted from the solution to produce a solid structure that offers an adaptive advantage to the producing organism, performing mechanical/structural or functional/defensive roles. Because of this wide range of essential functions, the biotechnological application of biominerals is extremely varied, making them a prime source of inspiration to biologists and chemists to create novel biomimetic materials [1]. Among their potential applications, biominerals can serve for environmental monitoring, specifically, marine bivalves are sensitive organisms that register environmental changes and they help in assessing i) pH variation in sea water [2], ii) the evolution of the watershed (depositional vs erosional processes) [3], iii) climate changes [4], and iii) the effect of metal dispersion caused by anthropogenic activities [5].

Bivalves build their shell by a biologically controlled process occurring at the interface between the organism cells and the environment, forming an organo-mineral hard tissue mainly made up of Ca-carbonate (aragonite and/or calcite) [6], and organic molecules (horny conchiolin in the external surface of the shell, chitin, polysaccharides, proteins and glycoproteins in the medium and inner layers) [7]. Bivalves incorporate actively trace elements via intracellular or intercellular transport ways [8]. In our study, we applied a multidisciplinary and multitechnique approach to investigate Zn incorporation into marine bivalve shells belonging to different genera (Donax, Glycymeris, Lentidium, and Chamelea) grown in minepolluted seabed sediments (Zn up to 10 g/kg). Samples were investigated by X-ray diffraction (XRD), chemical analysis, soft X-ray microscopy combined with low-energy X-ray fluorescence (XRF) mapping, X-ray absorption spectroscopy (XAS), and transmission electron microscopy (TEM). These bivalves grew their shells producing aragonite as the main biomineral, and they are able to incorporate up to 2.0-80 mg/kg of Zn. Zn is mainly located in the bulk of the aragonite crystal matrix but it is not hosted in the Ca-carbonate structure. We identified three main different Zn phases: Zn phosphate, Zn hydroxycarbonate (hydrozincite), and Zn cysteine whose relative content changes as a function of Zn concentration in the shell. Zn phosphate is the most abundant species in the shells with the lowest Zn content (Lentidium, with Zn concentration of 29 mg/kg and Zn_{phoph} of 51%; Donax, with Zn concentration of 27 mg/kg and Zn_{phoph} of 55%), whereas Zn cysteine becomes more relevant (up to 56% of the total species) in Chamelea, characterized by a higher Zn concentration (Zn 80 mg/kg).

Our findings show that investigated bivalves can synthesize different phases other than Ca-carbonate when exposed to high Zn concentrations, suggesting that the biomineralization process acts as a detoxification sink to remove Zn excess from the immediate environment. In addition to the elucidation of biomineralization processes, achieved results are relevant to develop quantitative biomonitoring techniques and paleoproxy tools. A deeper understanding will be achieved by XAS microbeam analyses at a microscale on shell cross-sections to observe potential variations in Zn speciation inside the bivalve shell, and through the analysis of the soft tissues combined to shell analysis to observe if potential correlations between the metal content and Zn coordination environment occur.

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- OS2·O5 –

From thiophene building blocks to conjugated molecular systems for OLEDs: an investigation by synchrotron spectroscopies

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Conjugated molecular systems are of growing interest in the field of organic molecular electronics [1], due to the possibility to combine building block molecules to form more complex structures tuned to the desired device efficiency and performance in OLEDs [2]. In a typical device, the photoactive material is made by donor-acceptor (D-A) counterparts designed by combining their electron donor and acceptor properties on two sites of the same molecule usually connected by covalent bonds through π -bridge linkers (D- π -A) [3]. Thiophene-containing molecules [4] are well-know electron donors which are considered suitable donors/ π -bridges in D- π -A molecular systems, capable to improve the light harvesting efficiency and charge transport properties, facilitating the electron migration from the donor to the acceptor counterparts. Moreover, the introduction of π -conjugated ring-annulated moieties, such as benzene, simultaneously extends the π -conjugation and improves the stability of the resulting electron-donors and π -bridges for the assembling of organic electronic materials.

The present study focused on the gas phase electronic structure characterization of building block molecules such as: Thiophene (T) [5, 6], benzo[b]thiophene (BBT) and dibenzothiophene (DBT) [7]. The final goal is the comprehensive gas phase electronic structure characterization of the 2,8-bis(diphenylphosphoryl)dibenzo[b,d]thiophene (PPT), a promising ambipolar host-guest layer recently introduced in OLEDs. This molecular system is formed by two diphosphine oxide moieties functionalizing the small dibenzothiophene (DBT) core. It is characterized by high triplet energy and is known as good vacuum sublimable electron transporting host material for blue OLEDs. The phosphine oxide groups act as breaking points of π -conjugation between the core and the outer groups, leaving the electronic structures of the compound practically matching those of the central DBT moiety. For this reason, we have also characterized the Triphenyl Phosphine oxide (TPPO) as model compound of the phosphine oxide groups in PPT acting usually as π -conjugation breaking points (see Figure 1 for all the chemical structures).

For this purpose, in this work we present a combined experimental and theoretical study of the electronic structure in the gas phase of T, BBT, DBT, PPT and TPPO by means of X-ray photoelectron spectroscopy (XPS) and near-edge x-ray absorption fine structure (NEXAFS) spectroscopy based on assignments resulting from density functional theory (DFT) calculations and its time-dependent generalization (TDDFT) in the linear response regime. The acquired knowledge about the building blocks is useful to predict, control and manipulate their behavior when introduced in bigger molecular systems like in PPT.



Figure 1. Molecular sketches of: Thiophene (T), benzo[b]thiophene (BBT), Triphenylphosphine oxide (TPPO), dibenzothiophene (DBT) and 2,8-bis-diphenylphosphoryl-dibenzothiophene (PPT).

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64

- OS2·O6 -

The Unconventional Nature of the Nematic Phase of Bent-Core Liquid Crystals Revealed by Xray Diffraction

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The great interest of liquid crystal (LC) scientists in the nematic (N) phase of bent-core mesogens originated in 2004, when two claims of biaxiality, based on nuclear magnetic resonance [1] and X-ray diffraction data [2], fueled an animated debate within the LC community. Indeed, nematic biaxiality is considered the *Holy Grail* of LC science, theoretically predicted in 1970, but never unequivocally proved in low molecular weight thermotropic liquid crystals [3,4].

At the same time, several studies pointed out other unique properties of bent-core nematics, such as their ferroelectric switching behavior [5,6], extraordinary sensitivity to external magnetic and electric field [7,8], and unconventional rheological properties [9].

A long series of X-ray diffraction experiments performed by our group at the ESRF has revealed that these remarkable properties are intimately related to the presence of nanosized clusters of molecules—known as *cybotactic groups*—featuring very short-range smectic positional order and biaxial (possibly polar) orientational order [10-12]. These clusters, which encompass a number of molecules of the order of 10^2 , permeate the entire N phase of bent-core LCs, even at temperatures exceeding 200 °C and in the absence of an underlaying smectic phase. Cybotaxis is thus an inherent feature of the mesophase, not classifiable as a conventional critical phenomenon. Without external interactions, biaxial cybotactic groups are randomly oriented and the phase is macroscopically uniaxial [13,14]. However, external fields (mechanical, electric or magnetic) can extend biaxial order over a macroscopic length scale. When the clusters are polar, this also results in the transition to a field-induced ferroelectric state [5,6]. In general, the macroscopic response of the cybotactic N phase to external stimuli is greatly amplified by its cluster nature—where the fundamental entities are groups of hundreds of molecules in a conventional N phase [7-9].



Figure 1. Typical XRD pattern in the cybotactic N phase of a bent-core LC (horizontally aligned) and its interpretation in terms of the structural parameters of a cybotactic cluster. The small-angle four-spot pattern is a signature of tilted cybotactic order.

Here we provide an overview of our research on this topic, including our most recent observation of cybotactic order in the N phase of some rod-like all-aromatic nematic LC [15]. This result raises fundamental questions on the intimate nature of cybotactic order and its implications for both calamitic and bent-core nematics.

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Young Investigators session

- YI·KN1 -

A new phase transition in laser-shock compressed gold from X-ray diffraction at the Dynamic Compression Sector beamline

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The use of lasers to induce extreme compression states enables the study of material properties and equations of state at unprecedented pressures and temperature conditions. By carefully designing the laser pulse shape (i.e. laser power vs time), one can tune the compression history of the sample and reach a specific pressure-temperature state. The combination of laser-driven compression and x-ray diagnostics allow us to probe these extreme pressure-temperature states in-situ, providing a unique picture of the transformations taking place in high-energy-density matter. Structural probes, such as X-ray diffraction (XRD) and X-ray absorption spectroscopy (EXAFS, Extended X-ray Absorption Fine Structure), have been developed at the Omega laser (University of Rochester, NY) [1,2,3] to investigate phase transitions occurring on nanosecond time scales as a result of laser-driven dynamic compression. More recently, synchrotron beamlines, have installed optical lasers to combine the bright and stable synchrotron x-ray radiation with laser-driven dynamic compression. Here we report about new experimental study of shock-compressed gold by in-situ x-ray diffraction at the Dynamic Compression Sector (DCS) at the Advanced Photon Source (APS) [4,5]. A high-energy laser (< 80 J at 351 nm) send ablatively-driven shockwaves through a polyimide ablator and the Au sample glued to a LiF window. Velocimetry measurements are used to determine the pressure using impedance matching techniques. X-ray diffraction is used to monitor the structural transformations induced by the shock compression and provides a clear evidence for a phase transition from the face-centered cubic to the body-centered cubic structure near 220 GPa. At pressures above 250 GPa, shock-induced melting is observed and is completed by 323 GPa, providing experimental constrains on the melting curve of gold along the Hugoniot [6].

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- YI·O1 -

Directional sub-fs charge transfer dynamics in 1T-TaS₂

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We have investigated the directional dependence of ultrafast charge transfer in the strongly correlated layered material $1T-TaS_2$ by means of polarization-dependent resonant photoemission spectroscopy (RPES) [1].

Absorption of p- and s- polarized X-rays leads to selective excitation of S 2s electrons into out-to-plane $3p_z$ and in-plane $3p_{x,y}$ orbitals, respectively. Quantification of the intensity ratios between Auger resonant Raman channels at constant binding energies and Auger channels at constant kinetic energies in the measured S $L_1L_{23}M_{123}$ autoionization spectra allows to clock the excited state wavepacket delocalization against the atomic core-hole lifetime.

The study was conducted for $1T-TaS_2$ in both its room temperature and low temperature (30K) phases, characterized by nearly commensurate (NCDW) and commensurate (CCDW) charge density waves, respectively.

We have found that, while anisotropic 2D charge transfer occurs in the NCDW phase, with slower out-of-plane than inplane electron delocalization, the CCDW phase shows isotropic 3D charge transfer, thus denoting surprisingly strong interlayer coupling [Fig.1].



Fig. 1: Charge transfer times in the low temperature (left) and room temperature (right) phases of TaS_2 for out-of-plane (purple circles) and in-plane (green triangles) excitations, as determined by the core-hole clock method [2].

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- YI·O2 -

Structural modifications in cerium oxide ultrathin films induced by reduction

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The catalytic applications of cerium dioxide often involve the formation of oxygen vacancies on the surface of the material. Understanding how the excess of charge occurring in the formation of an oxygen vacancy relaxes is still today debated by the community [1], [2]. Consequently, studying the CeO₂ structural modifications during reduction processes represents an important topic in view of the optimization of the material reducibility. For this purpose, we investigated the evolution of the short- and long-range structure of cerium oxide ultrathin epitaxial films using x-ray absorption spectroscopy at the Ce L₃-edge and grazing incidence x-ray diffraction, during reduction induced by thermal treatments in vacuum on well-controlled ultrathin films [3]. At sub-nanometric thickness the film reduction is associated with a contraction of the Ce-O distance by 2-3%. The appearance of a phase with a (2×2) periodicity after a thermal treatment at high temperature is ascribed to the formation of a Pt₅Ce alloy. Films of approximately 3 nm thickness do not show significant structural modifications with the same thermal treatment, consistent with the hypothesis that reduction involves only the topmost surface layers and does not influence the bulk structure of the material.

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- YI·O3 –

Surface x-ray diffraction investigation of the interface structure of Yttrium doped Barium Zirconate proton conductor grown on different substrates.

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Heterostructures between different oxide materials offer an ample opportunity to probe into some of the exciting and intriguing phenomena exhibited by oxide interfaces. A short list of these unique properties includes high-mobility electron gas, superconductivity, metal-insulator transition, enhanced ionic and protonic conductivity. Such properties result from one or, in most cases, from the combination of different interface mechanisms such as epitaxial strain, strain relaxation, polar discontinuity, space-charge regions etc. [1].

Considerable efforts have been devoted to studying the effects of strain on the ionic conductivity to high- temperature proton conductors (HTPCs). HTPCs promise great potentials as solid oxide fuel cells (SOFCs) electrolyte membranes, considered a breakthrough for sustainable and renewable electrochemical energy conversion. Due to its chemical stability and high bulk proton conductivity in the low temperature range (300–500 °C), the perovskite oxide Y- doped BaZrO₃ (BZY) is probably the most representative proton- conducting oxide [2].

More recently, the role of the network of misfit dislocations in the proton conduction of the interface between NdGaO₃ and BZY was investigated [3,4]. Surface X ray diffraction measurements carried out on this system showed that the strain field related to the network of dislocations at the interface depends on the annealing in a wet atmosphere, pointing towards a role of the dislocations cores as a reservoir of hydroxyl groups.

In order to investigate the strong dependence between transport properties and structural defects, the interface structure between highly ordered, epitaxially oriented, $BaZr_{0.8}Y_{0.2}O_{2.9}$ (BZY) thin films grown on different substrates were intensively studied by synchrotron radiation-based diffraction techniques. Very thin films of BZY were grown on three different perovskite type substrates, NdGaO₃, SrTiO₃ and LaAlO₃. The degree of the lattice mismatch among the three different heterostructures results to vary from 8 % to 10 %. In these systems, the lattice relaxation occurs by misfit dislocations (MDs) at the interface between the deposited film and the substrate. Reflectivity analysis displays as common feature the presence of an interface region of few nanometers, extending both in substrate and film, compatible with elemental interdiffusion and high concentration of point defects. Surface x-ray diffraction (SXRD) measurements show the presence of MDs network that self-organizes in a somewhat disordered square network at the interface with a large inplane coherence length. The properties of these defective interfaces could be useful to fabricate novel dual miniaturized solid oxide fuel cells using state of the art microfluidic and microelectromechanical technology [5].

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- YI·O4 -

In Situ GISAXS Investigation of PtNi Alloy Under Operational Conditions of PEM Fuel Cells.

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In the last years, several Platinum-based bimetallic alloys have been studied as possible substituents of pure Platinum catalysts in Proton Exchange Membrane Fuel Cells (PEMFCs) to strongly reduce production cost. In particular, PtNi alloy was found to be a promising alternative to pure Pt due to its very good mass activity1 and its competitive catalytic activity2. Despite these advantages, the acid-based environment in which catalyst has to operate, causes the dissolution of the less noble metal and the consequent degradation of the catalyst layer. In this picture, in situ Grazing Incidence Small Angle X-ray Scattering, combined with Electro-Chemical AFM and Inductively Coupled Plasma Mass Spectrometry, is used to investigate the real-time kinetics of the surface degradation of PtNi alloy during electrochemical cycling voltammetry. In order to simulate the real fuel cell operation conditions, four different upper potentials have been used. Obtained results, allowed to describe the asymmetric Ostwald ripening process in electrochemistry the first time, A further investigation dependant on catalyst composition have also added to better describe the degradation of the aforementioned catalyst and to reveal in depth the structural and compositional changes during fuel cell operation.

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- YI·O5 -

Investigating chemical reactions in the millisecond time scale through coupled X-Ray Absorption and UV-Vis spectroscopies

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An important challenge in modern chemistry resides in uncovering the structural evolution of the species involved in fast chemical reactions, whose characteristic time scales range from the seconds to the milliseconds and below. Due to the extreme complexity of this task, it is of the utmost importance to develop new experimental strategies dedicated to the study of reactivity.

In this work, time-resolved energy dispersive X-ray absorption spectroscopy (EDXAS) and UV-Vis spectroscopy were combined to investigate the oxidation reactions of organic substrates by a selected non-heme iron activated species [1]. For the first time, pseudo first-order kinetic constants relative to fast bimolecolar reactions in solution were obtained by the time-resolved XAS technique. While XAS allows one to acquire insight on the local structure and electronic configuration of selected atoms, UV-Vis spectroscopy permits the unambiguos identity assignment of interchanging reaction intermediates: together, the two tecniques are complementary instruments for the study of chemical processes. The research was focused on sulfide and alcohol oxidation by the oxo-complex [N4Py•Fe^{IV}O]²⁺, generated by the reaction of the non-heme iron complex [N4Py•Fe^{II}]²⁺ (N4Py=N,N-bis(2-pyridylmethyl)-N-bis(2-pyridyl)methylamine) with peroxyacetic acid. The selection of [N4Py•Fe^{IV}O]²⁺ as the oxidizing agent was guided by the fact that non-heme iron complexes have attracted increasing interest as catalysts for the oxidation of organic compounds, thanks to their inexpensive and environmentally friendly nature.

The coupled XAS/UV-Vis approach was employed at the ID24 beamline at the European Synchrotron Radiation Facility (ESRF) to follow the oxidation of benzyl alcohol to benzaldehyde (Figure 1) and of a series of thioanisoles, differently substituted in the para position of the aromatic ring, to the corresponding methylphenyl sulfoxide (CH₃CN, 25 °C). Specifically, the XAS kinetic determination was applied to three aryl sulphides 4-MeO-PhSMe, PhSMe and 4-CN-PhSMe, whose oxidation by $[N4Py\bullet Fe^{IV}O]^{2+}$ is, respectively, decreasing in speed.

All reactions were carried out under pseudo-first order conditions with the concentration of the substrates largely exceeding that of $[N4Py \cdot Fe^{IV}O]^{2+}$. The rate of the iron oxidation state evolution during each reaction was determined by following the relative Fe K-edge energy shift in the time-resolved XAS spectra.

In all cases the kinetic constants values found by means of EDXAS were in good agreement with the k values measured through UV-Vis and with literature data.

The XAS technique, for the first time, allowed a quantitative determination of the kinetic constants of fast (in the millisecond to second timescale) bimolecular chemical reactions. These results make XAS spectroscopy an important tool to study fast complex chemical processes involving the oxidation of a metal center when the use of other experimental tecniques would be impossible.

Moreover, the application of multivariate data analysis to the time evolving XAS spectra will allow one to unveil the structures of fleeting intermediates and to gain crucial mechanicistic insights for the investigated reactions.



Figure 1. Oxidation of PhCH₂OH by $[N4Py \cdot Fe^{IV}O]^{2+}$ in CH₃CN at 25 °C followed by the coupled XAS/UV-Vis technique. (A) Time evolution of the XANES spectra at selected times from reaction start. (B) ΔE_0 vs time (the points with colored marks correspond to the spectra with the same color reported in panel A), where ΔE_0 is the difference between the K-edge position of the XANES spectra at time t and the edge position of the first XANES spectrum at t=0 s. (C) UV-Vis monitoring of $[N4Py \cdot Fe^{IV}O]^{2+}$ (downward triangles at λ =690 nm) and $[N4Py \cdot Fe^{II}]^{2+}$ (upward triangles at λ =513 nm) during the reaction.

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Copper Coordination Compounds Conjugated to Gold Nanoparticles as Innovative Anticancer Drugs: Structural Investigation Carried Out by Synchrotron Radiation-Induced Techniques.

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In recent years, the biomedical research of new metal-based anticancer drugs alternative to Pt(II) derivatives has been focused on complexes including, among other metals, gold, ruthenium, silver and copper. In particular, novel Cu-based antitumor agents have been studied according to the view that endogenous metals may be less toxic toward normal cells with respect to cancer ones (Figure 1a). In addition, copper(II) complexes of hexyl bis(pyrazol-1-yl) acetate ligands (Figure 1b) have been recently investigated for the development of a new and more efficient promoter for the Kharasch-Sosnovsky reaction to oxidize alkenes in allyl position. The synthetic strategy utilized ligands having soft donor atoms such as aromatic sp² hybridized nitrogen of pyrazolyl derivatives. Since such coordination compounds have low solubility in aqueous medium, it is necessary to design a strategic approach allowing for drug delivery. By conjugating the copper complexes with hydrophilic gold nanoparticles, it is possible to improve their solubility and stability in water, and consequently to increase their bioavailability. Moreover, these drug delivery systems allow the investigation of a slow and controlled release of copper complexes.



Figure 1. Molecular structure of Copper(II) complexes

In this context, we investigated the molecular and electronic structure of a selection of Cu(II)-coordination compounds (see Figure 1 for the molecular structures of complexes A and B) by means of SR-XPS and NEXAFS spectroscopy; the oxidation state and the local coordination chemistry of the metal ion was probed by Cu K-edge XAFS analysed in the near edge (XANES) and extended (EXAFS) regions. The pristine ligands were also studied for sake of comparison.

The combined use of complementary probes (XPS-NEXAFS-XAFS) is providing an accurate and reliable understanding of local coordination chemistry and electronic structure of Cu(II)-coordination compounds which are suitable to be the elementary building blocks to realize nanoassemblies by conjugation with hydrophilic AuNPs, along the route already successfully tested by some of us on model systems [1]. Here the results of multidisciplinary characterization of Cu(II)-coordination compounds and preliminary results on coordination compound/AuNPs interactions will be presented, discussing the further steps for the research.

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- YI·O7 –

Structural investigation of HgCl₂ solvation structure using X-Ray Absorption Spectroscopy

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The aim of this study is to obtain a complete description of the solvation complexes of the $HgCl_2$ molecule in different solvents, namely water, methanol (MeOH) and four different Deep Eutectic Solvents (DESs), made up from Choline Chloride (ChCl) mixed in a specific molar ratio with Urea, Acetylsalicylic Acid (ASA), Sesamol (SES) and Pyrogallol (PYR), by means of a combined XANES and EXAFS analysis. Accurate bond distances were obtained analyzing the EXAFS region of the absorption spectrum, while the quantitative analysis of the XANES region provided accurate informations on the tridimensional arrangement of the atoms around the photoabsorber and allowed us to determine the coordination number.

Knowing that the molecule does not dissociate in water [1] and assuming the model expected from previous theoretical studies [2][3], we found the same structure for the HgCl₂ solvation complex in H₂O and MeOH, while a totally different structure was found in the DESs, showing that these solvents have peculiar solvation properties since they are able to break the covalent Hg-Cl bonds. Furthermore, they show the same solvation properties towards the Hg-O molecule that shares the same solvation structure. The fitting results related to the two different geometries are reported in Figure 1.



Figure 1. Results of the fitting procedure. From the left to the right: XANES fit, EXAFS $\chi(k)$ signal fit, Fourier transform of the EXAFS signal. As an example the results for HgCl₂ in H₂O (up) and in the ChCl/Urea DES (down) are reported.

The Hg-Cl bond length in H₂O and MeOH is 2.31(2) Å, that is the same distance found for the HgCl₂ single crystal by means of an X-Ray diffraction study [4]. The Hg-Cl distance is 2.47(2) Å in the DESs: this much higher distance allows one to state that this molecule is dissociated in this solvents. Furthermore, the HgO molecule dissolved in one DES shows exactly the same absorption spectrum. This is an evidence that the DESs can dissolve also the HgO molecule in a solvation cluster that shares the same coordination number, the same coordination geometry and the same bond distances as the HgCl₂ molecule.

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- YI·O8 –

In-situ time resolved XAS investigation of Mg in magnesium-potassium phosphate cements

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Magnesium-potassium phosphate cements (MPCs) are chemically-bonded ceramics which set at room temperature through an acid-base reaction in presence of water, between MgO and an acid potassium phosphate. They attracted interest for a countless number of applications, ranging from nuclear waste encapsulation [1], bone repair [2], dentistry and in civil engineering as eco-sustainable fast repair materials for damaged structures [3]. During the reaction, a crystalline magnesium-potassium phosphate hydrate (MgKPO₄·6H₂O) forms by progressive incorporation of water, according to the following reaction:

$$MgO + KH_2PO_4 (KDP) + 5H_2O = MgKPO_4 \cdot 6H_2O (MKP)$$
(1)

In MKP, Mg is coordinated by 6 oxygen atoms from water molecules, in a slightly distorted octahedral coordination [4]. However, an amorphous precursor form first, and owing to the slow rate of the conversion into the crystalline product and to the progressive reduction in ion mobility with the progress of the reaction, it is always observed in the cement. Structural information on it is lacking, but it is of importance in order to understand the mechanism of the reaction, and, in turn, the development of the microstructure and the properties (e.g. mechanical, adhesive, dissolution) of the cement for applications.

A mechanism of the reaction has been proposed based on the nature of the products and kinetic analysis of synchrotron X-ray diffraction data [5]. Using quasielastic neutron scattering, nuclear magnetic resonance and time-resolved infrared spectroscopy, the hypothesis is that the amorphous precursor is an orthophosphate hydrate possessing structural motives of Mg similar to those in the crystalline phase [6-8].

In order to confirm this model, *in-situ* time resolved XAS experiments at the Mg K-edge have been performed at the LUCIA beamline of the SOLEIL synchrotron facility in Saint-Aubin (France). The experiment can be considered as state of the art because of the complexity of the investigated system (studied for the first time through *in-situ* XAS at the Mg K-edge) and of the peculiar set-up that has been used.

Various time-resolved measurements were conducted on samples with and without different types (and amount) of retardants, in order to better highlight the formation steps of the amorphous phases; in addition, spectra were collected on pellets of many Mg-bearing reference compounds (some of which have never been studied with XAS), representing potential candidates for the local chemical environment of Mg in the amorphous meta-stable phases.

Despite the time-resolved spectra suffered of low signal-to-noise ratio (all measurements were performed in fluorescence mode), we managed to successfully perform XANES linear combination fitting (LCF) analysis using the pure spectra of some of the Mg-reference compounds. LCF was performed at least 3 times on each spectrum and both on the raw and smoothed data, in order to test for the reproducibility.

The obtained results clearly highlight the effects of the retardant, allowing to identify the evolution of the amorphous through time and to better describe the oxidation state and coordination geometry of Mg in this meta-stable phase.

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- YI·O9 –

Iron rich amphiboles: a study on correlated structural and electrical properties

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In metamorphic rocks, Fe-bearing amphiboles carry important information on the crystallization conditions (G. Della Ventura et al., 2005); their HT processes are in addition strongly connected to the increasing electrical conductivity of subducting slabs at convergent plate margins (Wang et al., 2012). Amphiboles species like riebeckite (crocidolite) and grunerite (amosite) are also interesting technological materials, previously used in several technological applications due to invaluable thermal resistance characteristics. After the late '80s, however, due the discovery of their carcinogenesis effects these materials have been banned in many countries and their toxicity has been deeply studied (e.g., Turci et al., 2017).

The chemical/physical properties of the amphiboles and their behavior at high temperatures are associated to their loss of structural hydrogen. This process involves the oxidation of the iron atoms and the consequent release of protons at the crystal surface in the form of molecular water (Della Ventura et al., 2017). Although many studies have been devoted to characterize the oxidation behavior (e.g., Oberti et al., 2018, Della Ventura et al., 2018) and the associated structural adjustments (e.g., Welch et al., 2007), the dynamics of this process are still poorly constrained.

Here, we will describe a novel approach for the investigation of the oxidation process in amphiboles specifically tailored for these minerals (Della Ventura et al, 2018, Galdenzi et al, 2018). The method employs the X-ray Absorption Spectroscopy to monitor, with a high reliability, the Fe^{3+}/Fe_{tot} ratio in the sample during the heating experiment. We will also show new results on the conductivity anomalies in amphiboles, based on the analysis of data collected using *in situ* XAS experiments, performed while heating the sample and simultaneously measuring its conducibility. In addition to important understanding of the role of these minerals in geology and geophysics, this study reveals unexpected properties of the amphiboles that suggest the possibility to design new materials with outstanding properties.

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Satellite workshop: "Coherence of UV-SoftX beams, a contribution to its exploitation"

- SAT·O1 –

Examples of coherence in atomic and molecular photoionization by a single photon (synchrotron radiation) and few photons (FEL)

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Coherence has been defined in a recent publication as "*what makes a wave capable to produce observable interference and diffraction effects*" [1]. In a radiation source it depends on the source size and angular spread of the emitted beam and therefore is directly related to the brightness of the source. The effort done in new synchrotrons and FELs to increase the brightness, up to the diffraction limit, will have as a by-product an increased coherence of the emitted radiation. In the presentation two examples of how coherence can be exploited in atomic and molecular physics will be discussed.

Inner shell photoionization of diatomic molecules and Young double slits experiments

The photoionization cross section of the inner shell of diatomic molecules displays an oscillating behavior. This observation has led to the consideration that the photoemission from these highly localized core electrons can be regarded as a molecular Young's double-slit experiment. The development of experimental methods in which the energy and momentum of the ejected electron correlate with both the polarization of the incident radiation and the energy and momentum vectors of the ionic fragment has enabled detailed insights on the basic phenomena leading to the observed interference [2].

Asymmetry parameters in two-photon photoionization at FEL

Coherent control involves driving a quantum system via two pathways to the same final state and manipulating the phase and wavelength of the exciting source to favour this state. Seeded FELs, like Fermi are longitudinally coherent thus their beams can be used to extend towards short wavelength the coherent control experiments performed in the optical region by table-top lasers. In the proposed example [3] the coherence of the two-colour emission is demonstrated in the photoionization of the Ne 2p by measuring the asymmetry of the photoelectron angular distribution.

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- SAT·O2 -

Terahertz and Infrared Synchrotron Radiation: Coherence helps its use?

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Terahertz (THz) and Infrared (IR) Synchrotron Radiation (IRSR, 0.5 meV-1 eV) beamlines have been developed in the last thirty years in all II and III generation synchrotron machines and in many free-electron lasers [1]. THz and IR radiations are in resonance with most of the fundamental excitations in condensed matter, allowing to measure their characteristic energy and lifetime. Examples of applications range from the superconducting gap in superconductors, insulating gap in semicondutors, surface plasmons in metals, inter- and intra-vibrational modes in molecular solids and in macromolecules of biophysical interest [1]. Moreover, the intrinsically high brilliance of IRSR allows to perform spectromicroscopy at the diffraction limit, with a spatial resolution down to few microns. Single cell spectroscopy in Biology strongly benefits of this spatial resolution, together with high pressure spectroscopy in Solid-State Physics and Chemistry.

The developing of new machines with sub-ps electronic pulse duration and strongly reduced electronic emittance sets new opportunities for IRSR like time-resolved spectroscopy at low-energy [2]. Moreover, the coupling among IRSR with AFM based techniques allows to go well beyond the diffraction limit opening to terahertz and infrared radiation the nanoscale world [3]. Spatial and temporal coherence are however a challenging for low energy spectroscopy thus in this talk, I will discuss the existing and future projects on IRSR in Italy and the limitations and opportunities determined by temporal and spatial coherence.

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- SAT·O3 -

Microtomography with Coherent Synchrotron Radiation: Mapping the Human Brain

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The exceptional properties of synchrotron sources and in particular the high spatial coherence provide the foundation for very effective x-ray imaging techniques. The performances are unprecedented, ranging from advanced spatial resolution to high contrast and chemical specificity. In addition, there is a constant decrease in the image-taking time that opens new opportunities in the life sciences. This is also a new strategic aspect in synchrotron research, which traditionally emphasized brightness-based applications rather than massive data acquisition. Thanks to fast image taking, formerly impossible tasks are becoming realistic. One example is the full map of a human brain on the scale of neurons and connections, targeted by the new Asia-Pacific multinational research enterprise "SYNAPSE". The presentation will start from the elementary foundations of synchrotron radiation coherence, then briefly present relevant experimental techniques and recent achievements, and finally analyze the practical objectives and strategies of SYNAPSE.

- SAT·O4 –

Some odd consequences of self-coherence in the photo-diffraction and photo-absorption processes

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While the photo-emission process is inherently inelastic, and therefore at first sight impervious to any effect of coherence of the incoming photon beam, in reality a closer investigation reveals that some coherence effects depending on the single photon self-interference might indeed be observable. All hinges on the old adagio of Quantum Mechanics stating that, if the same final state can be reached by different pathways, the probability for its observation is obtained by taking the modulus squared of the sum of the probability amplitudes of the various paths, leading to the mechanism of self-interference.

To this purpose I review the two-slit and the usual crystal (Bragg) diffraction experiments, highlighting that in both cases the interference patterns are due to the self-interference of the single incoming photon. Guided by these two examples, I try to construct the photo-emission equivalent of these experimental set-up and discuss the related diffraction patterns. For comparison the case of Coherent Diffraction Imaging is also discussed, underlining similarities and differences.

- SAT·O5 -

Measuring linear and nonlinear response by the photoelectric effect: first order diffraction and higher-order in 3D and 2D systems

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Experiments with XFEL sources impose to understand the emergence of quantum-optics phenomena at X-ray energies. A discussion of the light sources as defined through the photoelectric effect detection, following J. Stohr's AOP-2019 paper, is presented and novel results obtained at SACLA on noble gas clusters show how angular correlations in first-order diffraction emerge as signals capable to support fine structural characterization even when multiple photons are simultaneously scattered.[2] Pump-probe results on cluster phase transitions will also be shown.[3]

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- SAT·O6 -

Opportunities for spatial coherent spectroscopies in the VUV-X ray energy range

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The rush toward diffraction limited synchrotron radiation rings provides transversely coherent beams which open new avenues to the structural and electronic characterization of materials.

The task to transfer experimental methods and to translate the physical meaning of classical coherent spectroscopy based on UV-Vis laser sources to the VUV-X ray wavelength range is of primary importance for accessing the nanometer spatial resolution.

The ELETTRA 2.0 project [1] presents as a key parameter a high degree of transversely coherent radiation in the VUV - X ray energy range that can be exploited by the synchrotron users community.

The aim of the talk is to introduce on the ground of simple physical concepts the production of spatially coherent radiation, the interaction of coherent radiation with the matter (scattering and four wave mixing), and the conundrums that can be addressed by the coherent spectroscopies.

In particular, to favor the discussion, some hints of possible application of VUV-X ray coherent spectroscopies in plasmonics and cluster coherent oscillations [2], and photovoltaic semiconductors [3] will be presented.

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Poster Session

- P·01 –

Structural characterization of hybrid Au-CuO Nanoparticles and their role in Selective Benzyl Alcohol Oxidation

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Bimetallic nanoparticles (NPs) have received great interest over the last decade owing to their unique catalytic, optical, and magnetic features. The design of bimetallic NPs by advanced synthetic approaches offers an effective way to control their size, shape, composition, and crystal structure which in turn are able to fine-tune their physicochemical properties. NPs containing gold in the presence of another metal represent a new challenge in gold catalysis.

Among the promising metal pairs, Au/Cu NPs as alloys or core-shell structures have been investigated pointing out at times a positive beneficial effect in terms of catalytic performances and stability with respect to their monometallic counterparts [1].

Recently, in order to disclose the essence of the synergistic effect between gold and copper in oxidation reactions, the structural evolution of supported Au/Cu alloy NPs in the CO oxidation reaction has been deeply investigated by different research groups [2]. Despite experimental and theoretical efforts, the control of copper surface segregation (i.e., the thickness of CuO on the surface) in Au/Cu alloy NPs under oxidative conditions and thus their behavior in catalytic oxidations is still a challenge. As a matter of fact, the degree of phase segregation is strongly influenced by the reaction conditions and oxidative/reductive pretreatments, the substrates/metals interaction, the particle metal ratio, and the synthetic approach. Selective oxidation of benzyl alcohol has attracted both academic and industrial interest because of the application of benzaldehyde in perfumery, dyestuff, and agrochemical industries. Although the positive effect of Cu on the Au-based catalysts for selective oxidation of benzyl alcohol was already reported, a correlation between the structural properties of the AuCu bimetallic NPs and their catalytic activity in this reaction is still lacking.

Hybrid Au/CuO NPs supported on carbon by solvated metal atom dispersion (SMAD) for selective liquid-phase oxidation of benzyl alcohol to benzaldehyde were synthetized [3]. The SMAD approach has been proposed as an effective way for the preparation of supported bimetallic Au-based and Cu-based NPs with high control of their size/composition, avoiding the use of any surfactant or capping agent.

The morphological and structural features of SMAD-derived AuCu bimetallic catalysts containing different Au/Cu molar ratios were deeply investigated by high- resolution transmission electron microscopy (HRTEM), scanning transmission electron microscopy (STEM), electron energy loss spectroscopy (EELS), and X-ray absorption fine structure (XAFS) measurements disclosing the role of the local particles/structure/composition and their catalytic properties.



Figure 1. Representative STEM-Energy filtered maps for sample Au₁Cu₁₇.

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- P·02 –

Electronic and magnetic properties of quaternary spinel ferrites prepared by low-temperature hydrothermal synthesis: a combined XAS-XMCD investigation

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Quaternary spinel ferrites with the general formula $Zn_{(1-x)}Co_xFe_2O_4$ (x = 0, 0.2, 0.4, 0.6, 0.8, 1) were synthesised through a low-temperature and green protocol combining the coprecipitation of the metal salt precursors with oxalic acid and the subsequent treatment of the resulting suspension under mild hydrothermal conditions (T= 135°C) [1]. The obtained powders were characterized from a structural (XRD) as well as compositional (XPS, ICP-MS) point of view.

The analyses showed that the approach afforded nanocrystalline materials after short treatment times (24 hours) with excellent compositional control, allowing to control the value of x in $Zn_{(1-x)}Co_xFe_2O_4$ by simply varying the nominal stoichiometric ratio between the Zn and Co precursors.

Given that ferrites are a class of materials which can display numerous and useful magnetic, dielectric and catalytic properties based on their composition and structure [2], which make them attractive materials for a wide variety of functional applications, it was important to also investigate the electronic and magnetic properties of the synthesized compounds, as well as their inversion degree [3].



The electronic structure was assessed by soft x-ray synchrotron radiation XAS measurements at the $L_{3,2}$ edge (2p --> 3d transition) of Fe, Co and Zn atoms, confirming the expected oxidation state of the elements [4].

Co $L_{3,2}$ XAS spectra indicate that the co-existence of Co and Zn cations has no influence on the site selectivity of both cations. On the other hand, the site selectivity of the Fe ions strongly depends on the composition. In fact, Fe $L_{3,2}$ XAS spectra show that the occupancy of the Fe³⁺ cations in octahedral sites (*Oh*) becomes smaller, and that of Fe³⁺ cations in tetrahedral sites (*Td*) becomes larger with increasing x (decreasing Zn content).

XMCD spectra of the most representative samples (CoFe₂O₄, Co_{0.8}Zn_{0.2}Fe₂O₄, Co_{0.6}Zn_{0.4}Fe₂O₄ and ZnFe₂O₄) at Fe and Co L_{3.2} edges were measured at RT in remanence, after *in-situ* magnetization with a permanent magnet (0.45 T). A preliminary analysis of Fe and Co L_{3.2}-edge XMCD spectra show a ferromagnetic coupling between Fe and Co cations in the crystal lattice of CoFe₂O₄. The spectra under remnant magnetization conditions clearly show that CoFe₂O₄ and Co_{0.8}Zn_{0.2}Fe₂O₄ samples preserve a fairly large magnetization after the field removal even at RT. Conversely, no clear magnetic dichroism in remanence at RT was observed on the samples with higher Zn content (ZnFe₂O₄ and Co_{0.6}Zn_{0.4}Fe₂O₄).

Figure 1. (a) Fe L₃-edge XAS spectra of $Zn_{(1-x)}Co_xFe_2O_4$ samples at variable x concentration. (b) Fe L_{3,2}-edge XMCD spectrum of CoFe₂O₄ measured in remanence, after magnetization at RT.

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- P·03 -

Following crystallization of ZnS nanostructures in confined space by *in-situ* and time-resolved SAXS

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Miniemulsion is an innovative method to obtain, already at room temperature, crystalline inorganic materials by exploiting a reaction occurring inside the confined space of independent nanometric-sized droplets. Despite being a promising technique, to the best of our knowledge, no systematic study on the crystallization phenomena under miniemulsion conditions has been carried out yet. In this regard, we performed by Small-Angle X-ray Scattering (SAXS) an *in-situ* and time-resolved investigation of the crystallization process of ZnS synthetized by inverse miniemulsion [1]. The experimental setup for this experiment was composed of a reactor equipped with a probe-type sonicator, connected with a continuous flow equipment (Figure 1). While the reaction was carried out, the reaction mixture was continuously flowed thought a homemade measurement cell mounted in the SAXS beamline of the synchrotron facility Elettra (Trieste), to follow the structural and morphological evolution of the system in real-time. The obtained SAXS profiles were then fitted in order to get an insight of the dimension and the number of the formed particles with time. Moreover, the same setup was employed to investigate the miniemulsion without the presence of the ZnS precursors, and the effect of the surfactant concentration on the synthesis.



Figure 3: Experimental continuous flow set-up.

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Structure rearrangements induced by lithium insertion in metal alloying oxide spinel structure studied by x-ray absorption near-edge spectroscopy

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Carbon-coated ZnFe2O4 (ZFO-C) spinel ferrite nanoparticles can be used in electrodes for Li-ion batteries and are known to show capacities larger than those calculated for an ideal spinel structure. In this work, the local structure evolution and reordering of this material upon lithium insertion are studied using K-edge and L-edge x-ray absorption near edge spectroscopy (XANES). XANES simulations corresponding to different lithiation stages are performed using full multiple scattering (Fe, Zn K-edge, Zn L-edge) and ligand field multiplet (LFM) calculations (Fe L-edge). XANES simulations are compared with experimental spectra obtained on ZFO-C nanoparticles previously characterized by electrochemical measurements. It is shown that a satisfactory agreement for the XANES Fe and Zn K-edges of pristine ZFO-C bulk nanoparticles can be obtained introducing a mixed spinel structure with Fe and Zn partially occupying tetrahedral and octahedral sites. Upon lithiation, changes in the XANES spectra are interpreted introducing displacements of the cations as an effect of occupation of Li into empty lattice sites. In particular, comparison of the simulations with the XANES data indicates that reversible Li insertion is accompanied by a migration of the Zn and Fe atoms from tetrahedral to octahedral sites. Furthermore, by studying L-edge XANES spectra, we show that the relocation and valence change of metal ions occur at earlier lithiation stages at the surface of the active material, gradually extending to the bulk for larger Li uptakes.

- P·05 –

Structurally induced effects on electronic properties of the semiconducting one dimensional systems

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Semiconducting nanowires have recently been extensively studied and developed for applications in nanoelectronics, optoelectronics, solar cells and sensors using carries confinement [1-2]. The Si and Ge nanowires in particular can be promising candidates for one-dimensional superconductor-semiconductor hybrid systems that are one of the optimal platforms for realizing Majorana zero modes [3-4]. Condensed matter realizations of Majorana zero modes constitute potential building blocks of topological quantum computers. However, their electronic properties are strongly dependent on their surface and core structure. Hence, a detailed investigation of their possible effects on these properties are necessary prior to the utilization of such hybrid systems. Here, we have studied structural and electronic properties of doped Si and Ge nanowires with distinct structures, ranging from single crystalline to one with embedded Si quantum dots and percolative crystalline path. We show that the predesigned structure of the wires results in prominent single distinct electronic configuration and density of states. This leads to the observation of photoluminescence modulations and transport mechanism in these systems. We demonstrate that DOS modulation results in two different transport regime i.e., thermally activated tunnelling and variable range hopping in these systems [5]. We further show that observed transport properties are the result of the geometry of the systems with a large internal surface and a significantly high density of states. These results improve the understanding of the different electronic transport mechanisms in semiconducting nanowires and can lead to advanced hybrid systems design.

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- P·06 -

Structural evolution of Lithium Manganate cathodes during charge/discharge cycles

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Surface Nanoparticles modifications have been observed on alumina coated LMO cathodes with respect to the uncoated nanoparticles cathodes during the first cycle of charge/discharge.

During discharging (lithiation), when at low voltages the disproportionation reaction is favored, scanning electron microscopy has revealed the presence of holes formation in the nanoparticles while similar effects were not visible in other phases of the voltammogram.

We put in relation this observation with the non perfect Al_2O_3 coating of the nanoparticles used for the electrode where channel of ions transport are activated, contrarily to uncoated nanoparticles, showing a deep reaction of the carbon based electrolyte with the oxide, on a larger extent than usually considered for the cathde electrolyte interphase. The non thermodynamic proton transfer process at the basis of the present effect was recently predicted by Choi et at [Phys.Chem.Chem. Phys 2018, 20, 11592] by first principle density functional calculations.

The x-ray absorption analysis (Mn L2,3, F and O K-edge) was also able to describe the chemistry at the interphase formed at hgh voltages when strong fluorinated by-products are differently observed along the vertical profile at variance with the coatings. Al2O3 coating results fully effective for stopping the strong reduction processes occurring during charging at high voltage of the battery, when O-Mn couple react with organic species, making Mn capture and electrolyte reaction with the oxide surface possible, and an electrolyte interphase and Mn dissolution might occur.

We followed the transition also by Raman to detect the signatures of the transformation, observing a reversible modification of the surface character of the nanoparticle from a spinel to a layered. In conjunction with soft X-ray spectroscopy this study is particularly suitable to detect modification of the active material at the frontier of the nanoparticle, where the interphase between electrolyte and active nanoparticle is formed, during phases of oxidation/reduction that are crucial for the cyclability and safety of the whole battery.

KeyWords: XANES, Scanning Electron Microscopy, Raman Spectroscopy, Al2O3 Coat

- P·07 –

Charge density wave and framework instabilities in monophosphate tungsten bronzes

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In the broad field of the low dimensional metals, peculiar electronic phases, such as superconductivity, charge and spin density waves (C-SDW), are investigated. More specifically, the complete understanding of the transition from the high-temperature phase to the CDW one is still a controversial object of study. In this regard, the monophosphate tungsten bronze is a family of oxides, $(PO_2)_4(WO_3)_{2m}$, where the electronic, magnetic properties can be tune by *m* and each member shows a CDW instability with different characteristics [1]. The structure is composed by empty perovskite slabs separated by a monolayer of phosphates. The thickness of the slab, linked to the *m* index, defines the sequence of charge density wave phases that appear on cooling. The instability of the system can be explained with the superposition of a structural one, given by the empty-perovskite-like structure, to an electronic one. Three different members are studied in order to explain the family behaviour. The member m=2, which presents a quasi-1D instability due to its peculiar structure, a single zig-zag chain of WO₆ surrounded by the phosphates. Two higher members which present a more difficult case: m=6 and 8. For these members, the origin of the instability comes from the WO₆ slabs framework, realised as correlated displacements of tungsten atoms along the octahedral 4-fold axis direction (W-O-W-O direction).

The instabilities and their origin can be studied thanks to the combination of diffuse scattering (DS), inelastic x-ray scattering (IXS) and *ab-initio* calculations. The DS technique allows a fast localisation of the regions of interest, since it can explore a vast angular region of the reciprocal space. The results can be further analysed through IXS, which allows identification of the origin of the diffuse pattern, namely elastic, inelastic, quasi-elastic or the combination of those. As example, the structural instability of the member m=8 can be seen in the diffuse maps as strong planes, see figure 1. The diffuse patterns are linked to relatively soft phonons modes, which were studied through IXS [2].



Figure 1. 3D DS reconstruction at RT for the high-phase of the member m=8: a) layer parallel to HK0 plane and b) layer parallel to H0L plane. The visible diffuse planes are related to the structural instability of the perovskite-like structure.

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- P·08 -

New internally heated diamond anvil cell for fast heating and cooling rates at high pressure

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Nowadays, fast heating and cooling rates (in milliseconds or even less) at static high pressure (HP) is possible using pulsed laser heated diamond anvil cells (DAC). However, such devices are usually employed for measurements above 1000K [1]. High temperature (HT) experiments with diamond anvil cells in the moderate temperature range (up to 1500 K) are usually realized using internal or external resistive heaters [2]. However, most of these heaters were designed for relatively slow heating ramps [2], and not suitable for performing fast heating cycles due to the possible instability of complex heating assembly at HT.



Figure 1. Example of XAS data measured at 300K and 1200 K by using the internally heated DAC loaded with a Ge sample. The well known shape change and red shift of the absorption edge shows successful melting of Ge at 3.5 GPa.

Recently, we developed a new HT diamond anvil cell allowing for combined x-ray absorption (XAS) and diffraction measurements (XRD) in a wide range of temperature and pressures [3]. The cell is resistively heated by using a self-heating gasket, and allows fast heating and cooling rates at HP, thus suitable for studying melting/crystallization dynamics when coupled with time resolved XAS setup (second and sub-second ranges). The temperature and its distribution inside the sample are evaluated by analyzing the black-body radiation signal, showing negligible temperature gradients. Initial test measurements were carried out recently on elemental Germanium using the available setup at the ODE (dispersive EXAFS) beamline of synchrotron SOLEIL [4,5]. Results show successful fast monitoring of melting (see Fig. 1) and crystallization of Ge at several pressure points up to 15 GPa.

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- P·09 -

Collapse of itinerant ferromagnetism in CoS₂ under pressure: an x-ray absorption spectroscopy study

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Cobalt L-edge x-ray absorption spectra (XAS) and x-ray magnetic circular dichroism (XMCD) of CoS_2 have been measured at low temperature (4 K) in order to characterize the electronic and magnetic structure with a significant improvement in resolution as compared with previous measurements. The branching ratio of L₃ and L₂ x-ray absorption near-edge spectra was found to be consistent with a low-spin configuration (S=1/2). A total magnetic moment $\langle m \rangle = 0.78 \mu B/Co$ atom with the orbital part $\langle m \rangle = 0.049 \mu B$ has been obtained from the XMCD signal, consistent with the nearly half-metallic character of CoS_2 and with the itinerant nature of the ferromagnetism. The behavior under pressure of CoS_2 was studied by Co K-edge XAS and XMCD experiments performed up to a pressure of about 30 GPa using diamond-anvil cell at a temperature of 10 K. No evidence of structural phase transition was observed, while the intensity of the XMCD signal was found to decrease continuously for increasing pressures, becoming negligible in the 8~10 GPa pressure range, a fact consistent with the collapse of itinerant ferromagnetic ordering. The gradual change in the electronic and magnetic structure upon application of pressure was also monitored by the near-edge XAS evolution, found to be in agreement with full multiple-scattering calculations under uniform contraction of distances, and by the blue-shift of the K-edge energy. The Co K-edge energy was found to shift to higher energies (up to 0.64 eV at 30 GPa) and a change of slope was observed at pressures around 5 GPa that may correspond to the disappearance of half-metallicity, in agreement with previous studies.



Figure 1. Pressure dependent XMCD spectra are shown for increasing pressure. The data of totally suppressed XMCD signal after 10 GPa are not given. The topmost XAS recorded at ambient pressure is shown for comparison.

- P·10 -

X-ray probing of surface anchoring in films of bent-core liquid crystals

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Bent-core mesogens (BCMs) are a class of thermotropic liquid crystals (LCs) characterized by a nonlinear shape and exhibiting a wide range of unconventional properties [1]. In particular, their bent shape and transverse molecular dipole result in a marked predisposition to stratification. This tendency strongly favours the formation, throughout the nematic (N) phase, of nanosized clusters featuring smectic (Sm)-like positional order and biaxial (and polar) orientational order (cybotactic order) [2]. Consequently, these materials are among the most promising candidates in the quest for the much sought-after biaxial [3] and ferroelectric [4,5] N phases.

Unfortunately, BCMs also exhibit unusual anchoring properties which result in a difficult control of the molecular director by conventional surface treatments, hampering the study and possible applications of these materials. For conventional rod-like LCs, the molecular orientation is efficiently controlled by treating the confining surfaces with specific alignment agents (*e.g.* surfactants, rubbed polyimide films, oblique SiO_x deposition). Despite the nanoscale mechanism is not always fully understood, these treatments allow a very fine control of the surface anchoring. Unfortunately, aligning BCMs with conventional approaches has proved quite difficult and also when a uniform alignment is obtained, its nature is often unclear, making the interpretation of the experimental results ambiguous [6,7].

Here we present a systematic study of the alignment of BCMs (fig. 1a) on different solid substrates under different alignment agents, spanning from ultra-thin films prepared using the Langmuir-Blodgett technique, to spin-coated thicker films $(10^{1}-10^{2} \text{ nm})$. The challenging investigation of BCMs' surface anchoring was performed by a combination of grazing-incidence wide-angle X-ray scattering (GIWAXS) (fig. 1b) and X-ray reflectometry (XRR) (fig. 1c), a powerful experimental approach to investigate both in-plane and in-depth molecular order in LC films.



Figure 1. (a) Molecular structure of the investigated BCM. (b) Cartoon of the GIWAXS experimental set-up with the corresponding pattern: the green arrow represents the incident X-ray beam at the grazing angle μ . (c) XRR data and corresponding fit for a thin LC film deposited on a silicon substrate. The inset shows the corresponding molecular bilayer structure.

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High Pressure Intrusion of Electrolyte Aqueous Solution into Si-LTA Zeolite

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Heterogeneous lyophobic systems (HLSs) are obtained through the intrusion of a non-wetting liquid -forced using high pressure- into a porous hydrophobic material. This implicates a transformation of the applied mechanical energy into the interface one. When the pressure is released, the system can induce the expulsion of the liquid out of the pores (extrusion), thus restoring the initial energy. In dependence on the material/liquid system [1], and on how the system behaves when pressure is released, the energy can be completely restored, dissipated or absorbed, and thus the system displays a spring, shock-absorber, or bumper behavior, respectively.

In the last decades, many works explored the energetic performances of HLSs based on hydrophobic pure silica zeolites intruded by water [2]. These materials show a huge variety of framework-types (different pore systems, and sizes) guarantying to potentially design a multitude of devises displaying different energetic behaviors, and thus exploitable in many fields. Recent researches indicate the use of electrolyte aqueous solutions instead of water to improve the performances of Si-zeolites heterogeneous lyophobic systems. In fact, higher values of the intrusion pressure can be achieved, and therefore higher stored energy. Once all silica chabazite is intruded by NaBr electrolyte aqueous solution (2M) the intrusion pressure increases almost twice in comparison to what found for water intrusion. Pressure increases even more using NaCl or CaCl₂ 2M or 3M aqueous solutions [3].

Due to these reasons, we decided to investigate the behavior of the pure silica zeolite LTA using the same electrolyte aqueous solution as non-wetting liquid (NaCl and $CaCl_2 2M$) in order to understand the framework-type influence on the intrusion.

Investigations were performed by means of porosimetry and X-Ray Powder Diffraction (XRPD) *in situ* during intrusion/extrusion cycles, with the aim to unravel the nature of the intruded species and their interactions with the zeolitic framework. Diffraction patterns were obtained from ambient pressure to 1.19 GPa for the system Si-LTA/NaCl 2M, and up to 2.15 GPa in the case of Si-LTA/CaCl₂ 2M. After pressure release, it was possible to acquire data only for Si-LTA/CaCl₂ 2M.

In both systems, the cell volume variation show a plateau after a first stage of compression, even if at two different pressures. In general, Si-LTA/NaCl 2M shows a higher compressibility, when compared to Si-LTA/CaCl₂ 2M. Cell volume variations were structurally interpreted on the basis of the extraframework/zeolite interactions. In both systems, both ions and H_2O molecules penetrated the zeolite porosities showing a similar evolution of the extra-framework intruded volume. This suggests that the different evolution of the cell parameters is mostly influenced by the different type, number and arrangement of the extraframework species rather than by their total volume. Despite chlorine ions are placed in the same position in both systems, with similar number and length of the bond distances with the framework, they interact differently with the cations. Indeed, in Si-LTA/NaCl 2M, the ions are not bonded each other, but are solvated, similarly to the initial aqueous solution. Instead, in Si-LTA/CaCl₂ 2M calcium and chlorine ions are at a bond distance of 2.8 Å, forming salt molecules. Our results confirm that nature and arrangement of the extraframework species and their interactions as a function of pressure strongly influence the cell parameter modifications.

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Structural characterization of Ga-Ferrierite, combining synchrotron high pressure XRPD and XAS experiments

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Among the many outstanding properties of zeolites, their catalytic activity is one of the most exploited in the industrial field and the number of reactions catalyzed by them has been extended. The future applications of zeolite catalysts could address to the synthesis of fuel from renewable biomass, in order to both increase the energy sources availability and contemporary to decrease the CO_2 emissions.

In particular, gallium-containing zeolites have been extensively investigated as they show unique catalytic performances in light hydrocarbon aromatization.

The impregnation or ion-exchange processes are the methods usually adopted to introduce gallium into both tetrahedrally coordinated framework (giving rise to Brønsted acidic sites) and extra-framework positions (determining the presence of Lewis acid sites) which can work separately or in a synergic way. Due to its size, gallium in framework positions is metastable; hence, any physical or mechanical treatment such as thermal treatment or impose pressure can cause the migration of Ga^{3+} to extraframework positions and its progressive aggregation in the form of isolated, dimeric and polymeric species up to oxide nanoparticles [1-3]. According to this, gallium migration leads to the appearance of a different type of Lewis acid sites [4].

The mobility of Brønsted and Lewis acid sites due to proton transfer mediated by the water molecules could improve the catalyst performances and has been already investigated in the past [5] but it still debated. The application of pressure can mechanically control the introduction of water molecules in the channel of zeolite as well as reversibly modify and control its chemistry [6].

In order to get a better understanding of the behavior of zeolites under pressure conditions, we have conducted Synchrotron X-ray powder diffraction (XRPD) and X-ray absorption spectroscopy (EXAFS) experiments at the Ga K-edge both at ambient condition and high pressure (using a penetrating transmitting media such as methanol: ethanol: water (16:2:1) mixture).

The investigated sample was a ferrierite zeolite exchanged with gallium (Ga-Ferr) and the aims of the study were :

- i) The detection and quantification of Ga⁺³ cations in framework and non-framework positions
- ii) The migration of Ga atoms to extraframework position and their progressive aggregation
- iii) The reversibility of the pressure-induced hydration (PIH) effect

The diffraction data collected at ambient condition highlighted the presence of gallium in two different extraframework position and its successful incorporation in the tetrahedral sites, as well as the minor presence (3.8 %) of GaO(OH). As a consequence, the structure of Ga-Ferr was determined by a two-phases Rietveld refinement in the *Immm* space group. The EXAFS refinement conducted on the first shell confirmed the presence of Ga^{+3} in the zeolite framework.

The high pressure XRPD and EXAFS experiments (data analysis currently in progress), have been performed from P-amb up to 5GPa upstroke and down stroke. A two phase LeBail fit was performed in the whole P range in the *Immm* space group, ruling out any P-induced phase transition and the almost completely reversibility of P-induced effects ; in fact, the features of the ambient-pressure pattern (Pamb) and the unit cell parameters are rather well recovered upon P release. The decrease of the volume cell up to 5 GPa is $\Delta V = -4\%$.

On the contrary, the examination of the spectra collected at the Ga K-edge with increasing pressure, evidenced a shift to higher R values accompanied by an intensity change of the EXAFS oscillations of the first peak of the Fourier transform modulus, related to Ga-O distances, above 4 GPa. The refinements of the EXAFS spectra are in progress and will give us a detailed and complementary comprehension of the Ga behavior.

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- P·13 –

High pressure behavior of the hybrid material AIPO₄-5+azobenzene: an *in situ* synchrotron Xray diffraction study

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The regular pore systems of nanometric openings exhibited by zeolite frameworks make these porous materials ideal host matrices for achieving supramolecular organization of photoactive species, leading to versatile building blocks for the realization of hierarchically organized multifunctional composite materials [1]. Organic/inorganic hybrid materials (like zeolites+colorants) are currently used in strategic areas, from sustainable energy technologies in solar energy harvesting to biomedical sciences. In these systems, photoactive molecules are organized in one-dimensional nanostructures inside the zeolite channels [2]. A recent study [3] has explored the response of these hybrid materials to compression. These investigations are crucial to enhance the application range of these materials - pointing out the stability and resilience of the supramolecular organization of dye molecules - and to unravel the effects of pressure on the optical properties of the hyperconfined species in the zeolite channels.

Among zeolites, the ones with AFI topology have been extensively studied with the aim to produce new hybrid materials with optical properties. Several studies [4] demonstrated that, after the incorporation and the linear alignment of dyes into AlPO₄-5 (AFI structure) mono-dimensional channel system, new spectroscopic properties were observed. The results indicated laser action in the system with properties tunable over a wide range.

In a previous work [5], the structural characterization of the composite material $AIPO_4$ -5+azobenzene dye has been performed (Figure 1), pointing out that, being $AIPO_4$ -5 starting material affected by Brönsted acidity, a consistent portion of the azobenzene molecules is protonated and interacts with the framework oxygen atoms.

In the present work, the high pressure-behavior of the same hybrid material has been studied by in situ synchrotron X-ray diffraction experiments, using both penetrating (methanol-ethanol-water mixture) and non-penetrating (silicon oil) pressure transmitting media, inside a diamond anvil cell.

The structural response of the hybrid system to compression has been compared to the behavior of the starting $AIPO_4$ -5 material, to evaluate the stability of the hybrid and the evolution of its optical properties, and to underline how the presence of azobenzene dye within the zeolite channels influences the compressibility of the $AIPO_4$ -5 phase.



Figure 1. - Azobenzene molecule inside the 12MR channel of AlPO₄-5.

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- P·14 –

A new vision of kinetic processes in geosciences: 3D and in situ 4D X-ray microtomography

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X-ray computed microtomography (μ -CT) has become an invaluable technique for geologists, with wide applications in various geological disciplines. X-ray μ -CT is a non-destructive technique and it is based on both conventional and synchrotron radiation sources (Baker et al., 2012a). This technique produces three-dimensional (3D) images of the internal structure of objects, determined by variations in morphology, mass density and/or chemical composition. It is a powerful tool for 3D investigation of several geological materials with spatial resolution at the micro- and submicron- scale. Furthermore, the morphology of unique and precious samples (such as fossils) can be investigated in a non-destructive way. The possibility to visualize and measure textural features of rocks in 3D is important for understanding and quantifying geological processes.

The past decade has witnessed significant advances in the *in situ* X-ray microtomography technique at high pressure and temperature (HP and HT) conditions. Nowadays, *in situ* experiments can be performed by combining a HP and/or HT apparatus with fast synchrotron X-ray microtomography (Baker et al., 2012b; Philippe et al. 2016; Prasek et al., 2018). Therefore, it is now routinely possible to characterize material and study kinetic processes under high temperature conditions (from ambient pressure to 1 GPa) with rapid acquisition times for tomograms (Prasek et al., 2018; Polacci et al., 2018). This provides direct visualization of rapidly evolving processes in disequilibrium systems, such as flowing liquids, degassing and bubble growth (Baker et al., 2012; Plese et al. 2018). Particularly, crystallisation and crystal dissolution kinetics can be revealed by *in situ* high temperature X-ray microtomography (Polacci et al. 2018).

The use of synchrotron radiation X-ray imaging in geosciences allows us to collect data with high spatial resolution, enabling highly precise quantitative analyses in rocks. X-ray phase-contrast imaging can also improve the visualization of features with small differences in mass density and chemical composition with respect to the rock matrix, so this technique is important for the analysis of multiphase geological samples.

This contribution provides an introduction to the principles of X-ray μ -CT and several examples of geologic processes studied in 3D and *in situ* 4D approaches. Furthermore, different factors affecting the image quality and several image processing methods will be discussed.

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- P·15 –

The evidence of mixing between basalt and rhyolite unraveled by microanalysis and X-ray microtomography

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Magma mixing is a widespread petrogenetic process. It has long been suspected to operate in concert with fractional crystallization and assimilation to produce rheological, chemical and temperature gradients in magmas. In particular, the injection of mafic magmas into felsic magma chambers is widely regarded as a key driver in triggering highly explosive volcanic eruptions. Understanding the mechanistic leading to such hazardous events is a scientific goal of high priority. Here we investigate a mixing event via the evidence preserved in mingled lavas using a combination of X-ray computed microtomographic and electron microprobe analyses, to unravel the complex textures and attendant chemical heterogeneities of the mixed basaltic and rhyolitic eruption of Grizzly Lake in the Norris-Mammoth corridor of the Yellowstone Plateau volcanic field (YVF). We observe evidence that both magmatic viscous interfingering of magmas and disequilibrium crystallization/dissolution processes occur. Furthermore, these processes constrain the timescale of interaction between the two magmatic components prior to their eruption. X-ray microtomography images show variegated textural features, involving vesicle and crystal distributions, filament morphology, the distribution of enclaves, and further textural features otherwise obscured in conventional 2D observations and analyses. The presence of mineral phases in both end member, for example, forsteritic olivine, sanidine, and quartz and their transport throughout the magmatic mass, by a combination of both mixing dynamics and flow imposed by ascent of the magmatic mass and its eruption, might have acted as a "geometric perturbation" of flow fields further fuelling mass exchange between magmas in terms of both chemical diffusion and crystal transfer.

- P·16 -

Earth and Environmental Sciences at LISA

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During the last years, several X-ray absorption spectroscopy (XAS) experiments at LISA beamline, performed by the beamline staff together with the users' community, have dealt with the investigation of mineralogical and environmental issues. Classical crystal-chemical problems such as cation ordering and trace-metal incorporation mechanisms as well as oxygen fugacity conditions during rocks and minerals crystallization have been addressed [1-4]. Specific attention has been also paid to the study of geomaterials with technological implications [5-7].

A number of works discussed the environmental implications of the presence of toxic elements and hazardous materials in sensitive matrices and their effects on the environment and on human health [8-11]. The users' community has indeed also put interest in the investigation of dust deposits of both natural and anthropogenic origin [12-14].

Several studies already benefited from the characteristics of the recently renewed optic elements of the beamline [15]. A key feature is the high photon flux ($\approx 10^{11}$ ph/s using Si(111) crystals) associated with the availability of SDD [16] and HP-Ge multichannel energy resolved fluorescence detectors, since we often have to deal with very diluted elements, frequently included in quite heavy matrices. The wide energy range attainable at LISA (4-90 KeV), which covers most elements heavier than Ca, allows to perform a great number of studies. X-ray Absorption Near-Edge Structure (XANES) studies, in particular those exploiting pre-edge features, took advantage from the high energy resolution of the Si(311) monochromating crystals. The beam can currently be cut down to a diameter of less than 100 µm with a flux in the range of $\approx 10^{10}$ ph s⁻¹ and a further reduction after ESRF-EBS upgrade is foreseen. The smaller beam size opens the way to the investigation of complex heterogeneous samples in a broad variety of fields.

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Structural investigations of niobium-doped bioactive calcium-phosphate glass-ceramics by means of spectroscopic studies

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Synthetic calcium-phosphate based glasses and glass-ceramics play a crucial role in the development of tissue engineering. These materials have a high biocompatibility with biological analogues, excellent ability to undergo varying degrees of resorbability [1] and due to their non-toxicity and relatively high bioactivity they are commonly used as bone and dental implants. A substantial research effort is devoted to improve synthetic calcium-phosphate materials physico-chemical properties, inter alia tune the degree of crystallinity which is mainly responsible for material solubility. One of the strategies is their doping with metal ions. The results found in the literature show that synthesized CaO-P₂O₅-Nb₂O₅ compounds exhibit a good biocompatibility, very low cytotoxicity in respect to calcium-phosphate doped with other metals and additionally can enhance human osteoblast function [2,3]. Moreover, a really few information on the structure of these materials can be found in the literature. Therefore, the detailed structural investigation by means of spectroscopic studies, *i.e.* infrared absorption spectroscopy, X-ray photoelectron spectroscopy, energy-dispersive X-ray spectroscopy and X-ray absorption fine structure spectroscopy, was realized to shed light on the relationship between structural parameters and dopant contents, preparation technique or sample morphology and porosity.

Set of CaO-P₂O₅-Nb₂O₅ samples with different Ca/(P+Nb) molar ratio and different amount of Nb ions, prepared by meltquenching (MQ) and sol-gel (SG) method, was measured. Fourier transform infrared (FTIR) spectra were collected by using PerkinElmer FT-IR/FIR Spectrometer Frontier in attenuated total reflectance (ATR) mode, X-ray photoelectron spectroscopy (XPS) measurements in the Ca2p, P2p, Nb3d, O1s and C1s energy ranges were realized by Omicron XPS Spectrometer and energy-dispersive X-ray (EDX) microanalysis was performed by using FEI Quanta FEG 250 SEM instrument with EDS detector. X-ray absorption fine structure (XAFS) Nb K-edge (18986 eV) spectra in XANES and EXAFS (up to 800 eV above the absorption edge) ranges were collected at the ELETTRA synchrotron (XAFS beamline) at RT using a transmission geometry. To obtain a detailed structural information about local niobium environment in the samples EXAFS data were analysed using the GNXAS software package [4,5]. Spectra of reference samples (like pure and commercial calcium phosphate compounds with various Ca/P molar ratio, niobium dioxide and niobium pentoxide) were also measured and analysed to construct proper model for data elaboration.

In this work, we show the results obtained for bioactive glass-ceramics with Ca/(P+Nb) molar ratio equal to 1.0 and with relative Nb contents reaching value up to 10 mol% of P ions. It should be emphasized that XANES spectra of all samples, independently on the synthesis method and Nb contents, are quite identical. Detailed EXAFS analysis show that in all samples octahedral coordination of niobium ions dominates (like in niobium pentoxide). This result was confirmed by XPS analysis, which showed that on the sample surface the contribution of Nb⁺⁵ ions can be even ten times greater than Nb⁺⁴ ions. Moreover, all samples exhibited calcium deficiency on the grains surface. On the other hand, in MQ powders niobium was rather homogeneously distributed over the grain volume and in SG samples accumulation of Nb on the grain surface was observed. Additionally, an increasing absolute niobium amount led to the more disordered Nb local structure. Subtle changes in niobium oxide sub-network continuity as a function of materials stoichiometry were also detected. To define the relationship between structural parameters and sample morphology, porosity and nanocrystallinity, the obtained results were combined with the data of X-ray diffraction patterns analysis, BET surface area measurements and SEM imaging.

We gratefully acknowledge the support of the SLL ELETTRA in providing synchrotron radiation facilities (XASF11.1 station) for 20160241 experiment.

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Mechanistic Study of the Nucleation and Conformational Changes of Polyamines in Presence of Phosphate Ions

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Polyamine Phosphate Nanoparticles (PANs) have great potential for the delivery of large therapeutics, such as plasmids and/or siRNAs, which can be complexed to positively charged polyamines through electrostatic interactions [1-3]. PANs are formed by a simple and straightforward one-step procedure, involving the mixing of polyamine solutions and phosphate ions. Their assembly is driven by electrostatic and hydrogen bonding interactions between the positively charged amine groups of the polyamines and the negatively charged phosphate ions. The aim of our work is to acquire a deeper insight into the interaction of polyamines and phosphate ions, and into the role that the ionic strength plays in the assembly of polyamines into nanoparticles. To achieve this goal, we evaluate the impact of the phosphate ion concentration and the ionic strength on the formation and growth of PANs using dynamic light scattering (DLS) and transmission electron microscopy (TEM) imaging; two techniques that provide valuable information on the changes in hydrodynamic diameter and size of PANs. We further use isothermal titration calorimetry (ITC) to elucidate the nature of the forces driving to PAN assembly. We perform synchrotron Small Angle X-ray Scattering (SAXS) experiments to investigate the association of polyamines with phosphate ions. SAXS allows us to trace the formation of the PANs at low phosphate concentrations, which are not detectable by DLS, and to study the nucleation process between phosphates and polyamines that leads to the generation of self-assembled nanoparticles, Figure 1. From Transmission Electron Microscopy (TEM) and Dynamic Light Scattering (DLS) the critical PB concentration for PANs formation was determined. Below this critical point, Small Angle X-ray Scattering (SAXS) studies revealed that small PAH-phosphate aggregates coexist with not complexed or weakly complexed polymer chains in solution and that the presence of the phosphate ions increases the Kuhn length of the polymer chains until that only spherical aggregates are present in solution. TEM, DLS and SAXS showed the increase of PANs size with ionic strength up to 250 mM NaCl. At higher NaCl concentrations, PANs disassemble into smaller aggregates. Isothermal Titration Calorimetry (ITC) showed that PAN formation is an exothermic process and the association of phosphates below the critical PB concentration is entropically controlled. The deeper understanding gained from this work into the mechanism of PANs assembly is a fundamental step toward optimizing these promising candidates as drug delivery vehicles.



Figure 1. Schematic illustration of PAN preparation in presence of phosphate ions, $[H_{(3-x)}PO_4^{-x}]$. In the sketch, single PAH chains are shown linked by the phosphate ions interacting with the amine groups of PAH. The size of the PANs increases as the concentration of $[H_{(3-x)}PO_4^{-x}]$ increases.

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- P·19 –

Sub and supramolecular investigation of the impact of tissue engineering's protocols on equine type-I collagen structural features

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The goal of scaffolds fabrication in tissue engineering is to mimic the microenvironment architecture of natural tissues, mainly composed by extracellular matrix (ECM). This network of fibrous intertwined with non-fibrous proteins guarantees biomechanical support to tissue growth. Type-I collagen is most representative protein of the connectives and, because of its characteristic hierarchical organization, confers toughness to the tissues. Moreover, due to its biocompatibility, type I collagen is commonly employed as anchorage biomaterial for cells in scaffolds fabrication, and it can be extracted by different species, i.e. bovine, equine and fish, and tissues, i.e. dermis, tendons and scales. X rays techniques are suitable for the investigation at sub and supramolecular scales of type I collagen in natural tissues, also providing helpful information about the modified structure in pathologies [1], such as corneal keratoconus [2]. In particular, Wide Angle X ray Scattering (WAXS) is useful to study the correlation among fabrication protocols, collagen's features at the atomic scale and biomechanical properties of collagen-based devices [3]. In order to evaluate the impact of extraction and fabrication methods on collagen at sub and supramolecular scale and the suitability for the regeneration of different tissues, chemiphysical studies have been performed on films made of equine tendons collagens, chemically and enzymatically extracted, and manufactured through two fabrication protocols: 1) dissolution in acetic acid (AA); 2) dissolution in acetic acid and homogenization (OMO). Physical crosslinking treatment (DHT) was also applied to increase films stability. Structural analysis by Wide Angle (WAXS) and Small Angle (SAXS) X-ray Scattering were carried out at the XMI L@b (CNR-IC-Bari), where a table-top synchrotron class X-ray microsource is available [4]; Fourier Transform-IR (FT-IR) and tensile tests were performed at UniSalento. WAXS and SAXS analyses revealed a preferential orientation of molecules in the raw collagen, regardless the extraction method. However, the chemical treatment allows to extract a more hierarchically organized collagen than the enzymatic one. Concerning films, the combination of X rays and FT-IR analyses highlights the effects of fabrication protocols on collagens molecules showing that each production step affects the extent of crystalline and nano domain and the lateral packing of collagen fibrils. In particular, it was observed the organization of a high % of smaller triple helices within a lower crystalline domain when films are obtained by the most aggressive processing (OMO), while tensile tests proved that the chemical fabrication protocol (AA) is the one that enhances both mechanical stiffness and supramolecular fiber organization of the films. Furthermore, in hierarchically organized collagens, nanoscale architecture act as a shield through which the fibrils organization protects the atomic scale structure from fabrication protocols effects (shield effect).

The present work shed light on the influence of the extraction and manufacturing protocols on collagen's sub and supramolecular structure, suggesting how to tune the biomaterial for the request characteristics by choosing the proper protocol for the starting material. These studies may represent a useful basis for the future optimization of collagen-basedh scaffolds for tissue engineering applications.

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- P·20 -

Brain and brain vessel X-ray synchrotron microbeams and microtomography for Chronic Pain studies and treatments

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Synchrotrons are the most powerful means currently in use, allowing for microtomographic reconstructions of biological materials in the field of bio-medicine. Concurrently, the extreme flexibility of X-ray modulation for tissue irradiation allows for planning of complex irradiation grid designs in oncological therapeutics with high rates of tissue sparing thanks to the use of microbeam and beamlet special geometric arrangements. Here we present results of microtomographic imaging of brain tissue and brain vessel structures as well as a therapeutic model of chronic pain by the use of specially arranged X-ray combs opportunely directed towards specific brain cortex areas in experimental animals. In the first experimental set, micro and nano tomographic imaging has been developed to compare microvessel structures in the somatosensory cortical area both in control and in chronic pain (CP) models. After a complex specific preparation including the injection of an X-ray opaque agent in the circulatory system of deeply anaesthetized rats and the following brain removal, a particular cortex-coring technique was applied to obtain brain sensory cortex cylinders (1.2 mm in length and 550 um diameter) to be analysed by Synchrotron microtomographic imaging focussed on the vessel trees in the two experimental conditions. A fourfold increase of neo-generated microvessels and capillaries was observed already at onetwo weeks after the generation of the chronic pain model (Figure 1A). This surge of neogenic vessels slightly faded in the next six months, yet persisting some trait of increase in the overall microvasculature density. In the second experimental set, our aim was the identification of potential novel therapeutic strategies in chronic pain, in line with our theoretic assumption [1] that CP has to be considered as a syndrome of abnormal connectivity on the somatosensory thalamocortical axis. Similarly to previous studies on epilepsy [2], we modulated the synchrotron generated X-ray microbeams to resect a significant portion of the cortical horizontal connectivity in the putative cortical region by 7 microbeams of 100 um width (Figure 1B) on primary somatosensory cortex of experimental rats with a CP model. After irradiation, the animals did not show any behavioral and electrophysiological sign of CP indicating that protocol effectively removed the abnormal hyperconnectivity supporting the typical dynamics observed in [1]. Therefore, the X-ray microbeams could provide translational insights for an innovative therapy of CP.



Figure 1. (A) Comparison of the neoangiogenesis and its fading chronic pain model (0.325 um of resolution) (B) Microtomographic imaging of microbeam sensory cortical transactions

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- P·21 –

Revisiting the probing depths of soft x-ray absorption techniques by Constant Initial State photoemission experiments

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An important parameter for correct usage and understanding of soft x-ray techniques is the probing depth, which is naturally limited by the energy of the probe (electrons or photons). For example, widely used techniques for soft x-ray absorption experiments such as total electron yield (TEY) and total fluorescence yield (TFY) can be used as surface-sensitive probes due to the limited ranges of emitted electron and photons at the typical energies under consideration.

Although those techniques have been exploited for many years, some confusion about the actual probing depths of the experiments persists, with scattered values differing up to one order of magnitude in the literature depending on the techniques and materials of choice [1,2]. For example, effective probing depths in the 2-10 nm and 70-200 nm have been used in a recent experiment for the interpretation of TEY and TFY spectra aimed at studying the evolution of the solid electrolyte interface in Li-ion battery electrodes [3]. Clearly, deeper understanding of the surface and interface properties could be obtained by using more precise estimates of the probing depths in different materials and in the typical energy ranges of the soft x-ray technique.

The CNR-IOM BEAR (Bending for Emission Absorption and Reflectivity) beamline at the Elettra synchrotron radiation facility[4] offers a wide range of available techniques for performance of accurate photoemission and photoabsorption experiments in the typical range 30-1800 eV for the photon beam. We have recently performed accurate constant initial state (CIS) photoemission experiments on selected samples at variable photon energy, within the framework of a larger research project aimed to obtain accurate and reliable measurements of the photoelectron mean free path at variable kinetic energy and ultimately of the probing depth of the TEY and TFY techniques. Investigated samples consisted in Al films covered with layers of Ge of variable thickness. The intensity decay of the main Al photoemission peaks was measured as a function of the kinetic energy of the photoelectron and of different Ge overlayer thickness. The mean free path curve has been measured in a wide kinetic energy range 30-1000 eV and compared with previous determinations using various techniques.

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105

- P·22 –

A Coherent Imaging XUV-FEL users end-station for the EuPRAXIA@SPARC_LAB Free Electron Laser

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A proposal for building a Free Electron Laser, EuPRAXIA@SPARC LAB, at the Laboratori Nazionali di Frascati, is at present under consideration [1]. This FEL facility will exploit plasma acceleration to produce ultra-bright photon pulses with durations of few femtoseconds down to a wavelength between 2 and 4 nm, in the so called "water window". The project is now focused on machine development, but it will host a user end-station to allow performing photon experiments in different areas [2]. The advent of FELs opened up the way for an unprecedented, wide class of experiments exploiting the peculiar features of these radiation sources. Key elements are the high peak brilliance and the short pulse duration, which is of the order of tens of femtoseconds. FELs can therefore allow high time resolution measurements and may provide a high signal-to-noise ratio. The main class of experiments that will be performed at the EuPRAXIA@SPARC_LAB FEL will include coherent diffraction imaging, soft X-ray absorption spectroscopy, Raman and photofragmentation measurements (Figure 1). These techniques will allow studying a variety of samples, both biological and inorganic, providing information about their structure and dynamical behavior. In this context, the possibility of inducing changes in samples via pump pulses leading to the stimulation of chemical reactions or the generation of coherent excitations would tremendously benefit from pulses in the soft X-ray region. High power synchronized optical lasers and a THz radiation source will indeed be made available for THz and pump-probe experiments. In order to perform the widest possible class of experiments, from coherent imaging, to diffraction and spectroscopy, emission, absorption, a top class experimental end-station, including a dedicated section with beam diagnostics and focusing devices and a highly flexible experimental chamber will be built [3].



Figure 1. A simplified layout of the experiments that will be performed at the EuPRAXIA@SPARC_LAB FEL

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- P·23 –

A photon beamline for the water window FEL at EuPRAXIA@SPARC_LAB

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A proposal for building a Free Electron Laser, EuPRAXIA@SPARC_LAB, at the Laboratori Nazionali di Frascati, is at present under consideration [1]. This FEL facility will exploit plasma acceleration to produce ultra-bright photon pulses with durations of few femtoseconds down to a wavelength between 2 and 4 nm, in the so called "water window".

The photon beamline we designed will deliver the photon beam from the undulators to the experimental area, optimizing the beam for the running experiment to allow a fine tune of the beam characteristics. The FEL radiation will be in SASE regime, at least for the first phase of the project, so it will present shot-to-shot fluctuations in intensity, spectrum and position. The radiation diagnostics are therefore chosen to be single-shot and not-intercepting whenever possible. The beam will be characterized by measuring its dimensions, coherence and positions both in transverse and longitudinal directions, its spectrum and its intensity. The main class of experiments that will be performed at the EuPRAXIA@SPARC_LAB FEL will include coherent diffraction imaging, soft X-ray absorption spectroscopy, Raman and photofragmentation measurements [2].

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- P·24 –

Generation of Coherent Sub-Picosecond THz Transition Radiation in Parasitic Mode to a Free Electron Laser

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We demonstrate that emission of coherent transition radiation by a ~1 GeV energy-electron beam passing through an Al foil is enhanced, both in intensity and frequency components, by the energy correlation established along the beam by coherent synchrotron radiation wakefield, in the presence of a proper electron optics in the beam delivery system. Analytical and numerical models, based on experimental electron beam parameters collected at the FERMI free electron laser (FEL), predict transition radiation with two intensity peaks at ~0.3 THz and ~1.5 THz, and extending up to 8.5 THz with intensity above 20 dB w.r.t. the main peak. Up to 80- μ J pulse energy integrated over the full bandwidth 0.01–10 THz is expected at the source, and in agreement with experimental pulse energy measurements. By virtue of its implementation in an FEL beam dump line, this work promises dissemination of user-oriented multi-THz beamlines parasitic and self-synchronized to EUV and x-ray FELs.



Figure 1. (a) Simulated electron bunch current profiles. (b) Calculated CTR spectra. CTR pulse energy integrated over the frequency range 0.01–10 THz and calculated from the above current profiles. Dots with error bars: measured pulse energy.

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Simple and Robust Free-Electron Laser Doubler for Full Control of Two-Pulse Two-color FEL operation

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We present the design of a Free-Electron Laser (FEL) doubler suitable for the simultaneous operation of two FEL lines, either in self-amplified spontaneous emission or externally seeded configuration. The doubler relies on the physical selection of two longitudinal portions (beamlets) of a single electron bunch at low energy, and on their spatial separa-tion at high energy. Since the two beamlets are naturally synchronized, FEL pump-FEL probe experiments are enabled when the two photon pulses are sent to the same experimental station. The proposed solution offers improved flexibility of operation compared with existing or designed two-pulse, two-color FEL schemes, as it allows independent control and continuous tuneability of the color, timing, intensity and angle of incidence of the radiation pulses at the user end station. Detailed numerical simulations demonstrate its feasibility at the FERMI FEL facility.



Figure 1. FEL doubler (not to scale): selection of electron beamlets in BC1 with a mask (red slices), and separation in the switchyard (SW) with a septum magnet.

A novel beamline for advanced photoelectron spectroscopy with narrowband extreme ultraviolet high harmonics at variable high repetition rate

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Spectroscopy in the femtosecond time domain can both reveal fundamental insight in the properties of materials and provide relevant experimental tests for functional systems. The quest for sources of ultrashort photon pulses (~100 fs) in the Extreme Ultraviolet (EUV) region operating with an adjustable repetition rate up to the MHz range has led, in this last years, to the development of high harmonic generation (HHG) coherent sources based on table-top lasers [1,2]. In particular, a comprehensive characterization of the photoelectron final state in ordered solids requires measurement, with a sub-picosecond time resolution, of energy, momentum and spin-polarization of the photo-emitted current, with an energy and a momentum resolution comparable to those achieved using advanced synchrotron radiation sources. The possibility to choose the optimal repetition rate for a given experiment (up to 200 kHz, or lower) makes it possible to explore a wide excitation-fluence range in pump-probe experiments, minimizing sample heating when relevant.

We have built and characterized a versatile twin-beamline for advanced pump-probe experiments based on a table-top laser HHG source operating in the EUV range up to 200 kHz repetition rate. The beamline is able to provide 10^{12} photons/sec in the range 15-35 eV, and 10^9 photons/sec up to 75 eV, with variable repetition rate, allowing one to measure shallow core level photoemission spectra in combination with valence band ones.

In the poster I will present in detail our experimental setup and show our latest results concerning EUV pulse generation (time duration specification, HHG conversion efficiency, thermal effects) and discuss the most challenging aspects we faced during the experimental work.

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- P·27 -

Developing new beamline instrumentation at LISA.

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LISA (Linea Italiana per la Spettroscopia di Assorbimento di raggi X) is the new Italian Collaborating Research Group (CRG) beamline now operative at the European Synchrotron Radiation Facility (ESRF) [1]. The optical layout consists in a cylindrical collimating mirror, a fixed-exit, Energy-scanning double crystal monochromator, manufactured by strumenti scientifici CINEL S.r.L., and a second toroidal focusing mirror. The new optical configuration allows to cover a very wide Energy range, $4 \le 90$ keV, and provides a high flux of $10^{10} - 10^{11}$ ph/s (depending on the Si crystal pair: either 111 or 311), on a small beam spot, $< 200*200 \ \mu\text{m}^2$ FWHM. The beamline has two experimental hutches: the first one, EH1, located just after the optic hutch, is used for experiments with unfocused beam, such as XAS in transmission mode; the second one, EH2, centered at the focal spot of the second mirror, is dedicated to experiments needing the highflux focused monochromatic beam, such as XAS in fluorescence mode. To this purpose LISA is equipped with 3 energy resolved fluorescence detectors: two multi-element HpGe and one 4-channels SDD.

In this contribution we provide an overall description of LISA and we report about the tests of some beamline instrumentation carried out in collaboration with industrial partners. We present a new Multi Channel Analyzer (MCA) for the signal readout from the fluorescence detectors of the beamline, the new V1782 CAEN Octal 32k digital MCA, designed for high energy resolution semiconductor detectors, which integrates an advanced firmware algorithm for the processing of any kind of exponential signal or coming from charge sensitive preamplifier. This algorithm includes advanced tools for the baseline restoration and pile-up rejection. Furthermore, we describe the integration on the beamline of the BEST (Beamline Enhanced Stabilization Technology) feedback system, manufactured by CAEN ELS and distributed by S.RI. Tech, which is a powerful suite of tools conceived to control and stabilize the incoming photon beam position and intensity as well as to provide real-time powerful beam diagnostics data. The architecture of the BEST system relies on three main building blocks [2]:

- THE EYE: a digitizing master readout/input unit that can be either a TetrAMM (a 4-way fast picoammeter with high sampling speed that can be connected to a phBPM (photon Beam Position Monitor) or to an intensity monitor, such as a ionization chamber or a pin-diode) or an ENCbox (a dual input monitor that can read in real time either relative (quadrature) or absolute (BISS-C) encoders)
- THE MIND: a control and interface unit which reads the signal from the master readout/input and calculates the • necessary corrections to stabilize the beam intensity and position
- THE ARM: an output device, called PreDAC, which receives the correction/compensation digital data given by the BEST control and interface unit and drives the beamline optics.
- the cross check: the full deployment of a BEST system allows reading in parallel a further readout/input unit (slave) that can be used for an independent sanity cross-check of the beam characteristic with and without the feedback being active.

These cases represent a noticeable example of the fruitful collaboration between Italian industry and LISA.

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- P·28 –

The design of research infrastructures

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The framework programme for research and innovation, Horizon 2020, has foreseen a budget of 2,26 billions of euros for the enhancement and the promotion of European scientific infrastructures, recognising their importance as essential tool for enhancing the quality of scientific research and competitiveness in Europe. Research infrastructures are defined as facilities, resources or services used by researchers or companies for doing scientific research or enhancing knowledge and innovation in a specific area. Research infrastructures can be great equipment, data archives, electronic devices or other kind of structures. They can be precisely located, distributed in space or virtually defined: regardless their nature, a research infrastructure is an excellence for knowledge and innovation.

Nowadays all the most developed Countries make a huge investment in research infrastructures, being aware that such a big effort, in terms of cost, is widely justified, representing a driving tool not only for fundamental science but also for the industrial and technologic development - public of private - necessary to keep high levels of competitiveness at international level.

These infrastructures represent also the core of an advanced multidisciplinary research centre, able to encourage research in the fields of biotechnology, environment depollution, imaging, medical and science applications.

Ecourbanlab, Research Laboratory of DADU - Department of Architecture, design and urban planning, University of Sassari, directed by Prof. Massimo Faiferri, has been focusing for years on this topic, facing the design of great scientific infrastructures not only as functional spaces characterized by strict technologic features but also as spaces conceived according to quality for the well-being of workers and visitors, considering also their relation with the urban context, landscape and environment.

Enhancing the urban role of scientific infrastructures means opening up the space towards the community in order to transfer knowledge to the surrounding territory, providing operators, researchers and companies with a work quality not merely "operating" but also "contextual".

Nowadays it's undeniable how most of International Research centres are not closed places anymore, but they've become rather learning spaces open to the outer space. In this way can be created a direct teaching and a transfer of the results achieved, creating at the same time a social proximity with the territories and the communities able to better understand and accept public investments on great scientific infrastructures, more than many other public constructions more visible.

It's important to underline the need of an interdisciplinary research able to link the technologic dimension of great scientific infrastructures and the aspects related to architecture, urban planning, landscape, territory and design.

Scientific research infrastructures, conceived as a space with defined functional needs, but open to accept possible scenarios of implementation and flexibility.

According to this outline, the research group of Ecourbanlab (DADU) collaborates with the "Istituto Nazionale di Fisica Nucleare (INFN), especially with the "Laboratori Nazionali di Frascati", on the project EuPRAXIA *-European Plasma Research Accelerator with eXcellence In Applications-* and the proposal on a new Science Center LNF.



Figure 1. EuSPARC _ urban and architectural design

- P·29 –

V K-edge XANES spectra of V model compounds and V-bearing phosphate glasses: a Full Multiple Scattering study

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We present a systematic study on a set of V-bearing model compounds, representative of the most common V coordination geometries and oxidation states, analysed by means of vanadium K-edge X-ray Absorption Near Edge Spectroscopy (XANES) calculations in the Full Multiple Scattering (FMS) framework. The analysis and the calibration of the free parameters of the theory under the Muffin-Tin approximation (Muffin Tin overlap and interstitial potential) has been carried out by fitting the experimental spectra with the MXAN program [1]. The analysis shows a correlation of the fit parameters with the V coordination geometry and oxidation state [2]. By making use of this correlation it is possible to approach the study of unknown V-bearing compounds with rigorous preliminary information.

As an example we show the V K-edge XANES study of V-bearing phosphate glasses that allowed to obtain information on V oxidation state and coordination geometry even in complex amorphous systems.



Figure 1. Comparison between experimental and theroetical XANES spectra of a ^[4]V⁵⁺ model compound.

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