Società Italiana di Luce di Sincrotrone

Società Italiana di Spettroscopia Neutronica

Secondo convegno congiunto SILS-SISN

XIX Convegno Nazionale SILS ~ XXII Convegno Nazionale SISN

Trieste, 1-3 settembre 2011

Aula magna, sede 'Androna Baciocchi', Università di Trieste

ABSTRACT BOOK

Comitato Scientifico:
A. Balerna, L. Cantù, M. Celli, M. Cianci, G. Cruciani, A. De Francesco, C. Lamberti, R. Magli, C. Mariani, P. Mariani, F. Migliardo, A. Morgante, A. Orecchini, L. Paolasini, S. Turchini

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Final Program

Thursday, 1 September 2011

8:00-9:15	*Registration*
9:15-9:30	**Carlo Mariani (SILS) and Paolo Mariani (SISN)**: *Introductory remarks*
Session 1	
9:30-10:00	**I1 – A. TALEB-IBRAHIMI** (CNRS/Synchrotron SOLEIL, France): "Recent progress on advanced materials by SR based photoelectron Spectroscopy"
10:00-10:15	O1 – L. Paolasini "Giant magnetoelastic interaction in UFe_2"
10:15-10:30	O2 – C. Mazzoli "SCES investigation via X-ray magnetic resonant techniques"
10.30-11.00	*Coffee break*
11:00-11.15	O3 – M. Minola "Magnon dispersion in $(CaCuO2)_n(SrTiO3)_n$ superlattices studied with high resolution Resonant Inelastic X-ray Scattering"
11.15-11.30	O4 - M. Coreno "Photoionization Experiments in the Gas Phase"
11.30-11.45	O5 – A. Verdini "RESPED: a novel tool for novel surface structure studies"
11:45-12.45	**poster session**
12:45-14:00	*lunch*
Session 2	
14.00-14.30	**I2 - D. MORINEAU** (CNRS, Institut de Physique de Rennes, France): "Discotic and calamitic phases in nanotubes"
14.30-14.45	O6 – M. Amati "Oxidation of Supported PtRh Particles: Size and Morphology Effects"
14.45-15.00	O7 – M. Maccarini "Structure and dynamics of PEG coated Au-nanoparticles"
15.00-15.15	O8 – D. Orsi "An XPCS study of heterogeneous dynamics in a 2D gel"
15.15-15.30	O9 – R. Mancinelli "Acqua libera e acque confinate: somiglianze e differenze su varie scale spazio-temporali"
15.30-15.45	O10 – C. Ziparo "Neutron Diffraction Measurement of Molecular Hydrogen Population in Hexagonal Clathrate Hydrates"
15.45-19.30	*Guided tour to Fermi and welcome party at Elettra*

Friday, 2 September 2011

Session 3	
SIMPOSIO Grandi Infrastrutture e presentazioni progetti PiK	
9:00-9:20	C. Rizzuto (Presidente Sincrotrone Trieste)
9:20-9:35	C. Petrillo (delegato FP7 Capacities Research Infrastructure)
9:35-9:50	G. Rossi (delegato ESRFI)

9:50-10:05	E. Puppin (Presidente CNISM)
10.05-10.30	*coffee break*
10.30-10.45	A. Franciosi (Amministratore delegato Sincrotrone Trieste S.C.p.A)
10.45-11.00	L. Paolasini (in rappresentanza di F. Sette, Direttore Generale ESRF)
11.00-12:00	Presentazione Progetti PIK
12:00-13.00	discussione
13:00-14.30	*lunch*
Session 4	
14:30-15:15	**Incontro con responsabili dei CRG neutronica (IN13, BRISP, INES)**
15:15-16:00	**Incontro con responsabili di beam-line di luce di sincrotrone (ESRF, Elettra, Desy)**
16:00-17:30	*coffee break* and **poster session (clip on demand)**
17:30-19:30	Assemblee Generali (separate) SILS e SISN
20:30-23:30	*Social dinner*

Saturday, 3 September 2011

Session 5	
9:00-9:30	**I3 – J. R. HELLIWELL** (Univ. Manchester, UK): "The growth of the importance of synchrotron X-radiation and neutrons in macromolecular crystallography"
9:30-9:45	O11 – M.G. Ortore "Synchrotron SAXS and FTIR experiments monitor the effects of high pressure on α-synuclein amyloid fibrils"
9:45-10:00	O12 – L. Cantù "Nanoscale structural response of ganglioside-containing aggregates to the interaction with sialidase"
10.00-10.15	O13 – P. Calligari "*Stati corrispondenti* nell'adattamento delle proteine a condizioni ambientali estreme: un approccio combinato di simulazione molecolare, esperimenti e modelli teorici"
10.15-10.30	O14 – S. Nazzareni "High-pressure behaviour of gypsum: a synchrotron and neutron diffraction study"
10:30-11.00	*Coffee break* and **poster session** (continuation)
Session 6	
11:00-11:30	**I4** – **D. ARGYRIOU** (Science Director, ESS, Lund, Sweden)
11.30-11.45	O15 – E. Guarini "Efficient multiple scattering evaluation via Monte Carlo integration for ToF neutron spectrometers with extended detection geometry"
11.45-12.00	O16 – L. Sciortino "High resolution XRD and EXAFS analysis of nanocrystalline cobalt samples"
12.00-12.15	O17 – U. Bafile "Effetti non gaussiani nella dinamica *self* dell'idrogeno liquido: diffusione di neutroni e simulazione quantistica"
12.15-12.30	O18 – G. Bicocchi "SANS/VSANS investigation of porosity microstructure in rocks from a natural CO_2 reservoir"
12.30-13.00	*young researchers award and closing remarks*

INVITED PRESENTATIONS

Recent progress on advanced materials by synchrotron radiation based photoelectron spectroscopy

Amina TALEB-IBRAHIMI
CNRS/Synchrotron SOLEIL, L'Orme des Merisiers, Saint Aubin, Gif/Yvette, France

In this presentation we will report on High resolution ARPES, using the high performances of the new Cassiopée beamline at Soleil, which reveal novel electronic and magnetic signatures in advanced materials.
Materials with exotic properties, like thermoelectricity, high temperature superconductivity, giant magnetoresistance have attracted large interest recently.
The case of misfit cobaltates [1] or the newly discovered pnictides superconductors [2] demonstrates the role of many body interactions thought to be responsible for the exotic physical properties of these highly correlated systems.
Graphene is one of the hottest topics in solid state physics and advanced electronic materials. This material is extremely promising for applications because it makes feasible carbon electronics while circumventing carbon nanotubes problems, i.e. scalability and contact problems. The electronic band structure of graphene has been recently the subject of a great number of investigations. We will provide here direct experimental evidence of the linear band dispersion of epitaxial graphene grown onto the Carbon-face of SiC also using synchrotron radiation.

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[2] Brouet, V., Rullier-Albenque, F., Marsi, M., Mansart, B., Aichhorn, M., Biermann, S., Faure, J., Perfetti, L., Taleb-Ibrahimi, A., Le Fèvre, P., Bertran, F., Forget, A., & Colson, D. PRL, 2010, 105(8).
_Fuglsang Jensen, M., Brouet, V., Papalazarou, E., Nicolaou, A., Taleb-Ibrahimi, A., Le Fevre, P., Bertran, F., Forget, A., & Colson, D. _PRB, 2011, 84(1)
[3] _M. Sprinkle, D. Siegel, Y. Hu, J. Hicks, P. Soukiassian, A. Tejeda, A. Taleb-Ibrahimi, P. Le Fèvre, F. Bertran, S. Vizzini, H. Enriquez, S. Chiang, C. Berger, W.A. de Heer, A. Lanzara, E.H. Conrad PRL, 2009 ,103, (22). Hicks, J., Sprinkle, M., Shepperd, K., Wang, F., Tejeda, A., Taleb-Ibrahimi, A., Bertran, F., Le Fevre, P., de Heer, W. A., Berger, C., & Conrad, E. H. _PRB, 2011, 83(20)

«Discotic and calamitic phases in nanotubes»

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Calamitic and discotic columnar liquid crystals are of special technological interest, according to their self-organization tendency and high charge carriers mobility. More specifically, the design of ordered nanowires obtained from their impregnation in nanoporous templates with aligned channels is promising for new functional materials applications.

Meanwhile, the manipulation of liquid crystals in nanostructured systems raises exciting new questions for basic condensed matter physics. In this contribution, we will discuss the profound modifications of the phase behavior, self-assembling tendency, and molecular dynamics studied by a variety of neutron scattering methods and by molecular simulation for a series of liquid crystals confined in porous silicon and aluminum oxide nanochannels.

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‘Criticality of an isotropic-to-smectic transition induced by anisotropic quenched disorder’,
G. CHAHINE, A.V. KITYK, K. KNORR, R. LEFORT, M. GUENDOUZ, D. MORINEAU, and P. HUBER, Phys. Rev. E, 81, 031703 (2010).

‘Pore dimensionality effects on the dynamics of a nanoconfined liquid-crystal’,
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"The growth of the importance of synchrotron X-radiation and neutrons in macromolecular crystallography"

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Synchrotron radiation (SR) techniques and facilities are continuously pushing the frontiers of faster crystal structure determination, automation, wavelength range usage, smaller crystal sample size (including powders and polycrystallography), larger protein molecular weight and complexity, as well as better diffraction resolution. Higher resolution can also come from complementary chemical and biological crystallography studies. The new research specialism of probing functional states directly in crystals, via time-resolved Laue and freeze trapping structural studies, has been developed. Mutiple static crystal structures has long been a capability and becomes ever easier to achieve with 'high throughput' crystal structure measurement being routine. The current number of Protein Data Bank depositions is approximately 65000 X-ray crystal structures, about 90% of the total, and 75% of these are from synchrotron radiation facilities. The new X-ray laser technology brings further excitement and challenges towards single molecule and also femtosecond time-resolution X-ray diffraction. Overall, SR X-ray biological crystallography is complemented by neutron protein crystallographic studies aimed at cases where much more complete hydrogen and hydration details (as deuterium) are needed to help understand biological mechanisms such as with enzymes and has involved synergistic methods developments between SR and neutron Laue crystallographic methods. Recently improved neutron reactor instrumentation including neutron image plate apparatus like the Institut Laue Langevin LAue DIffractometer 'LADI III' and the potential of new spallation neutron sources also show an exciting evolution of capability and scope for neutron biological crystallography. There is an expansion of PDB depositions and currently these total 46 drawn from 3 research facilities, one each in Europe, Japan and the USA. Overall, fundamental and applied ie industrial 3-D molecular science is still experiencing a tremendous growth and 3-D with snapshots to create 4-D viewing is seen regularly.

Science & Scientists at ESS

D. ARGYRIOU

(Science Director, ESS, Lund, Sweden)

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Abstract non pervenuto

ORAL PRESENTATIONS

Giant magnetoelastic interaction in UFe_2

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Abstract. Using the unique coverage of (Q, _) space available on the BRISP spectrometer, we have investigated the low Q dynamical response of a single crystal of UFe_2. A strong inelastic signal was found with a dispersion corresponding to the transverse acoustic phonon branch, forbidden in the first Brillouin zone. A detailed analysis of the neutron intensities as a function of temperature and an applied magnetic field reveals a possible magnetic contribution superposed to this signal, which could originate from the magnon-phonon interaction, explaining the anomalous magnetoelastic behavior in this compound.

SCES investigation via X-ray magnetic resonant techniques

C. Mazzoli, G. Ghiringhelli

After pioneering experiments on the interaction between X-rays and spins, the advent of third generation synchrotron machines has definitely shown the versatility of Magnetic Resonant Elastic and Inelastic X-Ray Scattering in the investigation of magnetic materials.

In particular, the techniques benefits of chemical selectivity, high Q resolution and sensitivity to the angular part of magnetic moment to access fundamental physics information, resulting in powerful tools, complementary to neutron diffraction.

Nowadays, the investigation of complex and elusive magnetic structures, even in externally applied electric and magnetic fields is possible.

Results obtained on forefront scientific cases as frustrated magnetic systems [1], collinear and cycloidal multiferroics [2] are presented. In particular, magnetic structures solution, phase diagrams definition and magnetic interaction patterns determination have been successfully achieved, directly contributing to the understanding of key mechanisms active in the aforementioned classes of compounds.

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Magnon dispersion in $(CaCuO_2)_n(SrTiO_3)_n$ superlattices studied with high resolution Resonant Inelastic X-ray Scattering

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Cuprate-based superlattices (SLs) can be considered as new, artificial materials belonging to the family of high-T_c superconductors, offering the opportunity of freely choosing the two building blocks [1,2]. We have studied $(CaCuO_2)_n(SrTiO_3)_n$ (CCO/STO) SLs in which the CuO_2 planes of the infinite layer CCO are alternated to the charge reservoir buffer layer of STO. Although not superconducting, these SLs constituted of two insulating materials show a relatively low sheet resistance at room T. Their peculiar transport properties make them particularly interesting for adding new experimental information to the old puzzle of high-T_c superconductivity. We devoted special attention to the crystal field excitations and to the magnetic excitations (magnons). These two families of elementary excitations can tell us how the electronic and magnetic backbone structures of the infinite layer gets modified at the interface to STO.

High resolution resonant inelastic x-ray scattering (RIXS) at Cu-L_3 edge is a powerful tool for measuring magnons in cuprates, as we have recently demonstrated both theoretically [3] and experimentally [4]. Moreover the study of magnons is interesting due to their possible connection with high-T_c superconductivity, as supported by our recent data [5].

Using the AXES spectrometer at the ID08 beam line of the European Synchrotron Radiation Facility (ESRF) we have carried out RIXS measurements at Cu-L_3 edge on CCO_n/STO_n SLs with n=2,3 and we have compared them with measurements on bulk CCO. RIXS data show very clear magnon dispersion in both SLs and bulk CCO. In particular, in the SLs we found a decrease of the superexchange coupling when n decreases, i.e. the in-plane magnetic coupling diminished when the interface are made more dense. Moreover the persistence of dispersing magnons even for n=2 gives a hint on the limits of low dimensional quantum magnetism.

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Photoionization Experiments in the Gas Phase

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Photon flux and energy resolution achievable at third generation facilities, such as the Gas Phase beamline of the Elettra storage ring (Trieste, Italy) [1], enable thorough studies of inner-shell electron photoionization, even with low density targets such as vapours of biotic molecules [2] and clusters [3]. I will discuss recent experiments where photoionization techniques have been applied to gas phase molecular targets of increasing complexity, ranging from molecules of biological interest, to metal containing molecules and clusters.

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Resonant photoelectron diffraction: a novel tool for novel surface structure studies

A.Verdini, L. Floreano, A. Cossaro

Conventional photoelectron diffraction (PED) is a wide used technique for studying the structure of surfaces and interfaces. The main advantages come from being able to choose the desired chemical state by means of photoemission and from probing the atomic position around the selected emitter. In same cases ordinary PED measurements on core level data can be hindered by the relatively low core level emission, or the desired peaks overlap with much intense, but undesired, peaks coming from the substrate, making impossible to obtain reliable PED patterns. In order to overcome this limitation, we collected the photoemission data in resonant conditions, where the emission is maximized by tuning the photon energy at the adsorption threshold of the selected atom. Therefore, it was possible to exploit the photoemission at resonance to increase the signal coming from the desired atom in the desired chemical state and to measure the angular distribution of the resonant photoemission signal, obtaining the resonant photoelectron diffraction (RESPED) patterns. Moreover, in the case of transition metals, the photoemission spectra are collected on the L2-L3 edges, with kinetic energies (about 500-800 eV) in the forward scattering regime, which can provide information from the simple analysis of the main peak postions in the RESPED pattern. RESPED patterns can be also compared to simulations, via the usual reliability factors minimization, in order to obtain a quantitative and more complete information on the structure of the system. Examples on different systems will be presented: the study of ion bombarded and reduced TiO_2(110) surface, where resonant photoelectron diffraction has demonstrated the unique capability of to map out the spatial distribution in the crystal sites of the Ti3+ defects [1]; in the case of the magnetite Fe3O4, which presents three distinct species for the cation *A*-Fe2+ ,*B*-Fe2+ ,*A*-Fe3+, it has been possible to assign the main spectral features to the three different Fe species, attributing unambiguously the structure near the Fermi level to the *B*-Fe2+ ions; the study of a 0.5 monolayer of Mn deposited on the CdTe(110) surface where the RESPED patterns clearly indicates that even at room temperature, the Mn atoms goes inside the bulk substituting the Cd atoms, and does not occupy the interstitial sites.

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Oxidation of Supported PtRh Particles: Size and Morphology Effects

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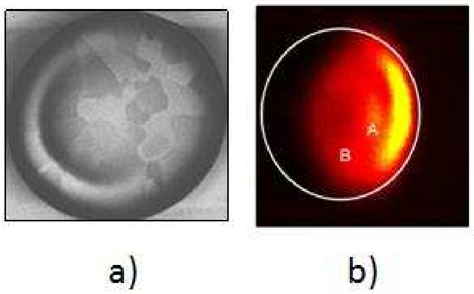
The chemical transformations of supported PtRh particles ranging in size from a few micrometers to a few nanometres, and nanocrystalline films have been studied under identical oxidizing conditions by means of different chemical and structural characterization techniques [1]; in particular the main technique used has been the scanning photoemission spectromicroscopy (SPEM) available at the EscaMicroscopy beamline of the Elettra Synchrotron Light Source. This novel experimental technique allows sample's chemical mapping with a spatial resolution below 100nm and the acquisition of photoemission spectra on regions with the same dimension, and allow us to determine the chemical state of single micro-particles (Figure 1). In particular we studied PtRh cluster deposited by PLD (pulsed laser deposition) on a tungsten single crystal (W(110)) covered by a thin magnesium oxide film (MgO).



a) b)

Figure 1) SEM (a) and Pt 4f SPEM map (b) images of PtRh alloy microparticle. The white circle (b) highlights the real size including the shadowed region at the left. A and B indicate the points where the spectra were measured.

Significant variations of the Pt and Rh atoms reactivity have been revealed by comparing the oxidation states of particles with different dimensions and, for the micron-scale particles, also within the same island (point A and B figure 1). It was demonstrated that a selected oxidation occurs: rhodium atoms undergo stronger and faster oxidation than platinum ones. Furthermore, the oxidation process is composed by many intermediate steps, in which metastable oxides are formed. Very small cluster's oxidation (<10nm diameter) is significantly faster then the bigger one (>100nm). Some morphological and structural clusters' modifications after long oxidation treatments were also investigated using a high resolution SEM (<2nm lateral resolution). Other measurements have been performed by using a Low Energy Electron Microscope (LEEM) that combines a high spatial resolution (<5nm) to a high sensitivity to surface structural modifications. In particular the behaviour of the clusters' polycrystalline structure has been studied during oxidation-reduction treatments. It has been shown that the clusters' surface is polycrystalline and that each nano crystals have different crystallographic orientation. After oxidation each nano-crystal undergoes a different oxidation rate. The diffraction pattern revealed that after a long oxidation the long range order of the particles' surface is completely lost. A characterization of the reactivity of the PtRh particles towards oxidation after an "ageing" process based on the repetition of many redox cycles has revealed a change in the stability of the oxides. Other experiments have been realized with SEM and EDX for studying the clusters' morphology at different annealing temperatures. The results have shown structural, chemical and morphology changes.

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Structure and dynamics of polyethylene glycol coated Au-nanoparticles

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Polymer-capped gold nanoparticles (AuNP) have many peculiar aspects like quantum size effects and single electron transitions. Their properties are highly dependent on their size and shape and upon spatial relationship of one particle to another. Coating nanoparticles with polymers tethered to their surface by means of specific ligands stabilizes them, and allows functionalization for specific applications in nanotechnologies, biology and biomedical studies [1], and can promote the bottom-up approach to the fabrication of nanostructures.

We studied the structure and the dynamics of a key class of polymer-capped AuNP, those coated with poly ethylene glycol (PEG AuNP). A novel synthesis was developed by ligand exchange procedure, which ensures the production of NP with little excess of (expensive) functionalizing ligand and high stability [2]. When dissolved in water, PEG AuNP are typical examples of mesoscopic solute in a microscopic solvent and the thermodynamic conditions of the solution depend on the extension and local properties of the solute-solvent interfaces. Polymer coated NP have homogeneous interfacial properties that can be modulated precisely by changing the type, the length, and the areal density of the grafted polymers, or by varying characteristics like temperature, salts and deuterium content of the solution, and can serve as model systems to draw a structure-dynamics relationship map on the mesoscopic scale.

The structural features of PEG AuNP were studied by small angle neutron scattering (SANS) as a function of temperature, deuterium content in solution, AuNP concentration, and of the length of the interfacial polymer chains. PEG AuNP functionalized with short (PEG400) and long (PEG2000) polymer reflected substantial differences in the structure of the polymer at the interface. The AuNP functionalized with the longer PEG showed a considerable gradient in the density of the polymers in the corona and in their hydration which has been demostrated to be sensitive to the concentration of heavy water in solution [3]. An intriguing result suggests the dehydration of the polymer as temperature is raised, with consequent shrinking of the tails and a reduction of the AuNP coated diameter. A similar behaviour is found when AuNP concentration in solution increases, and the average water content between the polymer tails decreases. This effect can be due to the competition between the AuNPs for water and results in a modification of the interaction between AuNP, too, as revealed by the analysis of the structure factor of the SANS data.

The dynamics of PEG AuNP in the nanosecond timescale was also studied by neutron spin echo (NSE) spectroscopy. NSE experiments gave evidence of two dynamical processes, one related to the translational diffusion of the nanoparticles (which agrees with the one evaluated by Stokes-Einstein equation), and a faster due to internal motion of the polymer chains. For comparison, NSE experiments were performed on PEG2000 polymer in solutions. Analogies and differences between free and anchored polymer will be discussed.

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An XPCS study of the heterogeneous dynamics in a 2D gel

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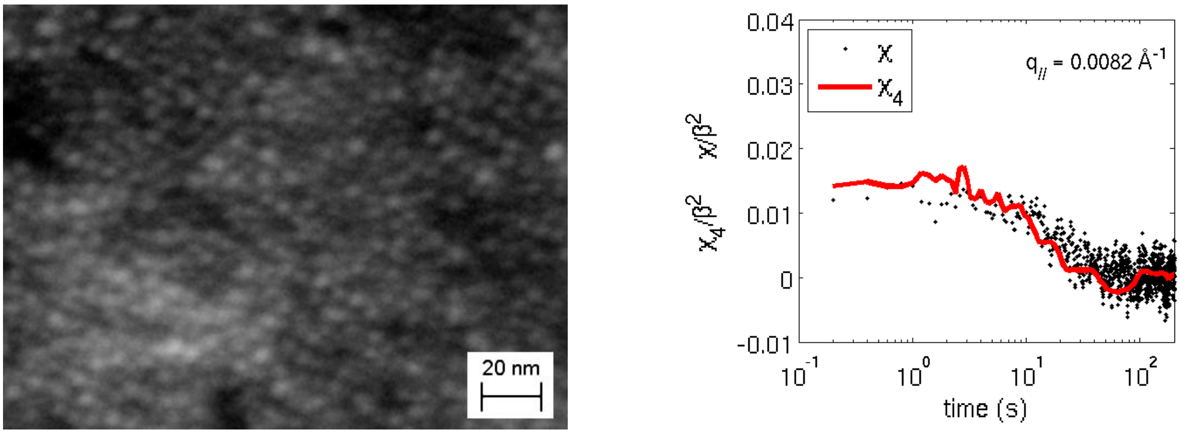
We studied the bidimensional confined model system provided by a Langmuir monolayer of gold nanoparticles (GNP) of 7nm diameter at the air water interface subject to dynamical arrest. By X-ray Photon Correlation Spectroscopy (XPCS) performed at the air/water interface we demonstrate heterogeneous dynamics and 2D superdiffusive behaviour on the nanoscale, similar to what we observed for layers of photosensitive azopolymers deposited on silicon[1].

Dynamical heterogeinity is characterized by the fourth order susceptibility χ_4, which is, at the best of our knowledge, for the first time directly accessed experimentally by our XPCS experiment, and allows a direct comparison with theoretical predictions.

We discuss our findings also in light of the semi-macroscopic properties probed by 2D interfacial shear rheology [2] measurements performed on the very same system: the sample shows a gel-like behavior as a function of both concentration and frequency, with a mainly elastic dynamic shear modulus.



Left: SEM image of a film of colloidal particles deposited on silicon. **Right:** the fourth order susceptibility χ_4 shows a well defined peak, on a time scale roughly 10 times faster than the slow (~60s) relaxation time of the collective 2D dynamics.

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Acqua libera e acque confinate: somiglianze e differenze su varie scale spazio-temporali

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Una delle anomalie dell'acqua è che essa non si presenta in nessuna forma amorfa (liquida o vetrosa) in una vasta regione termodinamica, detta *no man's land*. Questa zona è stata oggetto di speculazioni e congetture teoriche [1], tant'è che, negli ultimi anni, si è pensato di studiarla indirettamente con diversi espedienti, tra cui confinare l'acqua in matrici mesoporose (quali colloidi, silicati, emulsioni). In queste condizioni, infatti, l'acqua può essere sottoraffreddata a temperature più basse rispetto all'acqua di *bulk*. Tuttavia, come prevedibile, la natura chimica e l'estensione del confinamento - in casi estremi confrontabile con la scala di lunghezze della coordinazione tetraedrica - possono incidere drasticamente sulla stabilità e la "forma" della fase liquida.

Riguardo alla questione della somiglianza dell'acqua nello stato confinato con l'acqua nello stato libero, fenomeni fisici su scale spazio-temporali diverse danno risposte diverse. Ad esempio, i *patterns* di diffrazione dell'acqua nanoconfinata in matrici mesoporose ordinate, suggeriscono che, a temperature al di sotto del limite di nucleazione omogenea, l'acqua è in una fase amorfa, che cambia con la temperatura e si adatta alla geometria del confinante [2]; misure di dinamica al femtosecondo sullo stesso sistema sembrano mostrare[1] da un lato l'esistenza di un regime sub-diffusivo, dall'altro la persistenza di moti collettivi tipici dell'acqua e del ghiaccio. Circa il manifestarsi di arresti dinamici su scale temporali più lente (dal picosecondo in su), spesso chiamati in letteratura transizioni α-β [3] o *strong to fragile* [4], in misure di spettroscopia dielettrica *broadband* si distinguono comportamenti dell'acqua di interfaccia universali, da dinamiche più lente che dipendono, invece, dalla natura del confinante. Ciononostante, in alcuni casi (*hydrogels* e *xerogels*), proprio su tempi di rilassamento dell'ordine del secondo, si constata la possibile coesistenza, nella *no man's land,* di comportamenti tipici di fasi dell'acqua di *bulk*.

Lungi dall'aver risolto l'intricato *puzzle* dei rapporti tra acqua libera e acqua confinata, cercherò di riassumere lo stato dell'arte, anche alla luce di alcune evidenze sperimentali originali, derivanti da misure di spettroscopia neutronica e dielettrica su acqua confinata in emulsioni, xerogel, MCM41.

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Neutron Diffraction Measurement of Molecular Hydrogen Population in Hexagonal Clathrate Hydrates

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Clathrate-hydrates are crystalline structures, composed of hydrogen-bonded water cavities, hosting inside one or more types of guest molecules [1]. The structure of the water lattice is determined by the size of the guest molecule(s) and the composition of the gas mixture. They form spontaneously when water and gas are combined at low temperature and high pressure.

The most popular clathrates are made of methane and were discovered due to their capacity of occluding natural gas pipelines. Natural methane hydrate deposits have been found at the ocean's bottom and some industrial R&D technological activity is developing for their exploitation.

Recently, hydrogen simple (made of water and hydrogen only) and binary (made of hydrogen, water, and a second molecular species) clathrates, have been synthesized and have been suggested as potential candidates for hydrogen storage purposes[2].

Using present high pressure technologies, up to ≈5 wt % of molecular hydrogen can be stored in simple clathrate-hydrates with cubic sII structure.However, the high pressure value (≈2000 bar) required for these compounds calls for a different solution. This was found by adding a second molecular species to form a binary clathrate. In this case, for example, a large THF molecule can stabilize the cubic structure which forms at much lower pressure (50-100 bar).

Beyond the cubic sI and sII structures, which are composed of relatively simple deodecahedral and esakaidecahedral polyedral cavities, more promising structures are under investigation to test for a possible increase of the hydrogen capacity. As a matter of fact, using a larger molecule that THF, a binary sH clathrate hydrate can be formed which could potentially increase the hydrogen content be more than 40%.

Recent studies have been dedicated to the formation and stabilization of these clathrate structures, where the large molecule fills the largest cavity [3,4], but not much was known about small cage occupation by the hydrogen molecules. To this aim, we have measured the small and medium cage hydrogen occupancy on a sH structure using neutron diffraction. Measurements have been carried out on the INES diffractometer at ISIS (UK) [5], on a powder sample, prepared in our laboratories, and composed of totally deutereted water, deuterium and TMBE (Terth Methil Butil Ether) at a temperature of 20 K. A Ritveld refinement of the various diffractograms (taken as a function of temperature) gives us the possibility to determine the amount of molecular deuterium contained in each cage.

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Synchrotron SAXS and FTIR experiments monitor the effects of high pressure on α-synuclein amyloid fibrils

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It has been recently shown that high-pressure plays a specific role in driving the formation and dissolution of highly ordered and β-sheet-rich aggregates referred to as amyloid fibrils, which are the hallmarks of several neurodegenerative diseases, like Alzheimer, Parkinson and systemic amyloidosis [1]. In particular, it has been demonstrated that the fibrillation process can be reversed by hydrostatic pressure, for example by performing consecutive cycles of compression/decompression under aggregating conditions as in the case of transthyretin and α-synuclein fibrils [2].

Because the pathological relevance to Parkinson, we used SAXS and FTIR techniques to monitor the high hydrostatic pressure effects on stability and dissociation of α-synuclein fibrils, produced from the wild type protein and from two different mutants (A30P and A53T), which show a different fibril reaction pathways.

The whole experiments performed at Elettra synchrotron confirm that fibrillation can be tuned by consecutive cycles of compression/decompression under aggregating conditions (see the figure with FTIR results for the α-synuclein wild type fibrils). In particular, FTIR data indicates that pressures higher than 3 kbar induce transitions in the amount of fibril, random, helix, and turn structures, as it was provided from Amide I deconvolution, while SAXS curves show that moderate pressures - below 1.5 kbar - slightly modify fibrils' sizes and hydration features, without changing the average shape. The different sensitivity of amyloid fibrils toward high pressure seems to indicate the existence of packing defects in the fibril core, suggesting that pressure dissociates amyloid fibrils because they possess water-excluded cavities.

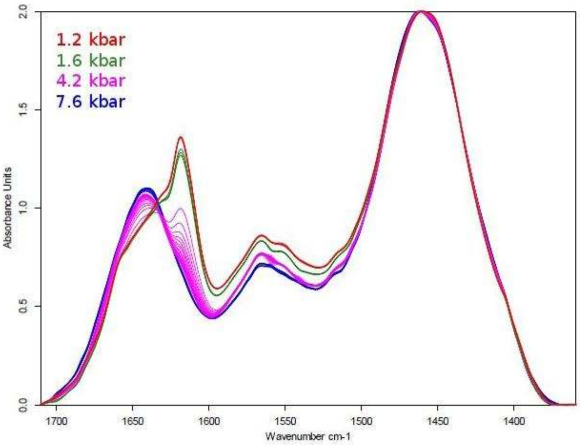

Figure 1: FTIR spectra of wild type α-synuclein fibrils during compression, as in the legend.

Noticeable is the fact that fibrils produced from the wild type α-synuclein were differently susceptible to pressure dissociation than the Parkinson's disease-linked variants, and that each species showed distinct reversibility. These findings suggest different dissociation mechanisms and intermediate states, hinting at the possibility that mutant fibrils would be more easily dissolved into small oligomers by the cellular machinery. Because the most cytotoxic species are the small aggregates rather than the fibrils, our results gain physiological importance to the determination of therapies against amyloid diseases.

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Nanoscale structural response of ganglioside-containing aggregates to the interaction with sialidase.

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It is well known that ganglioside aggregates curvature strongly depends on headgroup structure, being their amphiphilic balance crucially affected by steric, hydration and charge interactions.

A lot of information has been collected along the years on the packing properties of gangliosides, in monocomponent and multicomponent colloidal aggregates, with "stationary" composition, that is, when the system finds its optimal structure at the moment of lipid dissolution in aqueous solution.

We directly followed the structural change in model aggregates, induced by on-line molecular modification of already-packed gangliosides, namely the one brought about by a sialidase, acting on the ganglioside GD1a and leading to the lower-curvature aggregating GM1. We applied different scattering techniques (laser, X-ray, neutron scattering) being sensitive to different structural aspects of the aggregate, and followed their time evolution.

We found that, while chemically undergoing the enzymatic action in both cases, the aggregated structure could be either very stable, in single component systems, or structurally responsive, in mixed model systems. Moreover, while in progress, the sialidase-ganglioside interaction seems to define a time lag where the system is structurally off the smooth route between the initial and the final states. We can imagine that, in this time lag, the local structure could be very sensitive to the environment and eventually readdressed to a specific final structural fate.

"STATI CORRISPONDENTI" NELL'ADATTAMENTO DELLE PROTEINE A CONDIZIONI AMBIENTALI ESTREME: un approccio combinato di simulazione molecolare, esperimenti e modelli teorici.

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L'adattamento degli organismi viventi a condizioni ambientali estreme Ë senz'altro una delle aree piu' interessanti della biologia molecolare. In questa comunicazione presentero' il caso di una proteina, il Fattore d'Iniziazione 6 (IF6), prodotta da un archea-batterio proveniente dai camini idrotermali presenti nei fondi oceanici (condizioni ambientali estreme di alta pressione e alta temperatura). In particolare, mi soffermero' sui recenti risultati ottenuti in esperimenti di diffusione di neutroni e simulazioni di dinamica molecolare svolti sulle IF6 prodotte da organismi adattati a condizioni ambientali molto diverse[1].

Proporro' quindi l'analisi delle proprieta' dinamiche e strutturali della IF6 come esempio concreto per l'applicazione di due modelli teorici recentemente sviluppati: il modello di dinamica Browniana frazionaria[2] e un metodo recentemente sviluppato per la caratterizzazione della struttura secondaria delle proteine[3]. L'adattamento strutturale e dinamico, interpretato attraverso tali metodi, sembra suggerire l'ipotesi di un'evoluzione molecolare che proceda attraverso la creazione di "stati corrispondenti" atti a mantenere invariate, a differenti condizioni ambientali, le proprieta' molecolari delle proteine. Seguendo questo principio, mostrero' come le IF6, studiate nelle condizioni ambientali fisiologiche per i diversi organismi da cui sono prodotte, mostrino tra loro caratteristiche strutturali e dinamica molto simili.

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High-pressure behaviour of gypsum: a synchrotron and neutron diffraction study

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Recently, strong developments and improvements of high-pressure (HP) experiments at large scale facilities (both synchrotron and neutron facilities) opened new scenarios on the accurate determination of physical properties of minerals at very deep conditions. High-pressure single- crystal X-ray diffraction (SCXRD) synchrotron experiments allow to determine small structural variations with pressure due to increase of the quality of data collection. In HP experiments the angular limitation access to the Ewald sphere, due to the diamond anvil cell, can be partially encompassed by the high intensity of the synchrotron X-ray beam using small samples and multiple mounting into the DAC. At the same time, HP neutron powder diffraction experiments could determine the hydrogen position (and hydrogen bonds evolution) directly both on deuterated and natural materials.

We performed high-pressure single-crystal synchrotron and neutron diffraction experiments on gypsum ($CaSO_4$ $2H_2O$) to study the HP behavior of this sulphate including the hydrogen bonds. Literature data [1-4] suggested a polymorphic transition at 4GPa and the structure of the new polymorph, gypsum-II, was recently solved [5]. SCXRD studies [4-5] suggested that water molecules play a key role on the phase transition.

We combined the HP neutron data with single-crystal and powder synchrotron diffraction data measured on gypsum up to 13 GPa at ESRF (Grenoble, France - ID09 and ID27 beamlines). We performed HP neutron powder diffraction up to 10 GPa at ILL (Grenoble- D20 beamline), loading a Paris-Edinburgh cell with NaCl as pressure calibrant and deuterated Ethanol/methanol as pressure transmitting medium and the same sample used in previous papers. Powder diffractions were collected with a radio oscillator collimator and each data collection was measured from 3 to 6 hours as P increased. The lattice parameters of gypsum at increasing P were obtained by refining the powder pattern by using the Fullprof software.

In the pressure range investigated we recognised two discontinuities in the *a* and *b* lattice parameters and beta monoclinic angle corresponding to the first phase transition at 4 GPa (already suggested [4-5]) and a second phase transition at around 7 GPa not clearly defined previously. A very good agreement was found between our XRD data set (SC-XRD in house, synchrotron SC- and powder XRD at ESRF, Grenoble) and the lattice parameters measured by neutron diffraction at D20 (ILL- Grenoble). We used the synchrotron XRD data to constrain the neutron refinement and decrease the refined variables, thus to focus in the H coordinates and occupancies.

Single-crystal XRD data [4] showed that the gypsum interlayer, where the water molecules are located, strongly decreases its thickness up to 3.94 GPa. The water molecule shares an oxygen with the Ca-polyhedron and hydrogen atoms (H1 and H2) form, at ambient pressure, weak hydrogen bonds with the oxygens belonging to S- and Ca-polyhedra. Neutron diffraction data suggest that increasing pressure the two hydrogens configuration changes: the coordinates of H1 move slightly from its position at ambient pressure whereas the y/b coordinate of H2 decrease significantly explaining the different compressibility of the two hydrogen bonds [4].

These new hydrogen bond configurations confirm that in the gypsum structure there is an increasing shift of the calcium-sulphate layer along *a* axis that lead to the phase transition and allow to retain water molecules at high pressure, namely to prevent the free movement of water molecules and should affect the dehydration condition.

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Efficient multiple scattering evaluation via Monte Carlo integration for ToF neutron spectrometers with extended detection geometry

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New generation reactor-based time-of-flight (ToF) spectrometers are typically characterized by very wide detection areas. The clear advantages in achievable count rates are however counterbalanced by some difficulty in the handling and reduction of huge data sets, especially when correction for various effects in real-geometry conditions are considered. Anisotropic multiple scattering evaluation, even in an approximate way, is surely the most demanding step in the general treatment of inelastic neutron data, and becomes quite a hard task when thousands of time channels and several tens of thousands of detection pixels are available, as it happens for new or upgraded neutron ToF spectrometers such as BRISP, IN4C or IN5 at the Institut Laue Langevin in Grenoble. For this reason, we refreshed our approach to multiple scattering calculations, in order to obtain reasonably accurate real-geometry results in nearly real-time conditions. Our new code, though conceptually originating from a long standing experience of Monte Carlo (MC) integration techniques to extract (unnormalized) double and single scattering intensities, is now made particularly efficient in computing time both by a careful application of the "importance sampling" method used to calculate some of the required MC integrals, and by the choice of programming languages which allow for a heavy but efficient use of matrix algebra in place of the (far slower) nested-loop logic required by more traditional languages. The concepts and approximations at the basis of the algorithm are presented, along with a general description of the program structure and implementation details. Application of multiple scattering correction to a real case will also be discussed.

HIGH RESOLUTION XRD AND EXAFS ANALYSIS OF NANOCRYSTALLINE COBALT SAMPLES

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Among metal nanomaterials, nanostructured cobalt samples are well-studied due to their peculiar magnetic and catalytic properties. At least two Co phases are described in the literature, the face-centered cubic (*fcc*) and the hexagonal close packed (*hcp*), both arrangements being often distorted by significant amounts of stacking faults. At room temperature the structure of metal Co is mostly *hcp*, while the *fcc* phase is prevalent above 477 K. The *hcp-fcc* transformation is reversible, with small changes in volume ($\Delta V/V=0.0036$) and in enthalpy ($\Delta H=440$ kJ/mol) [1]. Despite *hcp* cobalt is the stable bulk phase, several papers report that cobalt nanocrystals and films can present, also at RT, various degrees of *fcc* arrangement [2]; the *hcp-fcc* transformation is ruled by a process of stacking fault accumulation, that can effectively influence the magnetic properties [3].

Nanocrystalline Cobalt samples were prepared by thermal decomposition and SMAD (Solvated Metal Atom Dispersion), and characterized by HRXRD and EXAFS experiments carried out at ID31, BM26 and BM08 (ESRF). The XRD patterns were analysed by a structural model allowing for: i. stacking faults extending their statistical influence as far as the third neighbouring atomic planes; ii. microstrains and iii. particle size distribution. The model was fitted to the HRXRD data by a suitable modification of the Debye formula [4]. The EXAFS spectra were analyzed with the GnXAS package [5] and both the *hcp* and *fcc* arrangements were essential to obtain a satisfactory agreement with the experimental data, due to the different distribution of next neighbours that affects in particular the third coordination shell [6]. Only a few parameters were needed for the EXAFS analysis: i. the first-neighbour length, that determines in closed packed arrangements all the other next-neighbour distances, ii. the Debye–Waller factor, iii. the angles of the three body configuration and iv. the cluster size, accounting for the reduction of coordination numbers in small particles according to Borowski's equation [7].

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Effetti non gaussiani nella dinamica *self* dell'idrogeno liquido: diffusione di neutroni e simulazione quantistica

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La dinamica di singola molecola in liquidi ha trovato nell'Approssimazione Gaussiana (AG) uno dei più importanti schemi interpretativi. La ricerca di una verifica sperimentale della sua validità, di evidente rilevanza generale, assume un ruolo particolare nel caso dell'idrogeno liquido per la sua connessione con il problema, largamente studiato dai punti di vista teorico e algoritmico, della simulazione dinamica di fluidi semiquantistici. Tuttavia, soltanto negli ultimi anni sono stati fatti progressi significativi in questo campo sul piano sperimentale.

La diffusione anelastica incoerente di neutroni è la tecnica di elezione per lo studio della dinamica self e sfrutta le eccezionali proprietà di scattering dell'idrogeno. Descriviamo i risultati di un esperimento in cui, utilizzando due spettrometri dell'ILL e valendosi di una simulazione della funzione di autocorrelazione della velocità delle molecole, si sono osservate per la prima volta le condizione di validità della AG in funzione di Q ed è stata ottenuta una determinazione semiquantitativa della componente non gaussiana nella funzione intermedia di scattering.

SANS/VSANS investigation of porosity microstructure in rocks from a natural CO_2 reservoir

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Sequestration of CO_2 in deep geological reservoirs represents one of the potential methods to reduce anthropogenic emissions into the atmosphere. In the long term the injected CO_2 dissolves into the local formation of rocks and, when present, in saline deep aquifers, participating to a variety of geochemical reactions. The overall impact of these processes produces changes in mineralogy, texture, permeability and porous structure of the rocks, to a level which depends on the different lithologies present in the rocks.

Mineralogical changes can be investigated by considering what occurs in rocks and minerals with natural CO_2 accumulations, as analogues for geological sequestration. Also computer simulations, based on thermodynamics, kinetics and geochemical modeling [1, 2], can be beneficial. On the other hand, reliable data concerning the porous structure, which is so important to trap CO_2, can be hardly extracted from computer simulations.

In this context a valuable help can be provided by Small and Very Small Angle Neutron Scattering techniques (*SANS* and *VSANS*, respectively): they have been indeed demonstrated to be powerful tools for the determination of the microstructure and porosity of rocks from Ångstrom to millimeter sizes [3], proofing also the existence of fractal dimensions for the volume and surfaces interfaces between pores and rocks.

Here are presented the preliminary results of a *SANS/VSANS* investigation on rocks pertaining to a geological context (located in Eastern Tuscany, Central Italy) featured by a deep geological gas reservoir. The former reservoir was intercepted by a bore-well drilled in ’80 by ENI and is presently hosting 700 bar of supercritical CO_2. Texture and mineralogy of volcanic rocks samples, from drill cores corresponding to the top of the reservoir, were found heavily modified by the interaction with CO_2-rich fluids.

The combined neutron experiments, performed using the PAXE and G5bis diffractometers at LLB (Saclay, France), allowed to approximately investigate pore sizes ranging from ~60 nm to ~6 μm. Samples of host rocks (from drill core) and a selection of possible analogues of the same volcanic rocks, unaffected by CO_2 presence, were chosen for the experiments together with samples of rocks, from outcrops, corresponding to the geological layers overlying the reservoir. Globally these rocks are representative of a wide spectrum of different lithologies (as limestones, marls, evaporitic deposits bearing gypsum and volcanic rocks with intermediate-acid composition).

The information provided by these experiments must still be fully analyzed and integrated with other data (e.g. chemical composition of rocks and fluids [4]) in order to get a better understanding of: i) the role and the possible effects of CO_2 in determining the micro-porosity of these host rocks ii) the sealing effect of the sedimentary rocks overlying the reservoir which act as a barrier with respect to the CO_2-rich gases.

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POSTER PRESENTATIONS

0.5 wt.% Pd/C catalyst for purification of terephthalic acid: irreversible deactivation in industrial plants

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A systematic study on several spent catalysts, withdrawn from different terephthalic acid purification reactors loaded with the same fresh catalyst (0.5 wt.% Pd/C, type D3065, supplied by Chimet SpA), has been carried out. Spent catalysts characterized by different lifetimes, position in the catalytic bed, sintering degree, and types of contaminant (mainly S, Pb, and Mo) have been investigated by TEM coupled with EDS detection, XRPD, EXAFS spectroscopy, and CO chemisorption. The Pd sintering process involves all catalysts, irrespective of the nature and amount of contaminants that have no influence on sintering rate except for S poisoning. Pd sintering occurs following different steps, leading to the formation of larger crystals, aggregates, and agglomerates, the last being the primary cause of the loss of Pd surface area and, consequently, of the decrease in catalytic activity. Among the investigated contaminants, S and Pb are the worst, because they strongly interact with Pd, forming from surface adlayers (not detectable by XRPD, but visible by EDS mapping) up to bulk Pd_4S or Pd_3Pb alloys (easily detectable by XRPD). In both cases, the catalytic activity decreases. In contrast, Mo, Cr, Fe, Ti, and Al do not interact preferentially with Pd (no alloys have been detected, although the contaminants are present in relevant concentrations): They have been found to be spread on the whole catalyst surface. Accordingly, no direct effect of these contaminants on catalytic activity loss has been evidenced.

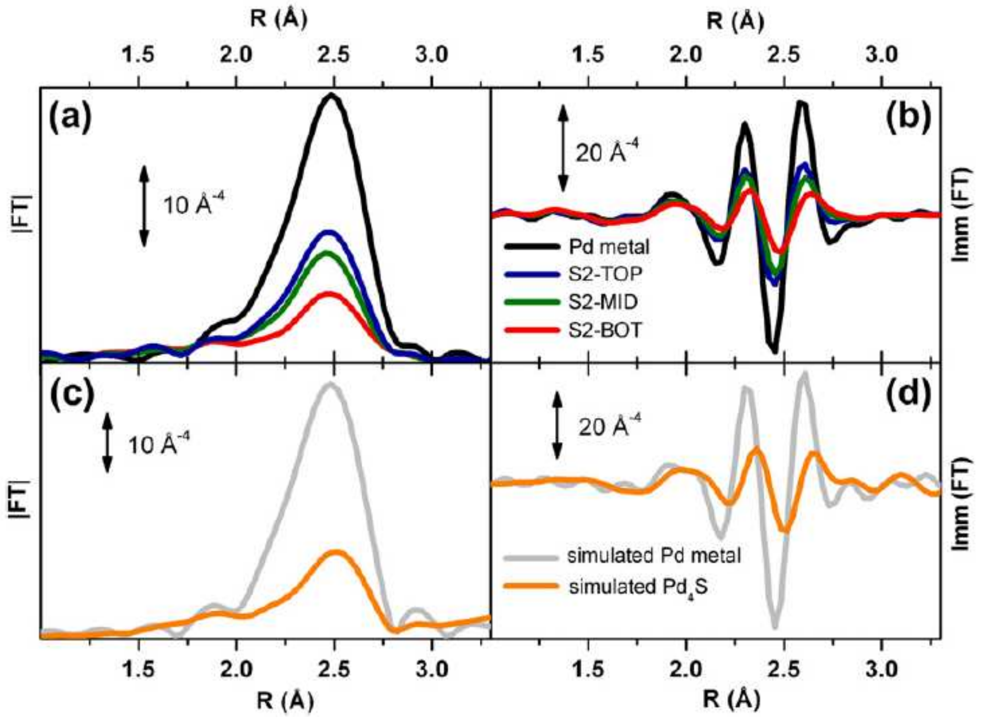

Figure Modulus (a) and imaginary part (b) of the k^3-weighted, phase-uncorrected FT of the EXAFS spectra of the samples contaminated by S: S2-TOP (blue curve), S2-MID (green curve), and S2-BOT (red curve). For comparison, the spectrum of bulk Pd foil (black line) is also reported. (c) and (d) As (a) and (b) for the simulated spectra, performed by FEFF6, of Pd metal and Pd4S bulk models.

Quadrupolar waves in uranium dioxide

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In presence of active orbital degrees of freedom, elementary excitations around a broken-symmetry state may include multipolar waves, but none of these exotic dispersive excitation branches had ever been identified. We show that quadrupolar waves constitute a major component of the dynamics of UO_2 in its magnetoquadrupolar ordered phase, and that many unexplained features in existing inelastic neutron scattering data, including a whole excitation branch, are associated with these propagating quadrupolar fluctuations [1]. Our model permits us to separate the role of Jahn-Teller and superexchange mechanisms as sources of quadrupolar interactions. Similar rich physics may be expected in other systems with active quadrupoles.

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Caratterizzazione non invasive di else di spade giapponesi in metallo (*tsuba*) tramite diffrazione di neutroni in tempo di volo XRF e SEM.

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La spada giapponese ha origini molto antiche che risalgono al 500 a.C. Fin da sempre si è trattato di una tradizione attenta sia nella lavorazione della lama vera e propria, che in quella di tutti i particolari che la circondano: oggetti curati con funzioni diverse che vanno dalla semplice decorazione, alla protezione della lama, alla difesa di chi la impugna. La *tsuba* (elsa della spada) è la parte che protegge la mano di chi impugna la spada. Costruire *tsuba* in Giappone era, ed è tutt'ora, un'arte; i produttori di *tsuba* spesso non erano gli stessi che forgiavano le spade, bensì specialisti del mestiere che si cimentavano in decorazioni sempre più accurate. Particolari lavorazioni e decorazioni con l'utilizzo di leghe metalliche di svariato genere, patine e smalti, le rendono oggetti d'arte unici, con un'attenzione quasi maniacale per ogni particolare; tanto da arrivare ad utilizzare leghe diverse per una stessa decorazione al fine di ottenere leggere variazioni cromatiche. Le *tsuba* analizzate in questo studio sono nove, tutte appartenenti alla sezione giapponese del museo Stibbert di Firenze. Risalgono ad epoche diverse: Edo (1603-1868) e Meiji (1868-1912); sono costituite da diversi materiali tra i quali ferro, acciaio e leghe di rame e argento. Al fine di caratterizzarne i tipi di decorazione e di lavorazione sono state utilizzate tecniche analitiche di tipo non invasivo. Essendo opere in esposizione al museo Stibbert, si è cercato di allontanarle il meno possibile dalla loro collocazione ufficiale, effettuando alcune delle analisi in situ. Le analisi in situ sono state realizzate con uno strumento portatile di fluorescenza a raggi X (XRF), con questa tecnica si è potuto ottenere un'analisi elementale qualitativa e quantitativa della parte superficiale (massima profondità 100 μm) delle *tsuba*[1,2]. Una sola *tsuba* è stata poi analizzata con un microscopio elettronico a scansione con microsonda EDX (SEM-EDX) che analizza il campione tal quale (senza campionatura). Anche in questo caso si è trattato di uno studio di tipo superficiale (profondità da 5 a 100 μm) che è stato poi comparato con la precedente analisi XRF. Successivamente è stata condotta una campagna di analisi presso la sorgente pulsata di neutroni ISIS del Rutherford Appleton Laboratory che si trova a Chilton-Didcot, in Inghilterra; utilizzando il diffrattometro a neutroni in tempo di volo (ToF-ND) INES [3]. La diffrattometria neutronica in tempo di volo è un'ottima tecnica analitica che utilizza i neutroni termici per indagare le proprietà microstrutturali dei materiali e ottenere un'analisi quantitativa media delle fasi presenti nel volume indagato. Questa tecnica, applicata recentemente ai beni culturali, offre importanti vantaggi: primo tra tutti quello di essere una tecnica non invasiva, poiché i campioni non hanno bisogno di essere pretrattati e possono essere misurati intatti; in aggiunta l'alto potere penetrante dei neutroni nei materiali indagati permette di ottenere analisi di bulk su campioni di qualche centimetro di spessore come ad esempio i manufatti metallici.

Con questo strumento siamo riusciti a riconoscere le fasi e gli elementi presenti all'interno delle varie *tsuba* e a quantificarne la distribuzione [4], ottenendo così un dato di struttura globale dell'oggetto: approccio non applicabile in modo non invasivo con altri strumenti. Infine con questa tecnica è stato possibile ottenere informazioni quantitative sullo stato di conservazione dell'opera d'arte, andando ad indagare, per esempio, le fasi di mineralizzazione e i prodotti di corrosione. I risultati ottenuti mostrano la particolarità di lavorazione di questi oggetti e il loro stato di conservazione e offrono spunti per caratterizzazioni sempre più specifiche analizzando un più ampio insieme di oggetti.

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Preparation and structural characterization of regularly ordered Ge quantum dot lattices in amorphous matrices

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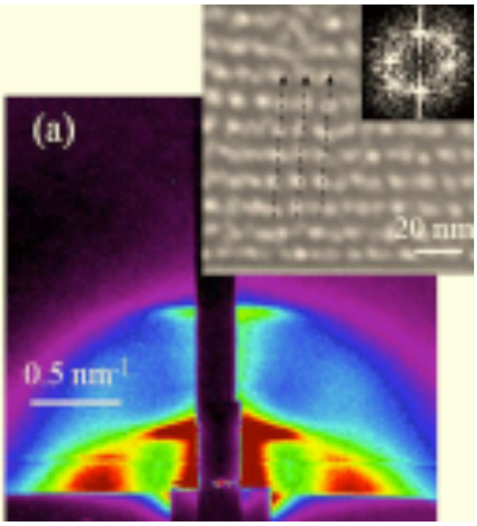
We compare the structural and optical properties of Ge quantum dot lattices in amorphous silica matrix obtained by two recently published techniques for the preparation of regularly ordered quantum dot lattices in amorphous matrices [1,2]. The first technique is self-ordering growth of (Ge+SiO_2)/SiO_2 multilayer at an elevated substrate temperature where diffusion and surface morphology effects drive the self-ordering. The second one is irradiation of (Ge+SiO_2)/SiO_2 multilayer by oxygen ions. The multilayer used for the irradiation is grown at room temperature in this case, resulting with no Ge clusters after the deposition process. The irradiation causes clustering of Ge and ordering of Ge quantum dots in the irradiation direction. We show that the size of the dots and their arrangement can be easily manipulated by the preparation parameters. The structural properties of the films prepared by these methods affect the quantum confinement of the charge carriers which is visible in the absorption properties of the films.



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Local structure of low – Z dopants and defects in semiconductors

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X-ray absorption fine structure (XAFS) can determine the local structure of most atoms in the periodic table. Recently, new opportunities to study dopants and defects in semiconductors have emerged, specifically for those based on low – Z ("light") elements, whose absorption edges lie in the soft X-ray range. This progress stems from improvements in the performance of synchrotron radiation sources and related instrumentation and in the development of computational schemes which are able to reliably simulate XAFS spectra.

On the ALOISA branch line of ELETTRA we have developed a mobile experimental station based on a windowless HP-Ge detector which allows to record XAFS spectra of low-Z dopants to concentrations down to 5×10^{19} at/cm^3; this set-up is available at only a very few other beamlines worldwide. Applications have included: i) the determination of the structure of N – H complexes responsible for the modification of the properties of dilute nitrides [1]; ii) the observation of nitrogen location in ZnO [2]; iii) the detection of B interstitial clusters [3] and SiF_4 molecules in Si ultra shallow junctions [4]; iv) the determination of the bonding geometry of O dopants in GaN [5]. In most cases data analysis was greatly aided by DFT calculation of equilibrium structures and spectral simulation with multiple scattering codes.

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Structure and dynamics of closed melting membranes

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We studied the dynamical and structural properties of large unilamellar vesicles (≈ 120 nm LUVs) of phospholipids (DMPC, $DC_{15}PC$ and DMPC : $DC_{15}PC$ = 1 : 1 molar mixture) in the temperature range around the chain-melting transition, ≈ 3°C wide, with 0.1°C resolution and 0.01°C accuracy. Small-Angle (SAXS) and Wide-Angle X-ray Scattering (WAXS) measurements show that across the transition the vesicle behaves as an ‘evolving membrane’, passing through several different states, each of them being characterized by different proportions of coexisting fluid- and gel-chains molecules. Noteworthy, no kinetics has been detected. On the same samples, a unique and very sensitive laser light scattering technique allows to determine the characteristic times of thermally induced shape fluctuations, connected to the elastic properties of the membranes. Results indicate a clear softening of the membranes in correspondence to the chain-melting transition, as indicated by a manifold increase of the corresponding fluctuation characteristic time. Meanwhile the overall size of the vesicle is not sensibly changed. This softening is likely to be due to the presence of structural defects, eventually driving to local morphological modifications.

The LDM beamline at FERMI@Elettra

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The high intensity of Free Electron Lasers (FELs) makes them particularly suitable for experiments on Low Density Matter (LDM): atoms and molecules entrained by a supersonic beam, as well as rarer species such as radicals, ions, clusters, and combinations thereof, can be conveniently studied, exploring both the linear and the nonlinear regimes of matter-radiation interaction at femtosecond timescales and short wavelengths.

FERMI@Elettra is a seeded source comprising two Free Electron Lasers (FELs) that will generate short pulses (25–200 fs) of VUV (FEL1: 12-60 eV) and XUV/soft-X-rays (FEL2: 60-300 eV; third harmonic: up to 900 eV) with close-to-ideal transverse and longitudinal coherence, and full polarization control (horizontal, vertical, circular). Its design includes a broadly-tunable user laser providing synchronized fs-pulses in the visible and near infrared, for pump-probe experiments.

The LDM beamline at FERMI@Elettra is a large collaborative project for experiments on neutral matter beams and, in prospect, trapped species and mass selected ions. Its initial design is based on the goal of exploiting the unique properties of the radiation pulses produced by FEL1/FEL2 while keeping the greatest flexibility in terms of target system and detection method. Its modular design will allow to easily generate intense beams of neutral atoms, closed-shell molecules, radicals, and pure/doped clusters, the latter ranging from ultracold helium nanodroplets to rare-gas clusters, atomic and molecular van der Waals clusters–especially water–and clusters of refractory materials such as metals and their oxides.

The modular design is intended to allow the use of a set of detectors (also working in tandem, when possible) for photoelectron/photoion spectroscopy, fluorescence emission, and photon scattering.

Metamagnetic transition and magnetic structure of the triple layer ruthenate $S_4Ru_3O_{10}$

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Using neutron scattering we have investigated the magnetic behavior of the triple layer ruthenate $Sr_4Ru_3O_{10}$. Magnetisation measurements on flux-grown crystals [1] point to a ferromagnetic transition at T_c=105 K with an antiferromagnetic component setting in at T*=50 K. In the *ab*-plane a metamagnetic transition is observed at about 2 tesla below T* whilst there is no transition when the field is applied along the *c*-axis. Floating-zone crystals [2] show similar features plus ultrasharp magnetoresistivity steps, a nonmetallic temperature dependence in resistivity for upward field sweeps, and a resistivity drop in temperature dependence for downward field sweeps. These features may suggest that the metamagnetic transition of $Sr_4Ru_3O_{10}$ occurs via an electronic phase separation process with magnetic domain formations. A neutron scattering study on single crystals [3] observed no metamagnetic effect in $Sr_4Ru_3O_{10}$, and no antiferromagnetic component whilst the ferromagnetic component was thought to be in the *ab*-plane and not along the *c*-axis.

To shed light on these contradictory results, we have studied the metamagnetic transition of $Sr_4Ru_3O_{10}$ using a good quality and well characterised floating-zone single crystal on the 4-circle diffractometer D10. The magnetic field was applied in the *ab*-plane (parallel to the [h –h 0] direction) and the scattering plane was defined by the [00l]/[hh0] directions of the crystal. A few selected reflections of the type (*hh*0) and (00*l*) were studied as a function of temperature. We analyze and discuss the results.

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3D refractive index reconstruction in quantitative x-ray phase-contrast tomography using a single-distance data

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X-ray propagation-based phase-contrast computed tomography (PPCT) is a nondestructive phase-sensitive imaging technique for visualizing interior features within samples, and for obtaining quantitative information on their three-dimensional (3D) geometries and properties [1]. The experimental setup of PPCT is identical to the absorption-based CT except for providing the beam is sufficiently spatially coherent, which is available from synchrotron radiation sources and micro-focus X-ray sources (with correspondingly low power), and increasing the sample-to-detector distance (SDD), to let the beam propagate in free space after interaction with the object [2]. Phase-retrieval is a technique for extracting quantitative phase information from PPCT [3]. In order to reconstruct the 3D refractive index of the object, typically phase-retrieval methods require at least two intensity measurements at different sample-to-detector distance (SDD). Therefore, this will sharply increase the experiment time and deliver a higher radiation dose to the samples, which could hinder their biomedical applications. Definitely, phase-retrieval employing only a single SDD PPCT data will boost its applications, and make the procedure much easier [4, 5].

Here, we report the investigations of a method which can quantitatively reconstruct in 3D the refractive index decrement of a quasi-homogeneous object using single SDD PPCT data. The method extends the Born-type approximation phase retrieval algorithm [6], which is based on the phase-attenuation duality ($\varepsilon = \delta / \beta$, with constant ε) and suitable for homogeneous objects, to tomography and we study its application to quasi-homogeneous objects. The noise performance and the influence of phase-attenuation duality hypothesis are also investigated. In simulation, the method allows to quantitatively reconstruct the 3D refractive index decrement for quasi-homogeneous and weakly absorbing samples and it performs well in the practical noise situation. Furthermore it shows a substantial contrast increase and successfully distinguishes different materials in a quasi-homogeneous and weakly absorbing sample from experimental data, even with inappropriate ε value. Data were collected at the SYRMEP beamline at the ELETTRA synchrotron facility, Italy. The energy of 14 keV, SDD=0.6 m and a CCD detector (Photonic Science, UK) with 2004 x 1336 pixels and an effective pixel size of 9 μm were used to acquire the data.

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Present challenges in Biocrystallography data collection and related instrumentation

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In the recent years new trends and challenges have appeared in biocrystallography. With the limited success of expression with recombinant technologies, mammalian proteins are increasingly purified directly from natural sources, with consequent heavy atom derivatization for phasing having a second golden age. One example is the homodimeric mammalian fatty acid synthase (FAS), a 270-kilodalton cellular multienzyme complex, which was purified from porcine mammary gland, and phased to 4.5 Å resolution with MIRAS with U and Pt[1]. In another case the molecular organization of cypovirus polyhedra, purified from insect cells, was elucidated with the 2Å crystal structure of both recombinant and infectious silkworm cypovirus polyhedra determined using crystals of 5–12 microns in diameter. The structure was phased using Au, Ag, Se and I derivatives[2]. At synchrotrons such projects require the provision of automation, microbeams, radiation damage issues and new strategies for data collections. Moreover, low-resolution structures may also be further investigated by complementing crystallographic information with *in-crystallo* spectroscopy. In fact by combining polarized EXAFS and x-ray diffraction data on PSII single crystals, the photosystem II (PSII) Mn_4Ca cluster, which catalyzes oxidation of water to dioxygen, was constrained in geometry and placed within PSII at resolution of 3.5 Å[3].

At PETRA III, the new 3rd generation synchrotron at DESY in Hamburg, the European Molecular Biology Laboratory (EMBL) is building state-of-art beam lines devoted to macromolecular crystallography. MX1 monochromator will be tunable over the energy range 5(4) to 17 keV to allow crystallographic data acquisition on a broad range of elemental absorption edges for experimental phase determination. In addition it will offer Si (311) for narrow band pass for new developments in phasing and *in-crystallo* spectroscopy. This beam line will also provide a very low beam divergence (0.2 mrad (H) x 0.15 mrad (V)) and variable focus size (20 to 100 microns) to adapt to challenging biological projects. We will discuss the challenges of modern biocrystallography data collection and how ideas and perspectives have been transferred into the design of MX1 beam line in particular.

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High pressure single-crystal synchrotron X-ray diffraction study of bloedite ($Na_2Mg(SO_4)_2 \cdot 4H_2O$): a contribution to the knowledge of asteroids and icy satellites

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Abstract

Bloedite $Na_2Mg(SO_4)_2H_2O$ is a common mineral in evaporitic marine sediments. Being one of the phases in the system H_2O-$MgSO_4$-$NaSO_4$, it has a large planetological interest. In fact, the density variations in the Mg-Na-H_2O system involve many aspects of the petrogenesis and physical volcanology of icy planets. Namely structural models of icy satellites are controversial since the crust-mantle differentiation are based on buoyancy forces not well known especially at different depth.

The bloedite structure consists of parallel layers of $MgO_2(H_2O)_4$ and $NaO_4(H_2O)_2$ octahedra, interconnected through SO_4 tetrahedra and hydrogen bonds. The Fundamental Building Block of the structure is the $[Mg(H_2O)SO_4^{--}]$ with finite hetero-polyhedral clusters linked by low-valence cations. We aim to investigate the HP behavior of bloedite in order to determine the equation of state (EoS), the density evolution and the water storage capability with P as well the evolution of H-bond in comparison with other sulphates.

The HP single-crystal diffraction was carried out on a bloedite gem quality crystal at ID-09 beamline of ESRF (Grenoble). A diamond anvil cell with 600 micron diamond culets, He as P medium and ruby chip as P calibrant was used. A flat panel detector, Mar555 (with a 555mm diagonal active area) allowed a very high quality of collected data. Lattice parameters and reflection intensities were obtained by Crysalis software and SHELXL software was used to refine the structure at different *P* up to 10 GPa. EoS was determined with data collected up to 12 GPa and EOS-Fit program. The second order Birch-Murnaghan (BM) EoS fit yields V_0 = 495.6(9) Å^3 with a K_0 = 40.5(7) GPa, whereas a third order BM EoS fit yields V_0=497.6(4) Å^3, K_0 =34(1) GPa and K'=5.8 (4) GPa-1. The lattice parameters compressibility are β_a = -0.0074(4) GPa^{-1}; β_b=-0.0069 (4)GPa^{-1}; β_c=-0.0054 (2) GPa-1 with an anisotropic ratio of 1:1.07:1.37. The bloedite resulted most incompressible along [001], the direction perpendicular to open sheet. The crystal structure refinements showed that the SO_4 tetrahedra are incompressible whereas the bulk modulus of MgO_6 octahedra is 90 GPa and that of NaO_6 octahedra is 42 GPa.

The H-bond evolution were followed through the measurements of O_{donor}-$O_{acceptor}$ distances. The longer distances O6-O1 and O6-O4 (2.854 and 2.955 Å at 0.001 GPa), have a compressibility ranging from 2.8(9) to 4.4 (7)10^{-4} GPa^{-1}, whereas the shortest ones, O5-O1 and O5-O4 (2.715 and 2.742 Å) have a compressibility of 7.7(6) and 9.2(7) 10^{-4} GPa^{-1} respectively. The arrangements of O5-O1 and O5-O4 are along *y* axis whereas O6-O1 and O6-O4 are along *x* axis with a strong component along *z* axis. This configuration explains the large compressibility of a and b parameters with respect to c lattice parameter.

The comparison of structural evolution of bloedite with Ca-sulphate, shows similarities and differences: the bulk moduli of bloedite and gyspum are quite similar, as well as the compressibility of hydrogen bonds. No phase transition was observed up to 12 GPa in bloedite which remains stable at very H*P* at room condition, whereas gypsum undergo to a phase transition at 4 GPa. The lack of a strong structural rearrangement, essential to compensate the dehydration process, would suggest that water remains in the structure of bloedite in the investigated *P* range, while the density increase of about 20 per cent over 10 GPa.

EVIDENCE OF THE ROLE OF Zn AND Fe CATIONS AS DOPANTS IN LEAD ANTIMONATE YELLOW BY X-RAY ABSORPTION SPECTROSCOPY (XAS)

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Naples yellow ($Pb_2Sb_2O_7$) is one of the oldest known synthetic pigments. It shows a cubic pyrochlore structure, obtained by roasting mixtures of Pb and Sb oxides. Naples yellow may exist also in a modified form obtained from a ternary mixture of Pb, Sb and Sn oxides ($Pb_2Sb_{2-x}Sn_xO_{7-x/2}$). Recent studies demonstrate that Zn oxide was also used to produce modified Naples yellow in Renaissance ceramic.

X-ray diffraction and Raman spectroscopy investigations of standard doped yellow pyroantimonates provided evidence that, in general, doping cations (such as Sn^{4+}, Zn^{2+}, Fe^{3+} or exceeding Pb^{4+}) induce significant structural modifications of the pyrochlore lattice of the pigment, suggesting that ternary cations enter the octahedral sites replacing Sb^{5+} ions.

Here we report on the results obtained by XAS investigations carried out at the GILDA beam-line of ESRF (Grenoble, FR) on the role played by Zn and Fe cations in modified Naples yellow, characterising the ions' local properties (interatomic distances, coordination number and oxidation state). The XAS study has been non-destructively carried out on different standard yellow pyroantimonates, as well as on Renaissance ceramic shards from the collection of the *Musei Civici di Pesaro* (Italy). XAS measurements at the Zn-K and Fe-K absorption edges evidenced that Zn and Fe enter the antimonate structure. A*b-initio* structural simulations based on Density Functional Theory were used to simulate both the structure around the metal (via a conventional structural relaxation) and the EXAFS spectra via a DFT Molecular Dynamics. The latter represents a novel and promising method for the analysis of point defects in crystals by EXAFS. The comparison with theory permitted to establish that in both cases the metal occupies the site of Sb. The same structure has been also observed for Zn cations in the yellow pigment of a Renaissance ceramic shard.

The study has been carried out within the joint research activities of the CHARISMA project supported by the 7th F.P. of EU.

Local order of amorphous phase change materials probed by EXAFS

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Chalcogenide alloys, like Ge2Sb2Te5 and GeTe, have recently received a considerable attention because their phase transitions between amorphous and crystalline structure (and vice versa) are accompanied with a huge variation in optical and electrical properties. Moreover, transition times on a nanosecond scale are reported in the literature and all these features have been profitably used in optical (e.g. DVD+RW disc) and electronic devices (i.e. PC-ram). Despite that, the phase changing mechanism is still not clear at a structural level and several models of the local order in the amorphous phase have been proposed. Furthermore, it is known that samples prepared under different conditions show a different crystallization kinetics. In this work, we have investigated by x-ray absorption spectroscopy (XAS) the local order around each component (K edges of Ge, Sb, Te) in three different amorphous GST 50nm thin films: as deposited, ion implanted and laser quenched. Deposition was performed by RF magnetron sputtering from stoichiometric target on a thermal oxidized Si substrate. Samples were irradiated at RT with 130keV Ge^+ ions at a fluence of 10^{14} ions/cm^2. Melt quenched amorphous was obtained by irradiation with a pulsed (12ns) Nd:YAG (λ=532nm) laser and an energy density of 180mJ/cm^2. Both irradiated samples exhibit a higher crystallization kinetics with respect to the as deposited film although, in a preliminary comparison, no major differences are detected in the XAS spectra.

A Fe K-edge XAS study of amethyst

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An X-ray absorption spectroscopy (XAS) study of the Fe local environment in natural amethyst (a variety of α-quartz, SiO_2) has been carried out. Room temperature measurements were performed at the Fe K-edge (7,112 eV), at both the X-ray absorption near-edge structure (XANES) and extended X-ray absorption fine structure (EXAFS) regions. Experimental results were then compared with DFT calculations.

XANES experimental spectra suggest Fe to occur mainly in the trivalent state. EXAFS spectra, on the other hand, reveal an unusual short distance for the first coordination shell: <Fe–O> = 1.78(2) Å, the coordination number being 2.7(5). These results allow to establish that Fe replaces Si in its tetrahedral site, and that numerous local distortions are occurring as a consequence of the presence of Fe^{3+} variably compensated by protons and/or alkaline ions, or uncompensated.

On the basis of DFT calculation the observed <Fe–O> bond length is compatible either with a tetrahedral Fe^{IV} or a Fe^{III} coupled to a monovalent (H^+, Li^+) charge compensating ion. Taking into account the XANES data, we suggest that Fe mainly occurs in the proton-compensated trivalent state. Fe^{4+} ions result to be non detectable.

Further studies are in progress to determine the position of Fe in quartz specimens of different colorations (citrin, green quartz, …) and having undergone thermal treatments (discolorated amethyst). In the latter case , namely, the <Fe–O> distance stretches to 1.85(1) Å in agreement with DFT calculations for tetrahedral Fe in quartz.

The Time-of-Flight Spectrometer for small angle inelastic scattering BRISP

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The neutron Time-of-Flight (TOF) BRIllouin SPectrometer BRISP for inelastic neutron scattering was developed and constructed at ILL's High Flux Reactor (HFR) for investigating a host of open scientific problems in the low-momentum region with relatively high incoming neutron energies (Q range between 0.3-1.6 $Å^{-1}$; incident energy in the range 20-84meV).

With this dedicated instrument the high-frequency dynamics of atomic nuclei and electron spins is studied in rather different materials ranging from biological and magnetic systems to disordered systems, like dynamically soft glasses, liquids and compressed gases.

The spectrometer began its experimental activity in the second half of 2007. Since then BRISP has shown its capability in approaching and providing data in a plethora of disordered and magnetic systems. Originally designed for the investigation of these kind of samples, BRISP has immediately found a natural experimental extension to the study of those systems that have attracted a growing interest in the scientific community in recent years e.g. confined liquids, glasses, and biological macromolecules (proteins, nucleic acids, lipid multilayers, liposomes, model systems to understand the collective dynamics in hydration water). In the present poster we present some example results showing the versatility of the instrument in the study of collective excitations in different systems and single particle dynamics in quantum liquids and solids.

Structure and bioactivity of calcium-phosphopeptides complexes.

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Casein phosphopeptides (CPPs) display the ability to form aggregates with calcium and promote the mineral uptake in models of intestinal cells. An optimal ratio between Ca^{2+} and CPPs is found to result in maximum bioactivity. A parallel study performed on living cells and by scattering techniques, in the same concentration range compatible with cell viability, has shown that the maximum bioactivity corresponds to maximum peptide- Ca^{2+} complexation. X- ray scattering allowed to estimate the dimension of the small calcium rich structures within the peptide- Ca^{2+} complex.

Dynamics of Physical Hydrogels Based on Partially Hydrophobized Hyaluronic Acid

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Hyaluronic acid (HYA) is a natural polysaccharide able to form viscous solutions or physical gels; it is largely used in biomedicine as the main component of scaffolds for tissue engineering and as basic material for drug delivery platforms. Chemically modified forms of HYA have been introduced to produce more 'stiff' gels improving their viscoelastic properties at low saccharide concentration. Among them, HYADD™ 4 is a chemically modified hyaluronate with 2–3 % of the carboxylate groups grafted with a hexadecylic amine moiety. The diffusive dynamics at the molecular level has been investigated in both systems by quasielastic neutron scattering. We have been able to investigate the dynamic behaviour of the solvent and that of the random saccharide network using spectrometers with different energy resolution ranging from ~ 10^{-3} to 10^{2} μeV: the spin-echo spectrometers: IN11 at the ILL (Grenoble), the backscattering spectrometers SPHERES at the FRM-II reactor (Munich) and IRIS at the ISIS neutron source (Chilton, UK), and the time-of-flight spectrometer NEAT at the Helmholtz-Zentrum (Berlin).

Only a small amount of water is closely associated to the 3-D network: water molecules within the large volumes of the gel scaffolding diffuse freely with a diffusion coefficient very close to that of bulk water. Only small differences appear in the local dynamics of HYA and HYADD polymer network probed at the ps time-scale.

AGGREGATING PROPERTIES OF MBP PURIFIED FROM BOVINE BRAIN.

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The myelin basic protein (MBP), is involved in myelin development and maintenance of myelinic membrane adhesion through the electrostatic interactions between the protein and the lipid bilayer. The 18.5 kDa isoform of myelin basic protein (MBP) is a major component of the myelin sheath in the central nervous system of higher vertebrates, and a member of a larger family of proteins with a multiplicity of forms and post-translational modifications (PTMs). The 18.5 kDa protein is the exemplar of the family, being most abundant in adult myelin, and thus the most-studied. It is peripherally membrane associated, located between the cytoplasmic apposition of surfaces of the oligodendrial membrane, but has generally been investigated in isolated form. It is a 169-residue water-soluble protein, which constitutes 30% of the total protein of the multilamellar myelin sheath. It has been extensively studied for its implications in multiple sclerosis disease. MBP has a single tryptophan residue and no cysteine residue. Moreover for the large number of charged residues throughout the protein's sequence and its low overall hydrophobicity, it has been classified as an intrinsically unstructured protein (IUP) (1), with a high proportion (75%) of random coil, but postulated to have core elements of β-sheet and α-helix. Moreover, in acqueos solution, the MBP's thermodynamically stable state is a flexible coil, with about 20% of secondary structure composed of β-sheet. On the basis of these statements and of our results we postulate that neutral pH conditions would lead the protein to assume a partially unfolded state that produced the formation of aggregates. Moreover, has been observed a further higher-order self- association of the protein into spherical structures called "spherulites" that, under polarizing light microscope, exhibit a "maltese- cross" extinction pattern and have been observed in brain sections from a rat model of Alzheimer's disease (2). The observed MBP spherulites show dimension variable, ranging from 41 to 61 μM, visible both under crossed and parallel polar light microscopy. Recently has been shown that MBP has an important role in one of the major pathways for β-amyloid clearance, and in particular in its proteolytic degradation. However, widespread and diffuse myelin breakdown has been reported in Alzheimer's disease patients, with levels of MBP significantly decreased in their white matter (3). The aggregation properties of MBP, evidenced by optical microscopy has been confirmed by Congo-red dye binding to protein aggregated state. In fact difference spectra titration of Congo red binding to MBP show clearly the formation of a complex between this dye and MBP fibrils. The experimental spectra evidence a net shift of the maximum of absorption of Congo red of about 75 nm towards longer wavelength, exhibiting the characteristic Congo red birefringence. The property of MBP to form aggregates organized in such structures, could therefore, award to the protein a further involvement in diseases correlated with the formation of amyloid.

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Stabilization properties of trehalose on lysozyme refolding kinetics in presence of strong denaturant.

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The protein stability provides a fundamental biotechnological element for successful utilization of enzyme for industrial and pharmacological application. At this regards the discovery of compounds capable of preserve protein's native conformation and, therefore, the equilibrium constants of biological reactions, represent one of the main elements of biological and biophysical application. In recent years, molecules called organic solutes or small stress molecules have attracted researchers attention. These founding arise from the observation that some life forms in nature, have successfully adapted to specific survival strategy, able to counteract severe environmental stresses[1]. Lysozyme is widespread in animals and plants. It is found in mammalian secretions and tissues, saliva, tears, milk, cervical mucus, leucocytes, kidneys and in egg white. It can act to some extent as an innate opsonin, or as an actively lytic enzyme and there are great interests about this molecule due to its possible utilization as a "natural" antibiotic and as a marker in the diagnosis of disease. Hen egg white lysozyme (EC 3.2.1.17) is a 129-residue protein stabilized by four disulfide bonds, with a molecular weight of ~14.3 kDa. Its native conformation displays four α-helix structures, which build the first domain. A second domain is made out of a three strand antiparallel β-sheet. Take into accounts these elements we analyze lysozyme conformational changes, dynamics and biological activity in presence of a strong denaturant and the same plus trehalose correlating the unique set of information carried out by ESI–MS hydrogen-deuterium (H/D) exchange experiments, activity measurements, circular dichroism and neutron spectroscopy. Protein refolding process is a kinetically competitive process between the folding and aggregation and the suppression of the this latter process is the key point for enhancing the protein refolding yield. The stabilizing influences of trehalose became clearly visible with the increasing of time of incubation. In fact the presence of 1.0M of trehalose in the reaction mix led us to obtain up to 70% of renaturation after 20 days of incubation from samples completely denatured, while this percentage is of only 47% in its absence. The same results were also obtained after 2, 5 and 10 days of incubation with an increase in the percent of refolding yield of 1.26-, 1.38-, 1.46-fold respectively in the presence of 1.0M trehalose. Further results arise through hydrogen exchange labeling experiments monitored by ESI-MS. In fact rate of exchange is very rapid in the case of the former, reaching up 72% of the total number of exchangeable protons after 1 hour of incubation, while the same result is obtained in about the double of time in the presence of the latter. It is evident that trehalose remarkably influenced this exchange and consequently the local protein environment and solvent accessibility to the amide peptide backbone, as shown also by neutron scattering mesearaments.

The present results demonstrate that trehalose is a feasible compound capable to reduced conformational changes induces by strong denaturant as evidenced by hydrogen exchange electrospray ionization mass spectrometry and circular dichroism measurements. Moreover the number of hydrogens exchanged, found in our experiments, is not as great as that in the fully reduced denatured protein, possibly because some hydrogens are protected in non-native helices, forming inaccessible cluster to solvent, able to clarify to high refolding yield of lysozyme. The presence of only one peak, in ESI-MS spectra, indicates either that both native and denatured lysozyme have only one conformation or that if multiple conformers exist, they interconvert rapidly compared to the exchange rate.

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Trehalose influences on autocatalytic cleavage of myelin basic protein.

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Myelin basic protein (MBP) plays a vital role in the structure and function of the myelin sheath. In human the 18.5-kDa isoform of MBP predominates, although it exists as a multitude of charge isomers resulting from extensive and varied post-translational modifications. In the myelin sheath, MBP is localized in the aqueous interstitial space sandwiched between two lipid bilayers, in strictly contact with the polar heads of the lipids. Additionally, MBP is capable of binding actin and anionic phospholipid bilayers simultaneously (1), indicating that MBP could potentially serve as a link between microfilaments and the cytoplasmic leaflet of the oligodendrocyte membrane. Recent literature data show autocatalytic cleavage properties of isolated and purified MBP, attributable to a single serine residue (Ser151) among the total of 18 seryl residues involved in the catalysis in pH condition near the neutrality.

Many of the reported studies in literature concerning this condition have concluded that MBP has little, if any, organized structure in aqueous solution, behaving essentially as a random coil. In contrast, theoretical predictions of MBP secondary structure indicate that it should have regions of repetitive secondary structure; in particular, α-structure and β-turns appear to have a high probability (2). So in order to partially elucidated this discrepancy we analyzed secondary structure in 18.5-kDa isoforms of MBP by FTIR spectroscopy. The data indicate that the protein shows, in this conditions, the predominancy of a disordered structure, although some elements of secondary structure (α-helix and β-turns) are present in its FTIR spectra. Starting from this experimental evidence we undertake a detail study of possible stabilization properties of the disaccharide trehalose on autocatalytic cleavage properties of MBP. The analysis of protein conformational states by SDS-PAGE, let us to state that trehalose completely avoid autocatalytic cleavage properties of MBP also after many days of incubation at 37° C at pH 7.4. In fact only after few hours of incubation in absence of the disaccharide the electrophoresis protein band completely disappeared with an evident smear of the band, characteristic of the autocatalytic properties of the isolated protein. On the other the band is well-defined and evident incubating the protein solution in the same experimental condition but in the presence of 0.4 M of trehalose, with the absence of degradation process up to three days, supporting the possible utilization of the disaccharide as compound capable of preventing autocatalytic cleavage of MBP. To further support these experimental evidences, we perform analysis of MBP enzymatic activity, according to its esterase-like ability to split ester bonds. The data reveal that samples incubated without disaccharide lose this activity in the early phase of incubation and almost all after one day of incubation, while it is preserved for over three day in the presence of trehalose.

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Effects of cationic distribution and spin-canting in $CoFe_2O_4$ nanoparticles on saturation magnetization.

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In the last years, the magnetic properties of nanosized particles of spinel ferrite oxides have been attracting a lot of interest for applications in biomedicine.[1] In these systems, the most relevant effect of the size confinement is the presence of non collinear (canted) spin structure. Besides, in ferrite oxides $MeFe_2O_4$, where Me is a divalent cation, a further effect is the particle size dependence of the cationic distribution in both tetrahedral (T_d) and octahedral (O_h) sites, strongly affecting the magnetic properties of the particles, e.g. saturation magnetization and magnetic anisotropy. Thus, the magnetic behaviour of ferrite nanoparticles assembly is due to a complex interplay of such effects.[2]

$CoFe_2O_4$, nanoparticles ($\langle D \rangle = \sim 6$ nm) prepared by a sol-gel autocombustion technique have been investigated through the combined use of DC magnetization measurements, Neutron diffraction and ^{57}Fe Mössbauer spectrometry (in high and low magnetic field). Neutron diffraction measurements give clearly evidence for the typical ferrimagnetic structure of the inverse ferrites while low temperature (10 K) Mössbauer spectra in high magnetic field (8T) show non-zero intensity for lines 2 and 5 and the presence of two Fe based components. This suggests a non-collinear ferrimagnetic structure in both T_d and O_h sublattices. The comparison between Mössbauer and neutron diffraction results gives new insights about the relation between spin canting and cationic distribution, allowing to justify the experimental value of saturation magnetization.

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SAXS investigation of early stages of precipitation in Mg alloys

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Abstract

Age-hardenable rare earth (RE) metal-based Mg alloys have received particular attention in recent years due to the interesting possibilities for their application in the aerospace and automotive industry [1]. A correlation between microstructure and mechanical properties was determined through the structural characterization of hardening precipitates formed during alloy thermal treatment, and different compositions have been proposed to overcome the problems of high temperature applications [2]. Although an extensive literature already exists on the transformation sequence in age-hardenable Mg–RE-based alloys [3–10] and advanced experimental techniques have been adopted to investigate the early stages of the phase transformations induced by thermal treatment [11], the initial formation of hardening precipitates in Mg–RE systems is not yet fully clear.

In order to better clarify this point, we have recently applied small-angle X-ray scattering (SAXS) to the study of the early stages of precipitation in two alloys: EV31 [12] and WE43 [13]. The evolution of the precipitates, in terms of size, volume fraction and number density, was determined *in situ* as a function of ageing treatment time at 150°C and 200°C.

The results of these experiments are presented and reliable hypotheses on the precipitation mechanisms and sequences are discussed, also on the basis of other experimental techniques such as TEM, DSC, microhardness, electrical resistivity and positron annihilation spectroscopy.

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SANS Study of Radiation Damage in Nuclear Steels

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Abstract

This contribution presents the results of recent studies carried out by means of small-angle neutron scattering (SANS) to characterize the microstructural radiation damage in ferritic/martensitic steels for nuclear applications (fission and fusion). It is in fact well known that complex phenomena occur in such steels under irradiation, such as the precipitation of new phases and the growth of microvoids and helium bubbles. SANS is therefore a very powerful technique for such studies, also because it allows to distinguish the presence of magnetic and non-magnetic defects via the separate analysis of the nuclear and magnetic SANS components.

The SANS measurements have been carried out at the D22 instrument at the High Flux Reactor of the ILL-Grenoble. The investigated material (Eurofer97, 9Cr 1 W, 0.2 V, 01 c wt%) had been submitted to neutron irradiation at 250°C up to an irradiation dose of 16 dpa (displacement per atom); for each irradiated sample a reference sample, submitted solely to the thermal treatment, was measured in order to isolate in the irradiated samples the genuine effect arising from the irradiation. The SANS data were the transformed to obtain the defect distribution (microvoids) by two different methods: cubic B-spline functions in logarithmic representation and Beaucage model based on a fractal representation of the investigated system, this second one providing a better quality fit. These results are presented and discussed with reference to microstructural radiation damage evolution as a function of the irradiation dose.

Investigation of the electronic structure of ETS-10 and ETS-4 using RIXS at Ti K-edge

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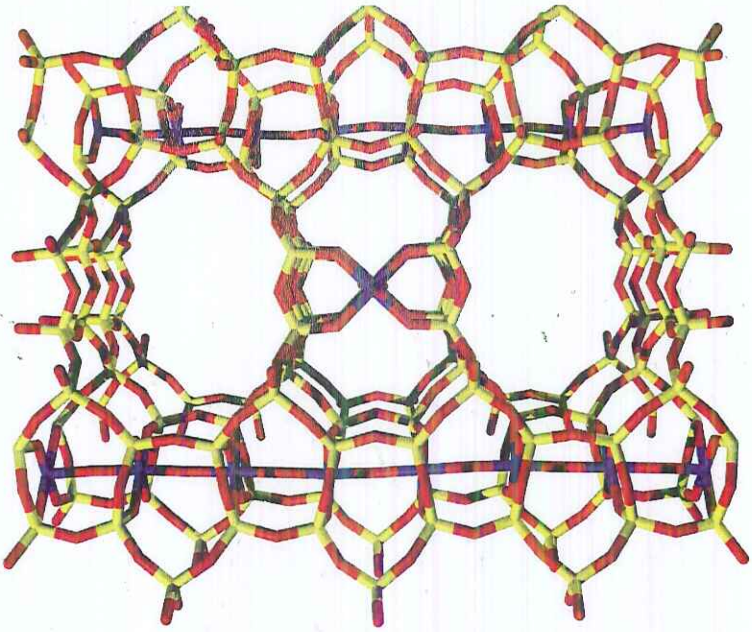
We present the study of the valence electronic states of Ti-zeotype materials like ETS-4 and ETS-10 using Ti K-edge X-ray absorption and emission spectroscopy. ETS-4 and ETS-10 are microporous Ti-silicalite that contain octahedral coordinated monatomic semiconductor –Ti-O-Ti-O-Ti-O- chains in their frameworks (see the figure: Ti blue, O red and Si yellow). The chains are isolated from one another by a siliceous matrix representing attractive systems not only for applications as quantum wire systems but also from the spectroscopic point of view. It will be shown that coupling the obtained experimental spectra with DFT and multiple scattering codes a complete overview of the electronic structures can be reached.



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Partnership for **S**oft **C**ondensed **M**atter

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A Partnership for Soft Condensed Matter (PSCM) between the ILL and the ESRF has been set up. It allows users to characterize samples before their experiments at both the ILL and ESRF and it facilitates the performance of complementary *in situ* measurements. The partnership is also developing complex sample environments for advanced surface and solution science experiments. Soft Matter laboratories at the moment are hosted both at the ILL and ESRF, while waiting for the construction of a new building that will host the Partnership from 2013 on.

Equipment for sample preparation and characterization is already available. Users who wish to use the facility in conjunction with neutrons or synchrotron radiation measurements should indicate this when making their request for beamtime.

The scientific and technical goals of the PSCM are the following:

- Development of most essential complementary techniques for the optimization of neutron and synchrotron experiments.
- Provision for delicate sample preparation onsite.
- Exploitation of the infrastructure for user service, in-house and collaborative research.
- Promoting complementary and innovative research using synchrotron and neutron techniques.
- Development of advanced sample environments for neutron and synchrotron research in Soft Matter.
- Training of early-stage researchers new to the field of neutron and synchrotron techniques applied to Soft Matter research.

In the poster a presentation of some recent results obtained with the use of PSCM equipment are shown, together with the information on the available instrumentation and future developments.

Academic Institutions are invited now to join the PSCM initiative. A draft of the Collaborative Partner Agreement can be downloaded from http://www.ill.eu/pscm

Lipid/saccharide complexes for drug delivery

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Cancer therapy is mainly based on the use of drugs with poor-solubility in water and high toxicity for healthy cells. Vectors, like lipid-based nanoparticles, have been developed to solve these limitations of conventional drugs. The size and surface characteristics of lipid/chitosan particles have been optimized to increase their circulation time in the bloodstream and to improve the biodistribution of the active species. The joint use of dynamic light scattering, Z-potential, small angle neutron (D11 @ ILL Grenoble and V4 @ HZB Berlin) and X-ray scattering (ID02 @ ESRF Grenoble) techniques gave a clear picture of the structure and of the morphology of these nanovectors. They are composed by a hollow core surrounded by a variable number of lipid bilayers with chitosan-water mixture sandwiched between two subsequent bilayers. This arrangement is similar to that observed in DNA-lipid complexes. The particle multilamellarity can be tuned by varying the chitosan/lipid ratio in the starting solution as well as by addition of lipophilic excipients like isopropyl-myristate. We showed that multilamellarity is also directly related to the loading capacity of the vectors: a higher number of layers leads to a higher amount of encapsulated drug. The connection between the lipid/saccharide ratio and the multilamellarity has been investigated and confirmed using a binary lipid mixture instead of commercial lecithin.

The amount of drug released by the nanoparticles, when monitored vs. time, exhibited a usual initial rise followed by a saturation that is reached within two hours for all the samples considered. In all the analysis performed a certain amount of drug is never released and appears to be permanently trapped within the particle. To obtain a full release of the drug it was necessary to degrade the particles by an efficient selective enzymatic degradation based on the knowledge on the structure of the particle outer shell. This work indicated that the correct functioning of the vectors and the tuning of their properties can be easily achieved once the internal structure was known. The results shown here indicated also that the combined use of advanced techniques allowed a detailed characterization of complex drug delivery systems.

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COMBINED STUDY OF STRUCTURAL PROPERTIES OF METAL-ORGANIC FRAMEWORKS CHANGING ORGANIC LINKERS AND METAL CENTERS

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Owing to high surface area, Metal-Organic Frameworks (MOFs) have shown good storage capacity. The high surface area of MOFs is accessible only upon removal of solvents from the pore and channels. Depending on the type of solvents and its bonding within the framework different methods have been developed to remove solvents without losing the crystallinity and porosity. Nothwithstanding, many MOFs are unstable to such treatment showing degradation of framework while some shows structure transformation from crystalline porous structure to crystalline non porous framework. For this reason there is an important work of engineering to find a good compromise between pore size and structural and thermal stability changing both organic linkers and metal centers.

In this work we present a combined theoretical and experimental study, applying both diffraction and EXAFS technique, on Zirconium based UiO-66 and UiO-67 and Hafnium based UiO-66 MOFs.[1-4] For each samples we studied the structure before and after solvent removal. We observed an high stability for all samples and similar behaviors for the different MOFs with the reduction of coordination and slight deformation of the metal center after the solvent removal.

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A PRELIMINARY TR-XAFS STUDY OF PYRIDINE PHOTODISSOCIATION IN Ru(bpy)$_2$(py)$_2$ COMPLEX

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The unique photophysical and photochemical properties of metal complexes have been successfully exploited in numerous medical and technological applications. Among these, we are currently studying cis–[Ru(bpy)2(py)2]Cl2, an anticancer agent which can be selectively activated in cancer cells by light. [1] The potential of this complex, and of similar derivatives, as cytotoxic agents depends on the excited-state features which control the nature of photoreaction intermediates and photoproducts. For this reason the structural determination of transient species is very important.

In the last years synchrotron-based time-resolved techniques are becoming successful in detecting ultrafast structural changes in molecules and match perfectly with our purposes. So we performed both pump and probe Wide Angle X–ray Scattering (TR–WAXS) and X–ray Absorption (TR–XAFS) experiments with sub-ns time resolution to investigate the light-induced process of our complex in water solution. A TR–WAXS experiment on the same system, in the sub-μs time scale, was able to detect the release of one pyridine (py) ligand from the metal centre and the subsequent coordination of a water molecule within 800 ns from laser excitation[2]. The goal of this new TR–XAFS study, with improved time resolution, is to obtain information on the progressive py dissociation and solvent molecule coordination.

Data were acquired at Argonne Photon Source (APS) on the beamline 11-ID-D, using a femtosecond laser (λ=351nm) as pump pulse, and X-rays as probe with 5 different time delays: 150ps, 500ps ,1 ns, 2 ns, 3 ns. Several spectra were acquired for each time delay to improve the signal to noise ratio. After data normalization, to each spectrum of the excited system was subtracted the corresponding spectrum of the ground state measured immediately before the pump excitation and then all differential spectra of the same time delay were averaged. Such differential approach was essential to enhance the small differences due to the high dilution of the complex in solution and of the further low percentage of the excited species.

We present here some preliminary results where it is possible to appreciate a trend in the $\chi(k)$ experimental curves as a function of the time delay. Furthermore it is presented a comparison with a differential spectrum of the aquo-photoproduct [Ru(bpy)$_2$(py)(H$_2$O)]Cl$_2$ on which a full structural analysis was performed. The analysis of the time-resolved spectra is still in progress but presented several difficulties to be overcome. In fact the uncertainty on the number and percentage of excited species increase the number of parameters to be optimized during the fit of the experimental curves. An important support will be given by TD-DFT calculations and by other TR-experiments on the same system.

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PICASSO: En route to digital detection for mammography with synchrotron radiation

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The Synchrotron Radiation for Medical Physics (SYRMEP) collaboration in Trieste, Italy is actively engaged in developing techniques in optimizing the quality of radiological examinations making use of X-rays generated by one of the bending magnets of Elettra Synchrotron Light Source with the following key features: (a) monochromaticity (0.2% bandwidth), (b) energy tunability in the range 8-32 keV, and (c) high photon flux.

One significant achievement was reached when the team has initiated the first clinical trial in mammography using phase contrast techniques [1-2]. Commercial screen-film systems have been used as detector for this study. The extraordinary characteristics of the beam however have pushed the development of a digital detector capable of exploiting these properties. In addition, the detector must be able to meet requirements for in-vivo mammographic sample imaging such as (a) fast acquisition time, (b) reasonably low dose delivered to the patient at (c) high spatial and contrast resolution.

For the said purpose, a double layer detector has been developed within the PICASSO (Phase Imaging for Clinical Application with Silicon detector and Synchrotron radiatiOn) project funded by INFN-Trieste. The detector is operated in the 'edge-on' configuration, coupled to MYTHEN-II single photon counting ASICs developed by Paul Scherrer Institut [3-4]. It is based on silicon microstrip sensors of strip pitch 50 μm, height 300 μm and depth 15-20 mm. The current detector prototype covers 21 cm in length, making it sufficiently large to accommodate in-vivo breast samples in the radiological hutch of the SYRMEP beamline of Elettra.

We report here the results of the detector characterization in terms of rate capabilities, contrast and spatial resolution using the new read-out system. Images of standard mammographic test objects and in-vitro breast samples were gathered in absorption and phase contrast modes at fast acquisition times. The results of the measurements are promising, and pave the way to clinical runs.

KEYWORDS: digital detector, mammography, silicon microstrip, synchrotron radiation

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Self-assembly and stability of G-Quadruplex: counter-ions, pressure and temperature effects

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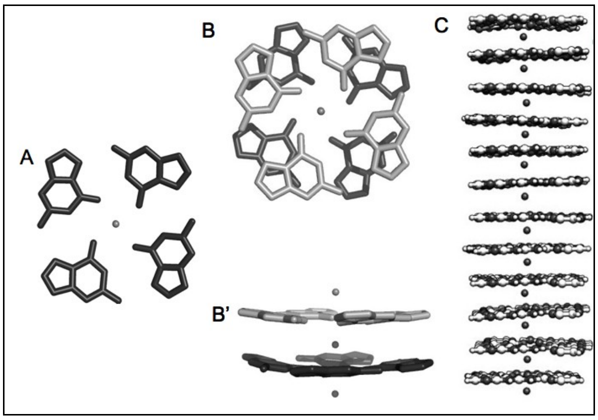
The important role of G-Quadruplex in biological systems is based on two main features: composition and stability of telomeres, and activity of telomerase. The G-Quadruplex structures are formed by supramolecular organization of basic units called G-quartets, that are planar rings constituted by four guanosines linked by Hoogsten hydrogen bonds. G-Quadruplex formation requires the presence of monovalent cations, since they stabilize the structure by coordination with the eight oxygen atoms in the central cavity of two adjacent tetramers.



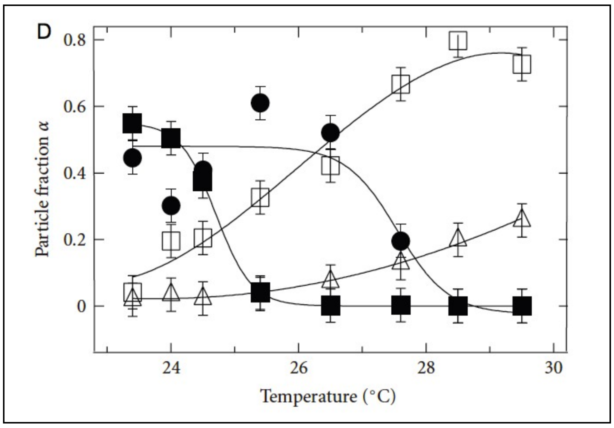


Figure 1 (left frame): **A**: G-Quartet, **B**: G-Octamer (top view)**, B'**: G-Octamer (side view), **C**: G-Quadruplex. **Figure 2 (right frame):** Temperature dependence of the fractions of guanosine molecules assembled in monomers (△), G-quartets (□), G-octamers (■) and G- quadruplexes (●)

We performed X-ray diffraction experiments on samples with several water contents (50-20% H_2O), at increasing pressures (ranging from 1 to 2000 bar). Results evidenced the presence of two phases (Cholesteric and Hexagonal) in diluted samples, while more concentrated samples (30-20% H_2O) presented just the hexagonal phase. In all the investigated samples compression increases the system disorder.

We also studied more diluted samples by small angle X-ray scattering (SAXS) in the temperature range between 20-60°C. Data obtained from SAXS measurements showed that more stable and larger particles can be obtained increasing the KCl counter-ions concentration. The temperature stability of the aggregates increases at increasing counter-ions content, too. In particular , SAXS results demonstrated the existence of two different quadruplex unfolding equilibria, one below and one above the octamer dissociation temperature.

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Magnon dispersion in $(CaCuO_2)_n(SrTiO_3)_n$ superlattices studied with high resolution Resonant Inelastic X-ray Scattering

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Cuprate-based superlattices (SLs) can be considered as new, artificial materials belonging to the family of high-T_c superconductors, offering the opportunity of freely choosing the two building blocks [1,2]. We have studied $(CaCuO_2)_n(SrTiO_3)_n$ (CCO/STO) SLs in which the CuO_2 planes of the infinite layer CCO are alternated to the charge reservoir buffer layer of STO. Although not superconducting, these SLs constituted of two insulating materials show a relatively low sheet resistance at room T. Their peculiar transport properties make them particularly interesting for adding new experimental information to the old puzzle of high-T_c superconductivity. We devoted special attention to the crystal field excitations and to the magnetic excitations (magnons). These two families of elementary excitations can tell us how the electronic and magnetic backbone structures of the infinite layer gets modified at the interface to STO.
High resolution resonant inelastic x-ray scattering (RIXS) at Cu-L_3 edge is a powerful tool for measuring magnons in cuprates, as we have recently demonstrated both theoretically [3] and experimentally [4]. Moreover the study of magnons is interesting due to their possible connection with high-T_c superconductivity, as supported by our recent data [5].
Using the AXES spectrometer at the ID08 beam line of the European Synchrotron Radiation Facility (ESRF) we have carried out RIXS measurements at Cu-L_3 edge on CCO_n/STO_n SLs with n=2,3 and we have compared them with measurements on bulk CCO. RIXS data show very clear magnon dispersion in both SLs and bulk CCO. In particular, in the SLs we found a decrease of the superexchange coupling when n decreases, i.e. the in-plane magnetic coupling diminished when the interface are made more dense. Moreover the persistence of dispersing magnons even for n=2 gives a hint on the limits of low dimensional quantum magnetism.

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ROLE OF WATER ON FORMATION AND STRUCTURAL FEATURES OF MAYA BLUE.

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The Blue Maya (BM) is an artificial pigment appeared around the 800 A.D , made and used in murales, pottery, sculptures by Mayas and other people in Mesoamerica [1]. BM is resistant to age, acid, weathering, biodegradation and even modern chemical solvents. The chemical reasons explaining how the compound becomes inert to the chemical aggressions are still under debate. Water seems to play a fundamental role in the interactions between indigo and clay.
For this reason the changes of the zeolitic, structural water during the formation of blue maya and the role played during the folding fenomena has been analysed in the present study by mean neutron inelastic scattering. We monitored the formation of Maya Blue by heating a palygorskite-indigo mixture and measuring the S(Q,W) response function on the IN6 neutron spectrometer at ILL, France. The recorded data gave rich information on several aspects of the processes. Because in our samples the incoherent scattering comes only from hydrogen atoms in this case the incoherent scattering (flat background in Q) is very sensitive to the amount of released water and gives information on the dehydration process. The simultaneous analysis of the elastic scattering and the incoherent scattering gave us a unique possibility to observe in parallel the dehydration process and the change of clay structure (folding). We observed that the folding temperature in palygorskite depends very much on the atmosphere (experiments were under vacuum). We quantified the amount of zeolitic water released during the Maya blue formation. We also demonstrate that a quite resistant pigment can be obtained by zeolitically dehydrating the palygorskite-indigo mixture by means of vacuum, without any thermal treatment.

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Structure of hyaluronic acid solutions

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Structural properties of hyaluronic acid and of a hydrophobically modified derivative were investigated by laser light, neutron and X-ray scattering. Samples of both polymers were prepared over a wide range of concentrations, 0.1 – 10% bw, spanning over both the dilute and the semidilute regime. The hydrophobic modification induces non covalent entanglement at very low concentration, lower than 1%, where the natural analogue, although macroscopically viscous does not show an intimate gel structure. Mixing the two species results in intermediate structures with maximum effect for equimolar mixture.

X-ray absorption spectroscopy on Cr and Ni surroundings to study the metal induced crystallization of amorphous Silicon thin films

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EXAFS investigation about the process of low temperature Metal Induced Crystallization (MIC) on a series of Me/a-Si and a-Si/M thin films on Fused Silica (FS) substrates (Me=Cr, Ni) have been carried out at BM08 GILDA Beamline of ESRF (Grenoble, F), in total reflectance and standard x-ray beam incidence.

The films were grown by electron beam deposition method and annealed at different temperatures, either during or after deposition. Significant changes in chemistry around the diffusing metal with temperature are observed.

EXAFS documents that in FS\Cr\a-Si series (where samples are *post-annealed* at 200, 300, 400, 500, 600, 700 °C for 1 hr) the metal Cr content (in presence of a unexpected significant oxide contamination) remains almost constant up to 500, while at 600 and 700 C there is sudden disappearance of metal chromium with the evolution of a new phase of $CrSi_2$, which is expected to act as nucleating agent for MIC process. On this films it was impossible to detect Cr diffused from the bottom layer to the upper surface also in samples post annealed for long time.

A similar deposition carried at 500 °C was measured in both ReflEXAFS and standard incidence geometry. It shows the presence of a small fraction of $CrSi_2$ in the a-Si layer in both top surface and bottom layers.

EXAFS analysis carried on Cr on top films (FS\a-Si\Cr) indicates that at 400 °C deposition temperature, most of Cr is diffused into the a-Si matrix and forms a stable $CrSi_2$. Apart from this, some part of Cr is oxidized as Cr_2O_3: this oxidized phase is predominant in the upper top layer, that is investigated in the total reflection geometry. Cr on the top is a favorable geometry for the diffusion of Cr in to *a*-Si matrix to start the metal induced crystallization process.

A similar set of measurements has been done very recently (July 2011) on Ni containing films. The main difference with Cr is the highest mobility of Ni into the a-Si layer, because the presence of Ni on the surface can be monitored in Total Reflectance geometry also in non annealed samples. It has been thus possible to monitor changes on the local environment of Ni at the upper surface of the a-Si layer, as a function of temperature and time of the post annealing process. An other difference is the lower content of contamination with metal oxides.

The analysis of Reflectivity curves, together with that of XANES and EXAFS spectra at Ni k-edge is in progress.

Femtoscale magnetically induced lattice distortions in multiferroic $TbMnO_3$

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The discovery of spin-cycloid multiferroics, in which the onset of non-collinear magnetic order leads to a spontaneous ferroelectric polarization, has generated considerable interest. While comprehensive, microscopic descriptions of their magnetic structures have been obtained, our understanding of the ferroelectric state itself is still emerging. Two competing theoretical scenarios have been proposed: one purely electronic, without ionic displacements; one based on anti-symmetric exchange interactions, with ionic displacements.
Experimentally it has hitherto proven to be impossible to resolve the individual ionic displacements. Here we report the observation of ionic displacements in $TbMnO_3$ which are found to be in the femtometre range. Our X-ray polarimetry technique uses an applied magnetic field to produce interference between charge and magnetic scattering, allowing the ionic displacements to be determined with high sensitivity on an absolute scale. Moreover, we show that the ionic displacements revealed by our experiments make a significant contribution to the ferroelectric polarization and arise from both symmetric and anti-symmetric interactions.

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Local environment of Er in ZnO-PbO Tellurite glasses

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Optical properties and structural parameters of Erbium doped tellurite glasses ($70TeO_2$ $(30\text{-}x)ZnO\ xPbO)_{0.99}$ - $(Er_2O_3)_{0.01}$ (TZPE) with x=5, 10, 15, 20 have been studied by different characterization techniques (EXAFS and Optical Spectroscopy) as well by the theoretical analysis (Judd-Ofelt method).

The effect of PbO addition and the changes in the optical properties were studied using the Absorbance and visible Photoluminescence. The variation in the optical properties has been attributed to the strong crystalline effect and to the asymmetry around the erbium ion sites in the tellurite glasses. The crystalline effect and asymmetry values around the Erbium ions decreased with increase of PbO mol%, as shown by the oscillator strength as well by the Judd-Ofelt parameter values.

EXAFS studies were carried out to probe variation of the local environment of Erbium due to ZnO substitution by PbO. EXAFS measurements were performed at the BM08-Gilda Beamline of ESRF (Grenoble,F). Structural parameters on the Er local environment were extracted for the first shell of Erbium ions only, the outer shells being too disordered to be quantified. The first shell for Er does not vary significantly with PbO addition, even though coordination number, Debye–Waller factor and 4th cumulant are slightly changing, with their values decreasing to a minimum at 10 mol% PbO and then increasing till a maximum for the 20 mol% PbO. The N values vary from 6.4 to 6.7. Er-O distance is constant at 2.34 Å.

The variation of optical properties with the PbO addition, however, show a continuous trend, and can not be explained only by the short range order of the first shell monitored by EXAFS.

Reflectivity on complex biomimetic membranes

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Biomembrane components are unevenly distributed within the aggregated structure. This basic observation hangs onto the possibility of applying several powerful non-invasive physical techniques to assess the structure of complex biomembranes, threatening the interest in their non-invasiveness by the oversimplification of the experimental model. The use of asymmetric model systems is rare, due to the difficulty of realizing artificial membranes with well defined heterogeneous composition and applicable for non-average structural investigation. In collaboration with the ILL in Grenoble, we have developed and tested an experimental model bearing forced membrane asymmetry in the form of single floating bilayer, that we investigated by neutron and synchrotron radiation reflectivity. The two coupled different monolayers are prepared by Langmuir-Blodgett/Langmuir-Schaeffer technique. We have tested the asymmetric phospholipid / cholesterol / ganglioside model system. In fact, gangliosides in real membranes reside in the outer layer, which has been invoked to provide the structural basis for the third-dimension static deformation of membrane portions. Also cholesterol transverse disposition may assume specific arrangement in asymmetric domains. The Angstrom scale of neutron accessibility is able to reveal the cross profile of the membrane. We present some experimental results, revealing the experimental crucial points and the potentiality of the technique. We plan to directly access the structural effect brought by a soluble enzyme digesting the glycolipid component.

Studio di antiche spade Giapponesi attraverso Imaging neutronico risolto in energia

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Sono stati analizzati quattro spezzoni di antiche spade Giapponesi appartenenti ai periodi Koto (987-1596) e Shinto (1596-1781) [1] attraverso Imaging neutronico risolto in energia. I campioni sono la parte inferiore della antiche spade, con punto di rottura individuato a circa 50-60 mm dall'inizio della lama. Le firme intagliate in corrispondenza (nome giapponese) permettono di identificare le maestranze. Lo staff del Museo Stibbert ha fornito i campioni che sono stati adoperati come test per la caratterizzazione non distruttiva attraverso metodi non invasivi.

Le misure di Imaging neutronico risolte in energia sono state condotte su tutte le spade utilizzando la beamline di ICON presso la sorgente neutronica a spallazione SINQ in Svizzera [2].

Una prima misura è stata condotta su un barra in ferro spessa 6 mm per mappare la posizione spaziale del Bragg edge 110 della ferrite. Sfruttando l'aumento del contrasto indotto selezionando due differenti lunghezze d'onda, rispetto a misure realizzate su fascio bianco, abbiamo evidenziato la diversa distribuzione della ferrite nel materiale. Le lunghezze d'onda adoperate sono state scelte immediatamente prima e dopo il Bragg edge 110 della ferrite [3].

Sono state acquisite le immagini delle spade sia in fascio bianco, sia alle lunghezze d'onda individuate.

Sono state realizzate le ricostruzioni tomografiche degli spezzoni di spade utilizzando il pacchetto software Octopus, progettato presso l'Università di Ghent. Attraverso le ricostruzioni tomografiche è stato possibile determinare la distribuzione di difetti, slags e fratture presenti all'interno delle lame. Sono state evidenziate le porzioni di alterazione superficiale e l'area di tempra lungo il filo.

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Neutron scattering reveals an enhancement of atomic fluctuations in amyloid fibrils

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Protein aggregation and growth of amyloid fibrils hinder protein function and are involved in the etiology of several neurodegenerative diseases. Whilst a large amount of biological and structural information are now available about the amyloid state of proteins, and in spite of the close relationship among protein structure, dynamics and function, much less is known about its dynamics and the differences with respect to the dynamics of native and amorphous aggregated states. Here we present the results of the first elastic and quasi-elastic neutron scattering study on the dynamics of mature amyloid fibrils compared with the native and amorphous aggregated states. We selected a model globular protein, Concanavalin A, for peculiar aspects of its structure: as it is an "all-β" protein, we aimed to minimize any dynamical effect related to changes in secondary structure, thus highlighting the role of the supramolecular aggregated structure. Neutron scattering data are complemented by a complete structural and conformational characterization obtained by means of Confocal and Atomic Force Microscopy, IR and Fluorescence spectroscopy.

The results here presented demonstrate that aggregation state can influence protein internal dynamics in the pico-nanoseconds time scale and that neutron scattering is a suitable technique to highlight this effect. In particular, aggregation does not influence the temperatures at which the main anharmonic onsets occur (thus implying that the energy barriers are not modified) and does not modify the low temperature local dynamics, but amyloid fibrils, differently from the amorphous aggregates, are characterized by mean atomic fluctuations larger than in the native state, at temperatures above the dynamical transition, where proteins become biologically active. Information on the shape of energy potential are deduced and discussed.

Will be presented further studies on different amyloid morphologies (obtained by changing the physico-chemical conditions of glucagon peptide solutions) and different amyloid architectures (obtained by freezing kinetical intermediates in the fibrillation process of insulin), currently in progress.

Detectors and advanced instrumentation for imaging and time-resolved experiments

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We present some applications of the 1D/2D delay-line detectors and advanced instrumentation which are developed by the Laboratory for Instrumentation and Detectors, Sincrotrone Trieste.

Our special attention is dedicated to time-resolved experiments. A series of beamline research references is shortly presented, in order to show the advances that have become accessible thanks to the use of new electronic instruments exploiting the multihit approach and providing the desired timing information about detected events in an extremely straightforward way.

Fe AND Mn SPECIATION IN MULTICOLOURED TOURMALINES

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Four multicoloured tourmalines, where the variation of colours occurs in concentric bands, have been analyzed by X-ray Absorption Spectroscopy (XAS) at the Fe and Mn K-edge, in order to investigate the oxidation state and the site location of Fe and Mn, with the final purpose of understanding the physico-chemical factors affecting their colour. The natural multicoloured crystals present only Fe and Mn as chromophore elements, but despite the quite simple chemistry, they show a variety of colors including hues of blue, pink, red and green. In zones where Mn is predominant, a pink color is observed, whereas Fe predominance induces green or blue colors. Interestingly, the presence of Fe and Mn has been recognized also in the colorless areas.

XAS measurements have been collected at beamline GILDA-BM08 of the ESRF. The beam size at the sample was 0.15 mm x 1 mm in order to be able to selectively measure the different coloured zones of the crystals. A 13-elements high-purity Ge detector allowed to collect the fluorescence spectra through a cross section of each of the samples. Detection of the Mn $K\alpha$ and Fe $K\beta$ X-ray emission lines allowed to selectively collect profiles of Mn and Fe abundances across the studied crystals.

Pre-edge peak analysis shows that Mn and Fe are dominantly divalent in all the measured samples. Pre-edge peak integrated intensities are compatible with the location of Mn and Fe in the octahedral sites. Preliminary theoretical XANES calculations also agree with the octahedral coordination of Mn and Fe.

For these samples, the change in colour appears related to the variation in the relative abundance of Mn and Fe rather than to variations of their oxidation state.

Functional phase contrast X-ray lung imaging in a preclinical asthma model: first feasibility study at Elettra

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Asthma is one of the most common chronic diseases in the world, currently affecting an estimated 300 million people worldwide [1]. Although, there is still no cure. A variety of asthma mouse models have been developed each capturing a part of the complexity of this multi-factorial and multi-cellular disease [2]. Preclinical research using animal models of pulmonary inflammation has proven to be crucial for a better understanding of asthma pathophysiology and for development and evaluation of novel therapy concepts.

X-ray based imaging is the major imaging method utilized in clinical practice. It outranges all other modalities in terms of spatial resolution. Nevertheless, along with the radiation dose applied to the patient it suffers from a poor soft tissue contrast and a low sensitivity hampering all functional imaging approaches.

Application of phase contrast x-ray imaging enables strong tissue interface enhancement accompanied with reduced dose due to the facts that phase shift is proportional to the used x-ray energy and about 100 times stronger than absorption in soft tissues [3]. Current developments show that its limitation to Synchrotron sources can be overcome and therefore it will be a big leap forward in next generation medical x-ray imaging [4,5].

At the SYRMEP beamline of Elettra we combined this technique with the application of barium labeled macrophages as functional contrast agent targeting inflammation sides inside the lungs of an acute asthma mouse model, demonstrating the feasibility of both high resolution and functional x-ray imaging.

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Structural and XMCD studies on Cu doped ZnO pellets and ferromagnetic films.

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Cu doped ZnO polycrystalline pellets (targets) were synthesized with Cu concentration varying from 2% to 10% by solid state reaction route. Using these targets, Cu-doped ZnO films with preferred orientation along c-axis were grown on single crystalline c-cut Sapphire substrates using Pulsed Laser Deposition technique. All these films were produced and characterized at University of Hyderabad and showed ferromagnetism, with saturation values increasing with Cu doping.

Element specific magnetic measurements at Cu K-edge were carried out using synchrotron radiation at ID12 of ESRF (F) by x-ray magnetic circular dichroism (XMCD). Structural characterizations were carried out by x-ray diffraction and x-ray absorption spectroscopy (XANES and EXAFS at BM08-Gilda) at Zn and Cu K-edge for targets and films, in addition to x-ray linear dichroism (XLD) at ID12 for films.

For targets, it is revealed that at low Cu content the most of Cu atoms substitute Zn inside the ZnO wurtzite lattice while, for the higher Cu concentrations, Cu starts to segregate as CuO. XMCD measurements on $Zn_{0.98}Cu_{0.02}O$ and $Zn_{0.9}Cu_{0.1}O$ pellets show a peak in correspondence of the very feable 1s->3d pre-peak at 9877 eV. The monitored 3d state of Cu is paramagnetic, with intensity decreasing with increasing Cu content. The paramagnetic behaviour shown by the pellets at Cu K-edge is in agreement with recent works on high quality Co-doped ZnO bulk or thin film samples, indicating that in absence of sufficient amount of point defects or carriers, a structurally excellent Cu-doped ZnO polycrystalline bulk sample can not exhibit RTFM.

On films, Zn K-edge XLD signals confirm the high crystallinity and c-axis orientation of the films, but Cu K-edge XLD signals are different and very little, especially for higher Cu content: this suggests that the local environment around Cu in these films is strongly deformed in respect to what can be expected for Cu going substitutional of Zn. XANES and EXAFS analysis confirm quantitatively this evidence.

In the element specific magnetic measurements carried out on films, we didn't observe any XMCD signal indicating that the Cu whole K-edge of films is not spin polarized. However, the films showed ferromagnetic behavior when measured by SQUID magnetometer: new XMCD measurements at low energy Cu L_3 or O K-edges are expected to better clarify this problem, because they can better probe the d-states of Cu.

Density of states measurements in disordered systems.

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We present a data treatment procedure [1], based on an iterative technique, properly developed to subtract the multi-phonon contributions from the dynamic structure factor in a self-consistent way. Through this technique the one-phonon vibrational density of states has been derived from the dynamic structure factor of different disordered systems, by means of the incoherent scattering approximation. We present results on glassy glucose ($C_6H_{12}O_6$) a nearly perfect incoherent scatterer, due to high hydrogen content. The data treatment procedure has been found to work well also for the more complex case of dry and hydrated DNA. In the latter case, the presented results will be also analyzed in comparison with the available data for bulk water.

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A simplified microscopic approach to describe the vibrational properties of glasses.

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A simplified microscopic approach has been developed [1], in which a model of interacting harmonic oscillators has been solved by a specifically numerical technique useful to calculate the dispersion curves, the dynamical damping and the dynamic structure factor in a first order perturbative approach. The self consistent treatment of the theory allows to compare the self-consistently calculated density of states to the experimental one. We present the comparison with experimental available data on two different continuous random network forming glasses.
The glassy germanium diselenide (v-GeSe2) [2]. Its vibrational dynamics has been investigated by means of inelastic neutron scattering. Three different neutron spectrometers have been employed, each of them providing different energy resolutions and spanning different portions of the energy-wave-vector (E,Q) plane.
The glassy glucose [3]. Both coherent and incoherent cross sections have been investigated by means of two inelastic scattering experiments combined with isotopic substitution.

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ENZYMES INVOLVED IN PURINE CATABOLISM

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Whilst the synthesis of purine bases is accomplished through a series of reactions requiring amino acid precursors and the investment of ATP molecules, most organisms are unable to produce energy or useful compounds from purine catabolism. In some species, such as in apes, birds and reptiles, the catabolic intermediate uric acid, which can cause gout in humans, is discarded. In most other species uric acid is enzymatically converted to S-allantoin, which in turn is degraded to the end products, CO2, NH3 and glyoxylate.

The three steps involved in the complete degradation of uric acid to S-allantoin in organisms different from humans have been elucidated very recently by comparative analysis of different genomes. We have carried out the characterization by crystallographic techniques of the three enzymes that catalyze the conversion of 5-hydroxyisourate (HIU) to S-allantoin and further on, to allantoate: HIU-hydrolase, OHCU-decarboxylase and PuuE allantoinase [1-3]. In addition, we have shown that the PucG protein from *Bacillus subtilis* catalyzes the transamination of an unstable intermediate and the end-product of purine catabolism, S-ureidoglycine and glyoxylate, to oxalurate and glycine. This activity enables soil and gut bacteria to use the animal purine waste as a source of carbon and nitrogen. The PucG-catalyzed reaction does not require addition of a keto-acid in the reaction mixture, representing a unique example of a transamination in which the same substrate ((*S*)-ureidoglycine) provides both the amino group donor and, *via* its spontaneous decay, the keto group acceptor [4]. Although the original function of PucG may have been the glyoxylate detoxification, its ability to use keto acids as amino group acceptors enables the recycling of the C and N atoms of purines.

Finally, HIU-hydrolase and transthyretin are closely related phylogenetically and structurally, while performing quite different functions: the second is in fact a plasma transport protein. The evolution of 5-hydroxyisourate hydrolase into transthyretin represents a remarkable example of adaptation of a new function by active site modification of an enzyme. On the basis of phylogenetic reconstructions and structural comparison of HIU-hydrolase and transthyretin, two mutations (Y116T and I16A) have ben shown to be crucial in order to induce the conversion of the enzyme into a binding protein.

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