MaMaSELF Status Meeting 2013

Tuesday, 21 May 2013 - Friday, 24 May 2013 Hotel Rigi Kulm

MaMaSELF

Book of Abstracts

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Dinner

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Lunch

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Departure

Evening Session Tuesday / 3

Possibilities at the Swiss Neutron Spallation Source SINQ

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The Swiss Spallation Neutron Source SINQ [1] is a modern user facility for neutron diffraction, neutron scattering and imaging experiments. It started user service in 1998. Presently, 14 instruments are open for outside users and one is at the end of the commissioning phase, two instruments are reserved for testing new components and crystals quality, one is operated by industry.

Together with the excellent sample environment ranging from high pressure, high field, very low and very high temperatures, computer controlled (low-temperature) sample changer to specialties such as in-situ measurements under hydrogen, and the present flux (4 times higher than in 1998 as a consequence of increased proton flux as well as upgraded target). An upgrade program for the instrumentation as well as the guide system has been initiated to strengthen SINQ's competence in the next decade.

We will present the present status of the facility; plans for the future upgrade program as well as highlights from the user service of the last few years.

[1] B. Blau, K.N. Clausen, S. Gvasaliya, M. JanoschekS. Janssen, L. Keller, B. Roessli, J. Schefer, Ph. Tregenna-Piggott, W. Wagner, O. Zaharko: The Swiss Spallation Neutron Source SINQ at Paul Scherrer Institut

Neutron News 20, 5-8 (2009).

Early Afternoon Session Wednesday / 4

Hybrid solar cells based on zinc oxide nanostructures

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Hybrid solar cells based on zinc oxide nanostructures Rui Wang, Kuhu Sarkar, Peter Müller- Buschbaum Keywords: mesoporous ZnO, P(S-b-AA) template, sol-gel synthesis

Abstract: Mesoporous zinc oxide (ZnO) structures in the form of thin films have been investigated in the present work. The promising electronic and optical properties of ZnO leads to its wide scale applications in various fields of which the area of hybrid photovoltaics interests us. In a hybrid solar cell, ZnO acts as the inorganic electron acceptor in combination with a hole-conducting organic polymer.

The main focus of this thesis would be to synthesize mesoporous ZnO network morphologies in the form of thin films. The mesoporous network provides large surface-to-volume ratio to enhance light harvesting capacity and the interconnected network reduces the probability of electron-hole recombination in addition. In order to design such a morphology, an amphiphilic diblock copolymer Poly(styrene-b-acrylic acid) is used as a template via solution based sol-gel route. The task is to find a proper morphology of ZnO network by adjusting the weight fractions of solvents and the ZnO precursor. Structural characterization of the thin films is done by scanning electron microscopy (SEM) and atomic force microscopy (AFM). Thickness of the films is investigated by white light interferometry and height profilometry. Optical properties of the films are studied by UV/Vis spectroscopy and photoluminescence.

Early Morning Session, Wednesday / 5

New coating process for SiC-Fibers and its effects on mechanical properties of SiC/SiC composites

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Fiber-reinforced ceramic matrix composites (CMCs) have the potential of operating at temperatures greater than 1100°C with minimal or no cooling, which will produce a variety of performance advantages. Achieving a CMC system with the required thermal and structural properties will depend on the ability to design and process the CMC so that it achieves the proper microstructure features. The three major constituents of any continuous fiber ceramic matrix composite are the reinforcing fibers, the matrix and a fiber-matrix interphase, usually included as a coating on the fibers. As with most other ceramic composite systems, a coating is applied to the fibers to serve as the fiber-matrix interface. Such a fiber coating is necessary to prevent chemical attack of the fibers during processing and to provide for a weak mechanical interface between the fiber and matrix for enhanced toughness and graceful failure. The state of the art coating is today most widely applied by chemical vapour deposition (CVD).

The aim of the present Master Thesis is to develop a simple method to coat ceramic fibers with BN. In recent years, some researchers had successfully used dip-coating method to prepare coatings on fibers. The dip-coating method, comparing with the CVD method, was simpler in operation, inexpensive and might obtain uniform coatings on both surface and interior fibers of 2.5D fabric, which had been widely used in ceramic matrix composites.

In this study, low-cost and harmless raw materials are employed to prepare coatings on carbon and silicon carbon fibers by dip-coating method with special attention directed towards coating thickness control. Thus, the dip-coated BN coatings could serve as low cost and anti-oxidation interphase for SiC/SiC composites.

In the first step continuous dip-coating equipment will be used to coat C-fibers initially and SiC fibers afterwards. The BN coating will be investigated by XRD, SEM, FT-IR, XPS and Raman spectroscopy. The influence of BN coatings on mechanical properties of SiC/SiC composites will also be studied by manufacturing SiC/SiC composites by Liquid Silicon Infiltration (LSI) route.

Early Afternoon Session Wednesday / 6

Electronic and atomic structure of graphene nanoribbons

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Epitaxial graphene on silicon carbide is a promising candidate for industry as it is grown on top of a technological substrate. Graphene ribbons are interesting for circuitry but when obtained by electronic litography their edges are rough and their transport properties are polluted by disorderrelated problems. High quality ribbons are obtained by combining lithography and an annealing procedure, and it is possible to settle metal-semiconductor-metal junctions on a continuous substrate of graphene. Here are studied the atomic and electronic structure of nanoribbons by Photoemission (ARPES) and Microscopy/Spectroscopy (STM, STS, STEM).

Early Afternoon Session Thursday / 7

Non-stoichiometric oxides for energy storage and transformation: structure and dynamics for low temperature anisotropic oxygen ion diffusion

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Non-stoichiometric, oxygen-deficient perovskites have been proposed as a potential electrolyte in solid oxide fuel cells, since they can theoretically operate at a lower temperature than current materials. The main structure of interest is the brownmillerite structure ABO2.5, where A is typically calcium or strontium and B is iron or cobalt. This structure undergoes a reversible topotactic intercalation reaction to form the perovskite ABO3, which can be achieved using electrochemical oxidation or by "chimie douce" techniques.

SrCoO2.5 is able to intercalate oxygen at a particularly low temperature; however the reaction and the transport pathways for oxygen atoms are not well understood, as the diffusion is anisotropic and related to lattice dynamics, and is complicated further by the existence of two intermediate compounds between the brownmillerite and perovskite phases. In addition, the related compounds SrFeO2.5 and CaFeO2.5 do not always behave in the same manner.

The aim of this thesis is to grow thin films of SrCoO2.5 single crystals in a mirror furnace, in order to observe the anisotropy of the oxygen diffusion, increase the sample's reactivity, and to determine why the reaction is not the same when using the related compounds previously mentioned. This information will be valuable not only for SOFC development but also for an improved fundamental understanding of ionic diffusion mechanisms in ceramics.

Early Afternoon Session Wednesday / 8

Synthesis and Characterization of Ferroelectric Materials for Energy Storage Applications.

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Barium titanate (BaTiO3) ceramics are ferroelectric materials that present high-dielectric-constants and have been highly study during the past decades due to their electrical and electronic applications. The synthesis process, particle size, and morphology of the material have shown an important influence on the properties of these electronic materials.

The present work aims to synthesizer nanoparticles of composition-modified barium titatante ceramic powder by soft chemical processes. In order to reach the highest value of dielectric constant, some thin layer of electric insulator materials will be deposited onto the surface of the nanopowders. The study and the understanding of the effects on the dielectric properties of the structure of such nanocomposites is a big challenge for future applications.

Late Morning Session Wednesday / 9

Hydrothermal synthesis of hierarchical porous material in the system Fe-O-OH

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This project aims to create the hierarchical porous material of iron oxyhydroxide by a hydrothermal method.

The idea is using schwertmannite as iron source, which is an iron (III) oxyhydroxysulfate with a somewhat variable composition and the general formula Fe8O8(OH)x(SO4)y•nH2O where 8 -x = 2y and $1.0 \le y \le 1.75$. Though schwertmannite can be synthesized by various biotic and abiotic methods, its structure cannot be clearly explained yet. The latest suggestion for the structure model is a defective akaganeite structure with broken channels and sulphate groups instead of chlorine. There should be amounts of defective sites at FeO4OH2 octahedral ribbons, yielding an open structure with high surface area.

While zeolites absorb cations, schwertmannite is classified in the group of anion-exchanger and also interesting as candidates for high active battery materials. In this regard, it is optimal for one single phase to have hierarchical pore system from micropores up to mesopores.

Based on disordered akaganeite structure of schwertmannite, we will perform synthesis with various bulky organic species such as Brij 58, cetylpyridinium chloride monohydrate, sodium salicylate and so on. Synthesis will be performed via hydrothermal routes. To determine the optimal condition of synthesis, a series of physical parameter, namely, the molar ratio of iron source and organic template, time and temperature, need to be considered. X-ray powder diffraction (XRD), chemical analysis, scanning electron microscopy will be measured to analyse the products.

Early Morning Session Friday / 10

From proteins towards polymer-protein conjugates: structure and dynamics properties for bio-technological application

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Polymers have specific, controllable properties such as mechanical strength, biocompatibility, and tailorability of their functional groups, which are important for biological application. When they are attached to proteins, proteinpolymer covalent conjugates combine the impressive biological activities of proteins with the tailorable structures and properties of synthetic polymers.

The aim of my research is to contribute to the description of interactions, structure and dynamical properties of a new class of polymer-protein conjugates, with special attention to protein stability and protein folding. A library of model proteins such as met-hemoglobin, interferone and/or lysozyme complexes with bio-compatibles polymers, with various architectures, will be synthetised. Microscopic properties of the complexes will be put in perspective with bio-functional properties, in order to elucidate preferential structures and relaxation modes of the proteins that are essential for folding and functionality.

In order to achieve the main assignment of the project a fully description of microscopic properties, of the conjugates, will be necessary. On one side, Optical Transient Grating technique and Light Scattering will enable a determination of the visco-elastic parameters, and relaxation modes on the nanosecond timescale. Measurements will be performed at the Laboratoire Interdisciplinaire de Physique (LIPhy) in Grenoble (coord. M. Plazanet). On the other side, structure and dynamics of the conjugates itself and protein/polymer will be investigated by X-ray and neutron scattering techniques. The use of deuterated polymers or proteins will make possible, through neutron scattering, the direct determination of the polymer/protein properties in the conjugates. Measurements will be performed on French and European large scale facilities (coord. D. Russo)

Comparison of different protein conjugates should lead to a variety of original results. With this project we wish to provide a valuable description of the properties of polymer hydrated protein for their potential application for bio-technology. The results could lead to the targeted design of original conjugates.

Late Morning Session Wednesday / 11

Continuous scans for X-Ray Ptychography

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X-Ray Ptychography is a lensless imaging technique that produces high-resolution two- and threedimensional quantitative maps through the

combination of multiple coherent diffraction measurements from the illumination of several overlapping regions on the specimen [1,2].

Recently, this technique has been show to be able to produce high-quality reconstructions even when sources of decoherence are introduced into the measurement system. These sources of decoherence can be of very different origin [3]:

1) mixed states in the probing radiation can include all sorts of mixing that manifest themselves as transverse partial coherence or finite longitudinal coherence

2) mixed states in the sample may result from quantum mixtures or stationary stochastic processes3) detector point spread can be viewed as a mixed state in the detector plane

This project aims to drastically reduce scanning time by introducing scans with continuous movement and interpreting the movement of the object as a partial coherence effect.

Several parameters are explored, such as exposure time per area, overlap of the scanned regions and different scan patterns.

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High-resolution scanning x-ray diffraction microscopy. Science (New York, N.Y.), 321(5887), 379🛛 82.

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[2]Dierolf, M., Menzel, A., Thibault, P., Schneider, P., Kewish, C. M., Wepf, R., Bunk, O., et al. (2010).
Ptychographic X-ray computed tomography at the nanoscale. Nature, 467(7314), 436\vee 9. doi:10.1038/nature09419
[3] Pierre Thibault, Andreas Menzel. Reconstructing state mixtures from diffraction measurements
Nature, Vol. 494, No. 7435. (06 February 2013), pp. 68-71, doi:10.1038/nature11806

Early Morning Session, Wednesday / 12

Cononsolvency in Thermo-Responsive Polymeric Hydrogels

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Temperature is one of the stimuli that can be controlled in various applications and more importantly in the field of biomedicine as the human body is thermo-regulated. For this reason thermosensitive hydrogels that can respond to temperature changes have been developed and widely explored in recent years. Block copolymers of various topologies have been designed for this purpose, the common feature of which is that they bear blocks exhibiting thermosensitivity in the temperature range of interest. This thermosensitivity usually relies on the reversible thermal phase transition of polymeric aqueous solutions characterized by a critical solution temperature. There are two cases. The polymer becomes insoluble by increasing temperature above the so called lower critical solution temperature (LCST) which in fact is a coil to globule transition, or in terms of interactions with water, a hydrophilic to hydrophobic transition. In the second case reverse phenomena occur and the critical temperature is named upper critical solution temperature (UCST).

Poly(N-isopropylacrylamide) (PNIPAM) is soluble in organic solvents, such as chloroform, acetone, methanol, and various other alcohols. It is also soluble in water, as long as the solution is kept reasonably cold. Heating an aqueous PNIPAM solution past 32 °C (the cloud point (CP) or LCST) instantaneously converts the clear solution into a milky suspension. However, in water/methanol mixtures, the could point is decreased, and PNIPAM collapses and precipitates. In order to study this phenomenon we carry out time-resolved mall-angle neutron scattering (SANS) experiments in Institut Laue-Langevin (ILL).

Late Morning Session Thursday / 14

Structure, local environment and reactivity of metal centers hosted inside hybrid metal- organic frameworks (MOF) investigated by spectroscopies FTIR, UV-Vis, in situ XAS and high resolution XRPD.

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Metal organic frameworks (MOFs) are a class of crystalline materials constructed by assembling metal-containing centers with multi-dentate organic ligands into a one, two or three-dimensional structure. High crystallinity makes it possible to tune the pore size from several angstroms to a few nanometres by controlling the length of the ligand. The MOFs being studied are UiO-67 MOFs synthesized by the group of Prof. Karle Peter Lillerud, University of Oslo and characterized in University of Torino under the supervisio of Prof.ssa Silvia Bordiga. The MOF studied comprises a Zr

based inorgnanic building brick and benzene dicarboxylic acid as the organic linker. Pt ions have been doped into the MOF in the form of Pt-complexes in varying concentrations.

Utra-high porosities (approx. 90%) and high surface area (6000m2/g), besides the presence of nanosized pores in the framework provides these MOFs with high potential in adsorption and catalysis. The samples are studied using FTIR spectroscopy, by sending probe molecules like CO, acetylene, ethylene etc to investigate the adsorption behaviour in time and changing equillibrium pressure as well as any modification in the chemistry of the MOF or the hosted Pt metal centers. The FTIR data will be complemented by UV-Vis spectra, DRIFTS and in-situ XAS measurements.

Structure analysis to be done by in-situ PXRD and elastic neutron diffraction.

Early Morning Session Friday / 15

Exchange bias of Fe/Tb multilayers

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Magnetic multilayers comprising of a transition metal (Fe) and a heavy rare earth metal (Tb) is known to show various magnetic structural ordering. These include antiferromagnetic, spiral and also twisted structures. A strong candidate for twisted

structure is Fe/Tb multilayer below 100 K. This is mainly owed of the fact that the Tb layer undergoes multiple phase transitions with temperature. In the bulk form Tb metal changes from its paramagnetic phase to an antiferromagnetic phase at around 227 K and simultaneously goes through a helical structure in between 229 K and 221 K. At around 213 K it finally goes to a ferromagnetic phase.

In a Fe/Tb multilayer it was reported that the Tb layer goes through a twisted state which shows a modulation with an applied magnetic field at 25K [K. Takanod et al. Journ. Phys. Chem. of Solids, 65, 1985, (2004)]. In this thesis work we intend to explore the effect of such multilple phase transitions on the exchange coupling with a Fe layer adjacent to the Tb layer. Such exchange coupling can be induced by field cooling the system from a paramagnetic phase of the antiferromagnet (Tb) layer to other phases.

Last Session Friday / 16

Neutron Imaging - Material research in real space

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Neutron imaging is a method that directly provides real-space information about the sample composition using neutrons as probing beam. In the standard configuration the resulting images represent the neutron shadow cast by the, for neutrons, semi-transparent sample. The basic principle is very similar to the more known X-ray radiography. The difference lies in the neutron matter interaction that provides a very different set of attenuation coefficients for the elements than provided by X-rays. Radiography is the basic mode for neutron imaging, but the method is not limited to the acquisition of two-dimensional images. Computed tomography using neutron projection data makes it possible to reconstruct the three-dimensional distribution of attenuation coefficients in the sample. On the other hand, processes can be followed in quasi-real-time modes. Depending on the installed instrumentation it is possible to reach voxel sizes of 13.5um for small samples while it is possible to support samples with dimensions up to 250mm at lower resolution. Most neutron imaging experiments are performed using radiography and tomography with a "white beam", but the use of optional energy selection devices in the beam makes it possible to perform Bragg edge imaging at different neutron energies. Neutron grating interferometry imaging can provide additional information about the sample by using the differential phase shift and the dark field information. The dark field images have proven useful in investigations of magnetic domains since it is sensitive to the small neutron scattering angles caused by the magnetic domain walls.

Early Afternoon Session Thursday / 17

Modification of Delamination Properties of Mica by new Synthesis Pathways

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Metal oxide-hydroxide coated mica is widely used for pearlescent vehicle pigments in industry. To produce a pigment with thinner layer, we need to prepare a better delaminating mica flake base. In our study, two kinds of mica and two series of synthetic mica samples between them are prepared by the simple one-step mixing, melting and crystallizing method. The sample A is with the composition which is used in industry now, the flour phlogopite KMg3(AlSi3O10)F2. And the sample B is found in the literature, a kind of soudium swelling mica with high-charge, its composition is NaMg3(Al2Si2O10)F2. Changing composition is based on sample A. In series C, different percentage of potassium in A is replaced by sodium to study the effect of sodium ions on delamination. And in series D, silicon is replaced by aluminum to study the effect of the different layer charge on mica's delamination. All the samples will be identified by X-ray or MAS-NMR. Their delamination properties will be studied with the help of a grinder and SEM. Each sample will be grinded under exactly the same conditions and by the same procedures, and we will compare the thickness before and after grinding under SEM.

Early Morning Session Thursday / 18

High Oxygen Mobility in Rare Earth Doped Ceria Compounds at Low Temperatures

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Ceria based oxides are regarded as the key materials for energy and environmental applications, such as three way catalyst in automobile emission systems, heterogeneous catalysis, oxygen sensors, solid oxide fuel cells etc. The great versatility in applications is achieved by the unique combination of oxygen transport capacity together with the ability to shift easily between reduced and oxidized states (i.e Ce3+-Ce4+). Doped ceria materials preserve the fluorite type structure which facilitate the rapid and complete refilling of oxygen vacancies upon redox reactions. Oxygen storage Capacity (OSC), decreasing the catalytic activation temperature and increase thermodynamic stability of these materials is enhanced by doping with other rare earth elements; particularly with its neighbour praseodymium. The change in the valence state of both Ce and Pr from 4+ to 3+ creates a defect ordered route for the mobility of oxygen anions within the lattice. Although, it is known that the oxygen vacancy concentration in Ce1-xPrxO2- δ increases with increased Pr content, the exact nature of the alteration in vacancy concentration and its effect on redox properties is not yet conclusive.

The goal of this project is to identify the valence states of Ce and Pr in various Ce1-xPrxO2- δ systems by XANES experiments using high brilliance synchrotron radiation. This information brings us closer to the description of the lattice defect formation. The study will be supported by diffraction experiments to identify the crystal phases, spectroscopic methods as a function of temperature to identify the phonon modes of defect formation as well as the catalytic activation at which the vacancy migration occur in Temperature Controlled Isotope 16O/18O Exchange Raman Spectroscopy.

Early Morning Session Friday / 19

Study of phase transitions on Intermetallic superconducting compounds

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The ternary stannide superconductors with the general formula A3T4Sn13[1] (A=Alkaline Earth or Rare Earth metal; T=Rh,Ir) having Quasi-Skutterudite structure have attracted a lot of attention due to Unconventional Superconductivity, non-Fermi liquid behaviour, Anti-Ferromagnetic (AFM) and Charge Density Wave (CDW) orders. The origin of the superlattice reflections in one such superconducting ternary stannide Ca3Ir4Sn13 at low temperatures has been investigated in the present work using Inelastic Neutron Scattering (INS) and Single-Crystal X-Ray Diffraction. Our data suggests the development of a CDW order associated with the freezing of a low energy phonon mode as the cause for the superlattice peaks below T^{*} \approx 38K. The existence of a possible Quantum Critical Point (QCP) in the phase diagram of these stannides [2] has also been explored by introducing suitable chemical doping.

 Remeika J.P. et al., A new family of ternary intermetallic superconducting/magnetic stannides Solid State Communications, Volume 34, Issue 12, June 1980, Pages 923–926
 Klintberg. L.E et al., Pressure- and Composition-Induced Structural Quantum Phase Transition in the Cubic Superconductor (Sr,Ca)3Ir4Sn13 Phys. Rev. Lett. 109, 237008 (2012)

Later Afternoon Session Thursday / 20

Low temperature magnetic structure and lattice anomalies at the commensurate-incommensurate transition of multiferroic YBaCuFeO5

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Ferroelectric materials have been known since almost one century ago [1]. While their potential for applications was rapidly recognized, the possibility of combining ferroelectricity with magnetic

order -preferably with ferromagnetism- has resulted in an enormous deal of interest during the last decade. Several new materials combining both types of order have been reported, although their promising multifunctionalities have been obscured by two facts: one one side, most of them are antiferromagnetic. On the other, their transition temperatures are too low for most practical applications (typically below 40K).

The oxygen-defficient double perovskite YBaFeCuO5 constitutes a remarkable exception. Spontaneous electric polarization has been recently reported to exist below an unusually high temperature of TC \approx 230K [2] coinciding with the occurrence of a commensurate - to - incommensurate reorientation of the Fe3+ and Cu2+ magnetic moments [3,4]. From a more fundamental point of view the observation of incommensurable magnetic order in a tetragonal material at such high temperatures is rather surprising. In particular, the nature of the relevant competing magnetic interactions and its possible link to low dimensionality or geometrical frustration is not understood at present. Although the existence of the spin reorientation in this material is know since 1995 [3] the low temperature magnetic structure has not yet been solved. Using neutron powder diffraction we have recently been able to propose a spiral model which satisfactorily describes the measured magnetic intensities below TC [4]. Also, investigation of the crystal structure showed the existence of small anomalies in the lattice parameters and some interatomic distances at TC. The relevance of these findings for the magnetoelectric coupling, the direction of the polarization, the modification of the different exchange paths in the structure and the stabilization of the incommensurate magnetic order

- below TC are discussed.
- [1] J. Valasek Physical Review 15, 537(1920)
- [2] B. Kundys et al., Appl. Phys. Lett. 94, 072506, (2009).
- [3] V. Caignaert et al., J. Solid State Chem. 114, 24, (1995).
- [4] M. Morin et al., in preparation

Late Morning Session Thursday / 21

Chiral Hybrid porous materials for enantioselective catalysis: synthesis and reactivity studied by in-situ x-ray power diffraction

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Hybrid porous materials have become during the past decade one of the most promising classes of synthetic

compounds. These materials have potential applications in various fields, from gas storage purification and separation,

heterogeneous catalysis, breathing or even controlled drug delivery. Making a judicious choice of the organic and

inorganic building units (BU) it is possible to introduce functional characteristic to this materials. In this project MOFs

(Metal Organic Frameworks) are functionalized by the introduction of chirality for enantioselective heterogeneous

catalysis. Following previous studies in Rennes on MOFs elaborated from original ligands, we synthesized three

new optically pure large spacers (L1,L2,L3) containing two or four carboxylate functions and chiral alkyle chains

grafted on a fluorene core which is until now very few used for MOFs synthesis. By combination with Cd, Cu and

Zn based inorganic BU we synthesized three new families of stable, porous (from 20 to 60%) and chiral MOFs. Most

promising 3D MOFs (Figure) present desolvated phases whose structures are still not determined.

Project will deal with in situ laboratory and synchrotron powder diffraction study on these new MOFs. MOF

activation and interaction with molecules relevant for enantioselective separation and catalysis (i.e.

butanol-2,

- benzaldehyde for further cyanosililation) will be studied. The insight will be of crucial importance in the
- understanding of enantios elective separation and catalytic tests currently in progress on these MOFs. Furthermore part
- of the project will concern synthesis of new chiral MOFs from commercial ligands (champhoric acid), determination
- of their structures and study of their reactivity from in situ laboratory and synchrotron powder diffraction in order to
- evidence interesting activated phases.

Early Morning Session Thursday / 22

Pr2NiO4+d structure, valence states and lattice dynamics investigated by synchrotron radiation.

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Oxides, exhibiting high oxygen ion conductivity, have gained considerable interest for their applications in Solid Oxide Fuel Cells (SOFCs). However, still today high operation temperatures of about 1000 °C are needed for SOFCs, requiring huge problems of mechanical and chemical stability. Unfortunately, a decrease in the temperature reduces activity of the solid electrolyte and reactivity of the cathode. Thus, a better understanding of the diffusion process on a microscopic scale is fundamental in optimizing SOFCs.

Perovskite type oxides, ABO3, and their derivatives, such as layered Ruddlesden-Popper nickelates, (LnO)(LnNiO3)n, where Ln is an alkaline earth or rare earth metal, show interesting ionic and electronic transport properties. In addition, oxygen mobility related to low-energy phonon modes has been observed in SrFeO2.5, which gives evidence of a phonon-assisted diffusion mechanism in solids. To investigate the high oxygen mobility present in Pr2NiO4+ δ , at already moderate temperatures, structure, valence states and lattice dynamics are investigated in the present master thesis project. In situ single crystal X-ray diffraction will be carried out in a special electrochemical cell to change stoichiometry in a controlled way. This will allow to correlate a crystal structure as a function of δ . XES will be carried out in situ in order to investigate changes in the electronic structure upon reduction of Pr2NiO4+ δ . Inelastic X-ray scattering will be used to correlate the existence of low-energy phonon modes with the oxygen stoichiometry. The synthesis of polycrystalline electrodes and single crystals are carried out at the University of Montpellier, all characterizations given above will be performed at the ESRF.

Late Morning Session Thursday / 23

Aspects of structure and dynamics of fiber DNA

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We study structural and dynamical behavior of DNA molecules by means of neutron scattering using the following ILL beamlines: IN3, IN5 and D22. A classical three-axis spectrometer, IN3, is employed in our experiment to obtain the information about DNA structure; IN5, the time-of-flight

spectrometer, is used to measure of the longitudinal phonons in our sample and SANS instrument, D22, helps us to determine the persistence length of a DNA molecule.

IN the first part of our work we investigate the acoustic dispersion curve in A-form DNA fiber sample using inelastic neutron scattering (INS) on a TOF spectrometer, IN5. The experimental results will be compared with the longitudinal phonons branches calculated by the force-field simulations [1].

The second part of a project concerns the measurements of DNA flexibility, which are fundamental in understanding the biological role of DNA. It would be interesting to investigate persistence length as a function of temperature up to the DNA denaturation temperature. The experiment will be carried out on D22 beamline with in-situ UV absorption spectroscopy [2].

The last part involves the measurements of fiber DNA structure under the osmotic pressure. We are going to prepare two samples, and one of them will be subjected to osmotic pressure, while another will be left under normal condition. Both of the samples will be investigated by neutron diffraction with IN3 spectrometer. The aim of this experiment is to compare the structures of both samples to find out if there are any drastic changes of DNA structure under osmotic pressure.

[1] Jessica VALLE ORERO "Dynamics and thermal behavior of films of oriented DNA fibers investigated using neutron scattering and calorimetry techniques", PhD Thesis, http://tel.archives-ouvertes.fr/tel-00734670

[2] Peyrard Michel et al., Proposal TEST-2217, D22 beamline ILL, "SANS from short chain DNA with in-situ UV absorption spectroscopy"

Early Morning Session, Wednesday / 24

Water diffusion on carbon systems

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The object of this thesis work is the understanding of some properties of water molecules adsorbed on carbon systems, especially graphite. Because of the different polar character, water and carbon do not mix very well, but this system is an excellent model to study spatial confinement of water on hydrophobic substrate in the nanometer scale.

Water and carbon are common and their physics and chemistry has been hugely studied, however the dynamics of water on carbon surfaces is far from being a closed topic.

To explore this system, methods providing both atomic lengthscale and pico- to nanosecond timescale information are crucial for the description of diffusional motion. Those are reachable only with quasi-elastic neutron scattering (QENS) and with quasi-elastic helium atom scattering (QHAS). The application of Neutron Spin Echo spectroscopy on surface diffusion is proved using the spectrometer IN11 in ILL, obtaining directly the real part of the intermediate scattering function. Thermally activated processes are investigated by varying the temperature of the system.

Moreover, simulations are fundamental to analyze experimental results. Force-Field Molecular Dynamics is a tool visualizing directly the motions of the molecules, suggesting then a correct physical interpretation to the neutron scattering results. Coverage- and temperature- dependent intermediate scattering function will be compared with the data-based results in order to establish a diffusion model for water on hydrophobic substrate.

FRM2 Research / 25

Materials Research and Applications at the High Flux Neutron Source FRM II

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An overview will be presented over the research activities at the High Flux Neutron Source FRMII in the fields of materials research, industrial and medical applications.

In three topics special emphasis is given to the unique design of the FRMII reactor, to the process of silicon doping on an industrial scale and thirdly to the production of technetium, a radiopharmaceutical for medical applications, which is foreseen to start in near future at FRMII.

Late Afternoon Session Wednesday / 26

Low temperature oxygen mobility applied to catalysis.

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Nowadays, much attention has been given to the fundamental and applied studies of low temperature ionic conductors. Thanks to the interesting properties and diverse applications possibilities, they are commonly investigated by academic and industrial research centers throughout the whole world.

From one hand, low temperature oxygen mobility mechanisms are widely investigated for a better understanding of this phenomenon in order to improve the efficiency of those systems. We want to underline the technological importance of these oxides, associated to a steeply increasing budget.

This project profits on a natural scientific symbiosis between universities, industries and large scale facilities, allowing to optimize synthesis, structural and microstructural control, as well as a characterization of the catalytic and surface properties, benefiting on the competencies of all involved partners.

Based on the practical case study of low temperature oxygen mobility applied to catalysis, importance of each part of the system will be presented and benefits coming from such collaboration will be shown.

Spectroscopic and diffraction method handled at the University of Montpellier 2 combined with neutron studies performed in PSI and ILL will be used as a tool for better understanding of highly efficient catalysts synthetized and characterized in Saint-Gobain, all in the frame of the French CIFRE-doctoral program.

Early Afternoon Session Thursday / 28

Study of biocomposite materials for automotive applications

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Polymer composites have been the dominant emerging materials over the past decades. The huge amount of composites applications have steadily enlarged and accordingly they are conquering new markets. Natural-fiber-reinforced composites are within a class of biocomposites that is arising as a viable alternative to the regular glass-fiber-reinforced composites, especially for automotive applications. Vegetable-fiber-based composites present interesting features such as low cost, low density which is crucial for light-weighting technologies and competitive mechanical behavior. Among many natural fibers, sisal is becoming a great filler for composites reinforcement. The goals of the present study are: to investigate the properties of a polypropylene biocomposite reinforced with 20% of sisal fibers, compare its characteristics with current glass-fiber-reinforced composites, and identify promising industrial applications. The material is being tested in terms of mechanical and thermal performances. The first results of flexural tests show that the sisal-based biocomposite presents higher ultimate tensile strength than the standard composites and comparable flexural modulus. The tensile testing revealed that the biocomposite supports a maximum load higher than the reference materials but its elongation percentage is lower resulting in a brittle behavior. Other important experimental analysis being employed at the moment are: heat deflection temperature, vicat softening point, izod impact strength, fogging and ageing tests. The properties obtained so far show a great usage probability to fabricate vehicle interior components due to its comparable profile to the materials being applied currently.

Late Morning Session Wednesday / 29

Polymeric nanoparticles for drug delivery.

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As the most promising drug carriers nowadays, high molecular weight nanoparticles (micelles) from water-soluble polymers are considered, because they have the appropriate size, good solubility in bio-acceptable solutions and biocompatibility.

The focus of the project is on the experimental investigation of drug carriers with the ability to release a drug in tumor cells or tissues. These are therapeutically highly potent polymer-drug conjugates based on the copolymer N-(2-hydroxypropyl) methacrylamide (HPMA) bearing the anticancer drug doxorubicin and a defined amount of hydrophobic moieties (cholesterol and it's derivatives). We focus on the influestructures of the cholesterol-HPMA linkage and cholesterol itself, their influence on the nanoparticle formation and behavior in solution. All cholesterol-derivatives were bound to HPMA by a pH-sensitive hydrazone bond and differed in the chemical structure in the vicinity of the bond. The hydrazone bond is relatively stable at neutral pH (blood pH), but breaks under mild acidic conditions, such as in the acidic intracellular environment (endosomes in tumor cells) and releases both the drug (doxorubicin) and cholesterol (which then is eliminated from the body). Using fluorescence correlation spectroscopy, the critical micelle concentration in very dilute solutions (blood simulation) will be determined, using dynamic light scattering, the average size of the nanoparticles and their stability in various environments will be studies, and (time-resolved) small-angle neutron scattering will provide detailed information on the micellar structures (core-shell). Modern model-free methods will be used for the data analysis of these complex systems.

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Réunion MaMaSELF Consortium

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Dr. Peter GLATZEL

Is the discussion about the electronic structure of CEO2 juast a misunderstanding?

Late Afternoon Session Wednesday / 32

Synchrotron radiation study of topological insulators at ASTRID

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The research of new materials with novel properties is one of the fundamental principles of the technological advancement. The discovery of peculiar electronic properties has often historically been proved to lead to huge leaps in the field of technology. Recently many of the predicted technological limits of the materials are close to be reached and the research has to be focused again on innovative materials.

In the last decade insulators with previously unknown electronic properties have been discovered: the so called Topological Insulators (TI). These materials, with the relevant quality to be insulting in the bulk but good conductors on the surface, represent a previously unknown state of matter. As added value the electron motion along the topological gapless surface states is coupled to the electron spin, making of these materials the most promising candidates in the field of spintronics and quantum computing. Moreover TIs are also believed to give rise to completely new physical phenomena.

The lack of knowledge in such recent field grants to the fundamental research the highest priority to support future engineering application. The exotic effects theoretically foreseen in particular topological systems require now a thorough experimental prove of the physics behind.

In this contest, as in many others, synchrotron radiation-based research has proven to be most effective and fruitful; thanks to the wide range of photon energies the synchrotron provides we can access information otherwise undetectable by any other mean.

This project is aimed to explore the electronic properties of new TI systems such as TI nanostructures and thin films and it profits of the constant access to the SGM3 beamline at the ASTRID synchrotron. We here present the main features of the topological insulators as well as the importance of synchrotron light based Angle Resolved Photoemission Spectroscopy technique; in the end a brief review of the most recent results is shown.

Early Morning Session Thursday / 33

Structural and Mechanical Characterization of High Temperature Shape Memory Alloys

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The NiTi alloy system has fueled significant interest for its Shape Memory and Pseudoelastic effects. The transformation temperature of the NiTi alloy family is unfortunately confined below 100 $^{\circ}$ C thus its application temperatures are limited. CoNiGa alloys were found to posses shape memory properties at elevated temperatures which make them promising contenders for high temperature shape memory applications.

We intend to do high resolution neutron diffraction and scan peak profiles of fundamental reflections of ten Co49Ni21Ga30 single crystals, which have been subjected to different numbers of loading cycles. We need to measure several points along the gauge length of the samples, because the accumulation of residual stresses varies along the specimen due to sample geometry. At each measuring point we will perform omegascans and omega-2theta scans of several peaks. Martensite formation results in strong splitting of (h00)- and (hh0)-type peaks, while (hhh)-type peaks are unaffected by ferroelastic splitting. Each peak-profile will be scanned in two orthogonal chi-orientations.Finally in order to get further insight into mechanical aspect of shape memory behavior, we also intend to do a variable temperature nanoindentation tests of the Co49Ni21Ga30 alloy and try to get a structure-property correlation in the material.We will also be able to study any size effect if at all present in the system of study.

Later Afternoon Session Thursday / 34

Resonant X-ray diffraction for multiferroic systems

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The aim of the present talk is to provide a pedagogical introduction to Resonant X-ray Diffraction (RXD) as a tool to characterize exotic (multiferroic, multipolar) order parameters. After a brief description of analogies/differences with usual x-ray diffraction and with x-ray absorption, the main focus is put on the interpretation of energy and azimuth scans. Finally, some examples of RXD signals are discussed to describe phase transitions in (possibly) multiferroic or (locally) magnetoelectric systems.

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Organic Solar Cells

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Is the discussion about the electronic structure of CeO2 just missunderstanding?

Last Session Friday / 37

Structure and miscibility investigation of PTB7:PC71BM BHJ thin films

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Currently, polymer-fullerene bulk heterojunction solar cells (PSCs) are attracting a great deal of attention and getting more and more important. It shows great promise as a new kind of renewable energy source due to its low-costs, lightweight, flexibility as well as its easy process of fabrication attracts many attentions.

In recent years, the power-conversion efficiency of state-of-the-art PSCs has exceeded 8% in the scientific literature . However, despite the relatively good performance, deep understanding of the

fundamental principles is still not well-known.To get an efficient organic solar cell, simply a twocomponent system used to separate the excitons is not enough. We need a three-phase-system, which compared to the two-phase-system, a new intermixed phase is added. The structural length scales are needed in the range of the mean exciton diffusion length (usually 10-20 nm).

In this work up to date the most promising system PTB7:PC71BM will be investigated. Samples with different blend ratios will be made as the Starting for the work. As for the basic characterization of the active layer, AFM will be used to get information about solvents' treated film topography and XRR works for vertical profile. The focus is the usage of grazing incidence small angle neutron scattering (GISANS) for the determination of structural length scales of the active layers and the miscibility between the two components. For a better analysis and understanding of the scattering data, the simulation software IsGISAXS may also be considered.

In addition, devices are prepared and characterized in terms of IU-curves and photophysical properties. Consequently, the morphology information such as structure length scales and molecular miscibility are resolved, and correlated with the final device performance.

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Tutorial Block Thursday / 38

Is the discussion about the electronic structure of CeO2 just missunderstanding?

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Ceria (CeO2) has been a benchmark system in experimental and theoretical X-ray spectroscopy for three decades. It is also of immense practical importance as a redox partner in many chemical applications including medicine because of its ability to do Ce3+ \leftrightarrow Ce4+ + e-. We have used the "advanced" spectroscopies HERFD, RXES and (indirect) RIXS to study the electronic structure of bulk and nanoparticles of CeO2. The presentation will discuss the techniques and demonstrate the information on the electronic structure that can be obtained.

The interpretation of X-ray spectra in ceria requires some theoretical finesse. Most theorists who took up this task use a single impurity Anderson model (SIAM) and agree that ceria is a homogeneous mixed valence compound, i.e. the charge that should be identified with the Ce ion is not 4+ as formally expected but somewhere between 3+ and 4+.[2] This has been proposed already in 1983.[1] At the same time, the macroscopic properties in general and chemical activity in particular are commonly addressed using density functional theory (DFT). These studies find sites of Ce4+ in bulk and Ce3+ and Ce4+ in ceria surfaces and nanoparticles. [3] At first sight, this is in disagreement with SIAM that rejects the idea of Ce4+ already in bulk ceria. Then again, it may only be a different way of describing electronic structure and the disagreement is limited to nomenclature. Such reflections are of broad relevance because SIAM and DFT represent two fundamentally different theoretical approaches to X-ray spectroscopy. The dilemma gains in practical importance when one attempts to describe the changes in electronic structure during chemical reactions, e.g. in ceria nanoparticles.

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Opening