

# Outreach Workshop on Functional Materials

19<sup>th</sup> September 2013

Paul Scherrer Institut, Villigen, Switzerland

## Abstracts:

### Strain effects in correlated transition metal oxides from first principles

*Claude Ederer (ETH Zurich)*

Transition metal oxides exhibit a wealth of fascinating and potentially useful properties, such as metal-insulator transitions, multiferroic behavior, or high-temperature superconductivity. The unique electronic structure of these materials generally leads to a very strong coupling between their structural, electronic, and magnetic properties. We are using first principles electronic structure calculations and combinations of such first principles calculations with model-based approaches to explore the unique properties of functional complex oxides. Here, I will address the question of whether epitaxial strain, which is present in most thin film samples as a result of the lattice mismatch between the thin film material and the substrate, is able to induce metal-insulator transitions in the prototypical correlated oxides LaTiO<sub>3</sub> and SrVO<sub>3</sub>. Furthermore, I will demonstrate how Wannier functions can be used to connect the realistic electronic structure calculated from first principles to simplified models, which allow to better understand the interplay between spin, orbital, and lattice degrees of freedom in complex oxides.

### Soft x-ray photoemission spectroscopy on buried interfaces

*Claudia Cancellieri (PSI, SLS)*

At the interface between complex oxides, unexpected electronic properties different from those of the constituent bulk materials can arise. A particularly interesting example is the appearance of 2-dimensional conductivity at the interface of the band insulators LaAlO<sub>3</sub> (LAO) and SrTiO<sub>3</sub> (STO) [1–3] above a critical LAO thickness of 4 unit cells (u.c.) [4]. A very recent related heterostructure is the diluted system of (LaAlO<sub>3</sub>)<sub>x</sub>(SrTiO<sub>3</sub>)<sub>1-x</sub>/SrTiO<sub>3</sub> (LASTO:<sub>x</sub>/STO) which also shows interfacial conductivity above a certain critical LASTO thickness which scales inversely to the LAO content [5]. The interfaces of LaAlO<sub>3</sub>/SrTiO<sub>3</sub> and (LaAlO<sub>3</sub>)<sub>x</sub>(SrTiO<sub>3</sub>)<sub>1-x</sub>/SrTiO<sub>3</sub> heterostructures have been investigated by soft x-ray photoelectron spectroscopy for different layer thicknesses across the insulator-to-metal interface transition. The valence band and Fermi edge were probed using resonant photoemission across the Ti L<sub>2,3</sub> absorption edge. We measured, for the first time to our knowledge, clear spectroscopic signatures of Ti<sup>3+</sup> signal at the Fermi level in fully oxygenated samples of LAO/STO and the related system of mixed LASTO:0.5/STO. Our results show that Ti<sup>3+</sup>-related charge carriers are present in both systems, but only for conducting samples. No Fermi-edge signal could be detected for insulating samples below the critical thickness. Furthermore, the angular dependence of the Fermi intensity allows the determination of the spatial extent perpendicular to the interface of the conducting electron density.

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### Interplay between superconductivity and magnetism in La<sub>2-x</sub>Sr<sub>x</sub>CuO<sub>4</sub> /

La<sub>0.67</sub>Ca<sub>0.33</sub>MnO<sub>3</sub> heterostructures

*Saikat Das (Department of Physics and Fribourg Center for Nanomaterials, University of Fribourg, Chemin du Musée 3, CH-1700 Fribourg, Switzerland)*

We studied the interplay between superconductivity and magnetism in La<sub>2-x</sub>Sr<sub>x</sub>CuO<sub>4</sub> (LSCO)/La<sub>0.67</sub>Ca<sub>0.33</sub>MnO<sub>3</sub> (LCMO) superlattices (SLs). By varying the Sr content and thus the hole doping in the cuprate layers, three SLs (x=0.0, 0.15, 0.30) have been prepared using pulsed laser deposition. Upon Sr doping, the cuprate layers evolve from the insulating parent compound with an AF order of the Cu moments at x=0, over the high temperature superconducting state at x=0.15, to a metallic state where superconductivity is suppressed again at x=0.3. The quality of the samples has been characterized by in-situ Reflection high-energy

electron diffraction and X-ray diffraction techniques. The polarized neutron reflectometry on these SLs reveals the existence of a so-called depleted layer with a strongly suppressed ferromagnetic Mn moment on the LCMO side of the interface with a thickness of about 10 Å. On the other hand, with X-ray magnetic circular dichroism measurements we observed an induced Cu moment on the LSCO side of the interface. With X-ray magnetic linear dichroism measurements we also observed the signature of an orbital reconstruction effect of the Cu states at the interfaces of these superlattices.

### **Orthorhombic LuMnO<sub>3</sub> thin films, a multifunctional multiferroic** *Christof Schneider (PSI)*

Materials featuring the co-existence of coupled magnetic and ferroelectric order allow the switching of magnetic moments by an electric field and vice versa. Experimentally, only a few multiferroic materials are known to be ferromagnetic, with the large majority being antiferromagnetically ordered. We studied thin films of orthorhombic LuMnO<sub>3</sub>, a material which is known to exhibit magnetically-induced ferroelectricity with an E type antiferromagnetic groundstate. In single crystalline like thin films grown by pulsed laser deposition on YAlO<sub>3</sub> substrates, we identify co existing and coupled ferromagnetic and antiferromagnetic orders. The ferromagnetism is located in a layer close to the substrate-film interface and extends over ~10 nm with a constant magnetic moment of ~1 μB, subsequently falling off towards the film surface. This single phase material with coupled ferro-, antiferromagnetic orders thus represents an important step towards a future utilization of multiferroic materials in spintronic device with a built-in exchange bias.

### **XMCD/XLD Study of the Magnetoelectric Coupling Mechanism in the Multiferroic Composite Co/PMN-PT(011)**

*Jakoba Heidler (PSI, SLS, Villigen)*

Multiferroic composites are promising candidates amongst the strategies to achieve electric field control of magnetism. In compounds consisting of ferromagnetic and ferroelectric (FE) layers strain can couple the FE phase via the piezoelectric effect to the magnetic phase employing magnetostriction. [Pb(Mg<sub>1/3</sub>Nb<sub>2/3</sub>)O<sub>3</sub>]<sub>(1-x)</sub>-[PbTiO<sub>3</sub>]<sub>x</sub> (PMN-PT) is a relaxor FE with strong piezoelectric properties near the morphotropic phase boundary x=0.3 [1] - Wu et al. reported on a remanent in-plane FE polarization for PMN-PT (011) in addition to the two out-of- plane polarization directions [2]. The impact of the FE order of PMN-PT (011) on the electronic and atomic structure of a Co top layer is studied using X-ray magnetic circular dichroism (XMCD) and X-ray linear dichroism (XLD) for Co and Ti respectively. We observe the development of a magnetic easy axis upon rotating the FE polarization to in-plane due to strain-mediated coupling (see Fig. 1, red curve). The data suggest an additional charge driven magnetoelectric coupling due to electron accumulation/depletion at the Co/PMN-PT interface (Fig. 1, green and blue curve). Moreover, the Ti data shows a change in the spectrum with applied voltage which is described with the help of multiplet calculations.

### **Muon-spin Relaxation Studies of Diffusion Processes in Battery Materials**

*Martin Mansson (LQM, EPF Lausanne)*

Solid state diffusion is a very complex mechanism and, up until recently, studies of such properties have mainly been conducted by macroscopic methods that do not yield true material properties. This has been a major problem for materials development regarding e.g. Li-ion batteries where the basic operational principle is based on diffusion of Li-ions. Although the microscopic diffusion coefficient of Li<sup>+</sup> (DLi) in solids has been frequently evaluated by Li-NMR, difficulties arise for materials that contain magnetic ions. As a result, it is very difficult to correctly estimate DLi by Li-NMR for most battery materials, particularly for positive electrode materials. Since DLi is one of the primary parameters that govern the charge and discharge rate of a Li-ion batteries, such situation is very unsatisfactory. In order to rectify the shortcomings of NMR and electrochemical measurements, we have developed a novel method that utilizes the muon-spin relaxation (muSR) technique to probe the microscopic ion self-diffusion constant (Dion) in a straightforward manner. In this poster, we will give an introduction to the method itself [1-2] but also summary our muSR work on Li-diffusion in battery cathode materials [3-6]. Furthermore, we will show that the method is not limited to studying only Li-ion diffusion but can also be extended to other groups of compounds [7] and applications e.g. vacancy order formation in transition metal oxides. Finally, we will compare our method to other available microscopic techniques that are able to study ion diffusion in solids, e.g. quasi-elastic neutron scattering (QENS), as well as make an outlook towards future developments.

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- [6] Phys. Rev. B 85, 054111 (2012)
- [7] Publication in progress (2013)

## **Lithium Transport through Nanosized Amorphous Silicon Layers**

*Erwin Hueger (TU-Clausthal)*

The talk presents an approach to use neutron reflectometry (NR) to measure non-destructively lithium transport through nanometer thin layers of, e.g., relevant electrochemical materials. Such experiments are interesting for research on nanostructured electrode materials to understand and improve high energy density lithium batteries. Beside the important role of Li diffusion for the insertion and removal of Li at electrodes, the determination of the Li permeability through ultrathin films is also of interest. This is especially true for devices where selective diffusion of Li is required. The selective filtering of Li is especially important for lithium-air batteries, Li ion selective electrodes, and sensors [1].

The methodology is demonstrated for 10 nm thin amorphous silicon layers covered by solid Li tracer reservoirs [2]. A multilayer with a repetition of five [Si / natLiNbO<sub>3</sub> / Si / 6LiNbO<sub>3</sub>] units is used for analysis. Two types of NR Bragg peaks are detectable. One type of Bragg peaks originates from LiNbO<sub>3</sub>/Si chemical contrast, the other one from 6Li/7Li isotope contrast. Diffusion annealing reduces the intensity of the Bragg peak resulting from the 6Li/7Li isotope contrast but not that from the LiNbO<sub>3</sub>/Si chemical contrast. This demonstrates that the Bragg peak decrease is a measure of the 6Li and 7Li transport through the Si layer. These results open the possibility to determine the rate determining step (diffusion controlled or interface reaction controlled) of the Li transport process and to quantify Li transport parameters (diffusivity and permeability) in nanometer thin layers as a function of (i) chemical composition, (ii) film structure (amorphous or nanocrystalline), (iii) confinement (thickness of the layer) and (iv) temperature (e.g. to determine activation energy).

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## **Using muons as microscopic spin probes for organic devices**

*Laura Nuccio (University of Fribourg)*

One future avenue that may expand the rapidly growing spintronic technology is to take advantage of the long spin coherence time and of the flexibility of organic semiconductors [1]. However, advancements in understanding the behaviour of hybrid organic/inorganic spintronic devices have been slowed down by the lack of experimental techniques able to directly measure the polarization of injected carriers in operational devices. We show how it is possible to use low energy muon spin rotation (LEM) to obtain a direct and depth-resolved measurement of the spin polarization of the injected charge-carriers in a fully functional organic spin valve. Muons act as local magnetic probes, directly measuring the magnetic field distribution at the implanted site. By measuring the local magnetic field with current on and current off it is possible to extract the contribution of the spin-polarized current. Using different implantation energies finally allows to obtain the depth-resolution [2]. Using LEM we were able to prove, for example, that it is possible to control the spin polarization of extracted charge-carriers from an OSC by the inclusion of a thin interfacial layer of polar material [3].

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## **Single-Ion Magnets: Playing with Molecule-Substrate Interactions**

*Jan Gui-Hyon Dreiser (Ecole Polytechnique Federale de Lausanne and PSI)*

Single-Ion Magnets (SIMs) [1-3] contain a single transition metal or rare-earth ion embedded in an organic ligand. In contrast to many other mononuclear molecular magnets, SIMs exhibit long magnetization relaxation times rendering them good candidates for future molecular spintronics or information processing applications. In order to exploit their properties they should be organized and addressable one-by-one [4], and one way to achieve this goal is to deposit submonolayers of SIMs on to surfaces. Interestingly, the properties of SIMs can be strongly modified upon adsorption on a surface with respect to the bulk crystalline phase because of molecule-substrate interactions [5]. It is thus important to understand how these interactions can be employed to

control magnetic and structural properties of the SIMs. We will present our most recent experiments with respect to these goals.

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### Phase change in stacked chalcogenide layers

#### *Alin Velea (PSI)*

Phase change materials (PCM) are promising substitutes for existing flash memories which have almost reached their miniaturization limit. The PCM memory storage is based on modification of optical and electrical properties at the transition from an amorphous to a crystalline state. Here, we report on single and bi-layer thin films of GeTe, SnSe and GaSb prepared by pulsed laser deposition on glass substrates. GeTe has been chosen because is one of the fastest phase change material with the switching speed of less than 10 ns. SnSe is very similar with GeTe, it has the same average number of valence electrons and almost the same band gap. Unlike GeTe which crystallizes in the rhombohedral structure, SnSe crystallizes in the orthorhombic structure. On the other hand, in the amorphous phase, SnSe is highly resistive which results in a lower current necessary to reset the memory cell. The third material, GaSb, is characterized by a remarkably high thermal stability and it crystallizes in a cubic structure. The variation of single layer resistance as function of temperature was measured by four-probe method in inert atmosphere. The bi-layer samples were annealed at different temperatures below and above their transition temperature. All the films have been investigated by Extended X-ray absorption fine structure (EXAFS) and X-ray diffraction (XRD). The EXAFS analysis at the Ga, Ge and Se K-edges reveals information about the changes in local atomic environments as a function of temperature. Complementary to EXAFS analysis, X-ray diffraction spectra of the as-deposited and annealed samples were recorded in transmission at 17 keV. At specific annealing temperatures, discrete changes in the atomic long range order of bi-layers were detected. In the case of GeTe/SnSe bilayers we observed that SnSe increases the crystallization temperature of GeTe. The formation of SbSn alloys in GaSb/SnSe bilayers at high annealing temperatures was evidenced.

### Electronic structure of impurity systems by resonant soft-X-ray ARPES: Application to the diluted magnetic semiconductor GaMnAs

#### *Vladimir Strocov (SLS, PSI)*

A fundamental benefit soft-X-ray ARPES (SX-ARPES) in the energy range around 1 keV is the photoelectron escape depth increasing by a factor of 3-5 compared to the conventional VUV-ARPES. Furthermore, this region covers the 2p and 3p core levels of the transition and rare earth metals, respectively, which brings another benefit of the elemental and valence-state specificity achieved through resonant photoemission. These spectroscopic properties of SX-ARPES, combined with advanced instrumentation since recently available at the ADDRESS beamline of SLS, have enabled the move of this technique from bulk materials to buried heterostructures and impurities.

We illustrate first applications of resonant SX-ARPES to impurity systems with the diluted magnetic semiconductor (Ga,Mn)As, which is considered as the paradigm spintronics material. Despite more than a decade of intense research and various theoretical approaches ranging the p-d exchange to double-exchange models, the mechanism of ferromagnetism in (Ga,Mn)As still remains obscured. Our resonant SX-ARPES experiments on the Mn 2p absorption edge have for the first time unambiguously identified the Mn 3d-derived impurity band (IB) inducing the ferromagnetism as located about 300 meV below the valence-band maximum and hybridized with the light-hole band of the host GaAs. These findings conclude the long disputed picture on the (Ga,Mn)As valence band structure. The non-dispersive character of the IB and its energy alignment relative to the GaAs bands unveil its origin as a split-off Mn-impurity state predicted by the Anderson model. Responsible for the ferromagnetism in (Ga,Mn)As is the transport of hole carriers in the IB. Our experiments are further extended to (InFe)As showing the ferromagnetism induced by doped electron carriers. These examples illustrate an enormous application potential of SX-ARPES to a wide range of functional materials from bulk systems to heterostructures and impurities.

#### References:

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## **Electron Dynamics in TiO<sub>2</sub> Nanoparticles Study by High Repetition Rate Laser Pump / X-ray Probe Technique**

***Mercedes Hannelore Rittmann-Frank (Laboratoire de Spectroscopie Ultrarapide, Ecole Polytechnique Fédérale de Lausanne, Lausanne, Switzerland)***

Electron migration and surface trapping are crucial in applications such as photocatalysis and solar energy conversion. Indeed for the former, the migration of charge carriers to the surface, where they can react with species adsorbed onto it, is the most important step.

To address the issue of charge migration, we performed ps time resolved X-ray absorption spectroscopy at the Ti K-edge on TiO<sub>2</sub> anatase nanoparticles suspension, using our recently developed high repetition rate data acquisition scheme [1]. After exciting electrons across the band gap at 355 nm, the transient spectrum (excited – ground state sample) at 100 ps clearly shows a localization of the electron at reduced Ti<sup>3+</sup> centres that are coordination-unsaturated (i.e. tetra- or pentacoordinated, as opposed to hexacoordinated for the bulk). These unsaturated coordination sites predominantly occur at the surface due to truncation effects [2].

We found that the reduced centres, generated within the 70 ps width of the probe pulse, decay typically on two time scales, which we attribute to tetra- and penta-coordinated sites that are promptly populated, as opposed to a cascade mechanism from shallow to deep traps [3]. Similar results were obtained upon injection of an electron into the conduction band from an adsorbed Ruthenium dye (N719, as in dye-sensitized solar cells) excited at 532 nm. This implies that whichever way the electron is delivered to the CB, its ultimate trapping sites are identical.

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