Engineering the electronic properties of manganite heterostructures and interfaces for oxitronic applications.

Oxide electronics (or "oxitronics") materials provide a plethora of possible applications and offer many opportunities for scientists to probe some of the most exciting and intriguing phenomena exhibited by oxide systems and oxide interfaces. Among these oxides, the ABO_3 perovskite structure yields a fascinating class of materials, where almost all kinds of physical properties can be found (metallic, insulating, superconductivity, magnetism, ferroelectricity, etc…). For instance, $BiFeO_3$ is exhibiting simultaneously ferroelectricity and antiferromagnetism, resulting in a rather unique room temperature multiferroic. The manganites, $AMnO_3$, such as (La,Sr)MnO_3 or $CaMnO_3$, have also a very complex phase diagram encompassing ferromagnetism and metal-insulator transition. Furthermore, new properties are observed for heterostructures based on thin films of manganites, notably due to the presence of interfaces (with 3d perovskite such as $BiFeO_3$, but also with 4d or 5d perovskites).
For instance, a giant modulation of the resistivity upon a control of the ferroelectric polarization has been reported for tunnel junctions based on a metal/$BiFeO_3$/$CaMnO_3$ structures [1]. More recently, interfaces based on (La,Sr)MnO_3 have been proposed as a possible spin to charge current converter. The $BiFeO_3$/(La,Sr)MnO_3 interface might also enable manipulation of spin waves that is an essential development for future magnon-based technologies [2]. For all these applications, the role of the structure and electronic structure reconstruction at interfaces is crucial and remains unknown on many aspects. Indeed, both structural and electronic structures can be very different from the bulk near the interface and often change at subnanometer scale (due to potential discontinuity at interface, to strain and strain relaxation at several nanometers of the interface, etc..).
The PhD student will have to investigate the structure and electronic structure of heterostructures and interfaces based on manganite thin films, by using a combination of X-ray (Soleil synchrotron) and electron (LPS-university Paris-Sud) based spectroscopic and microscopic techniques. Both techniques, when done at the state-of-the-art, can have spatial or in-depth resolution enabling the studies of interface heterogeneities.
The student will strongly interact with the Unité Mixte de Physique CNRS-Thales laboratory (Palaiseau) where samples will be grown and physical properties measured. The goal is to elucidate the role of interfacial mechanisms for a further engineering of the functionality through a tailoring of the electronic properties. The PhD thesis is part of the AXION program funded by the LabEx NanoSaclay.

Severals hetero-structures will be investigated.
A first series of heterostructures comprises an interface between (La,Sr)MnO_3 manganite and $BiFeO_3$. In such system, spin current to charge current conversion has been recently observed. Obtaining a strong spin-charge conversion is indeed a promising key element in order to achieve energy efficient device [3]. It is then important to understand the underlying interfacial mechanisms (such as a possible interfacial Rashba-Edelstein effect) that govern such properties. On that aspect, we will investigate several systems where the electronic structure at the interface will be engineered (by introducing an additional layer, inverted interface, strain) in order to modulate the spin-charge conversion. In particular, we will try to measure and control the energy position and the filling of the Mn-e_g band at the interface. In the same context, the potential of ruthenates and iridates (i.e. 5d and 4d transition metal oxide) as efficient convertors will be investigated at the interface with the same manganite. Indeed, 4d and 5d exhibit higher spin-orbit coupling that can be used to control the spin-orbit effect at the interface, notably by a strong hybridization and charge transfer with the Mn-e_g band at the interface [4]. In particular, it depends on the potential confinement, the orbital degeneracies and

structural reconstruction at the interface that will be investigated by high-energy photo-emission spectroscopy (HAXPES) and scanning transmission electron microscope with electron energy loss spectroscopy (STEM-EELS).
A second system comprises $BiFeO_3$ and the $CaMnO_3$ manganite. In such heterostructure, the electrical transport properties can be controlled in a non-volatile manner by switching the ferroelectricity of the $BiFeO_3$, which is also an energy efficient process [5]. The interface plays also an important role for such application and can control the possibility to reverse the $BiFeO_3$ ferroelectricity. On that aspect, it is crucial to understand the formation of defects at the interface and of domain and domain walls in the $BiFeO_3$ film by microscopic investigation [6,7]. Further strategy to control interfacial dipoles and potential will thus be developed.

During the PhD thesis, the student will have to investigate quantitatively the electronic and crystal structures of such heterostructures and relate them to the physical measurements and the device functionalities.
The work will be done using a worldwide unique STEM-EELS (Scanning transmission electron microscope-Electron energy loss spectroscopy) instrument. Such instrument enables for instance to quantitatively describe the interfacial structure (plane termination, structural distortions). New imaging techniques such as atomically-resolved phase contrast imaging (STEM-ABF) will be used in order to determine the reconstruction of the oxygen octahedra, that are known to play a crucial role in the electronic structure reconstructions [8]. The student will also use state of the art EELS capabilities in order to investigate the charge and orbital reconstruction within the heterostructure and notably at the interfaces. **Such work will be done in the STEM group of the LPS-CNRS under the supervision of A. Gloter.**
Synchrotron techniques and in particular, photo-emission spectroscopy (PES) related techniques, will also be used to reveal the electronic structure. For instance, high-energy PES (HAXPES) combined with standing wave geometry will give the opportunity to investigate the valence band evolution across the heterostructure. Such techniques require rigorous modeling of the X-ray interaction within the heterostructure, but can reveal the potential discontinuity associated to the various interfaces [9]. In addition, resonant (angle-resolved) photo-emission will enable to separate Mn and Fe electronic reconstructions. Furthermore, in-operando experiments, where heterostructures can be switched during the investigation, will be done. **Such work will be supervised by JP. Rueff from the SOLEIL Synchrotron.**
The sample and physical properties will be grown and measured at the Unité Mixte de Physique CNRS-Thales laboratory with whom the PhD student will strongly collaborate.

[1] H. Yamada, V. Garcia et al., *Giant Electroresistance of Super-tetragonal $BiFeO_3$-Based Ferroelectric Tunnel Junctions*, *ACS Nano* 7 , 5385–5390 (2013)
[2] Hämäläinen et al., *Control of spin-wave transmission by a programmable domain wall*, *Nature Communications* **9**, Article number: 4853 (2018)
[3] S. Manipatruni et al, *Scalable energy-efficient magnetoelectric spin–orbit logic*, Nature 565, 35 (2019)
[4] Okamoto et al., Charge Transfer in Iridate-Manganite Superlattices, Nano Lett. 17, 2126−2130 (2017)
[5] S. Boyn, V. Garcia et al. *Engineering ferroelectric tunnel junctions through potential profile shaping,* APL Materials 3, 061101 (2015)
[6] Bégon-lours et al., *Factors limiting ferroelectric field-effect doping in complex oxide heterostructures*, 10.1103/PhysRevMaterials.2.084405 (2018)
[7] X. Li, Q. Zhu, L. Vistoli, M. Bibes, A. Barthélémy, S. Fusil, V. Garcia, A. Gloter, *In-depth mapping of ferroelectric-field effect transistor switching at submicron and atomic-scales*, in preparation.
[8] X. Li, I. Lindfors-Vrejoiu, M. Ziese, A. Gloter, & P.A. van Aken, *Impact of interfacial coupling of oxygen octahedra on ferromagnetic order in $La_{0.7}Sr_{0.3}MnO_3/SrTiO_3$ heterostructures*. Scientific Reports 7, 40068 (2017).
[9] S.C. Lin et al., *Interface properties and built-in potential profile of a $LaCrO_3/SrTiO_3$ superlattice determined by standing-wave excited photoemission spectroscopy*, Phys. Rev. B 98, 165124 (2018)

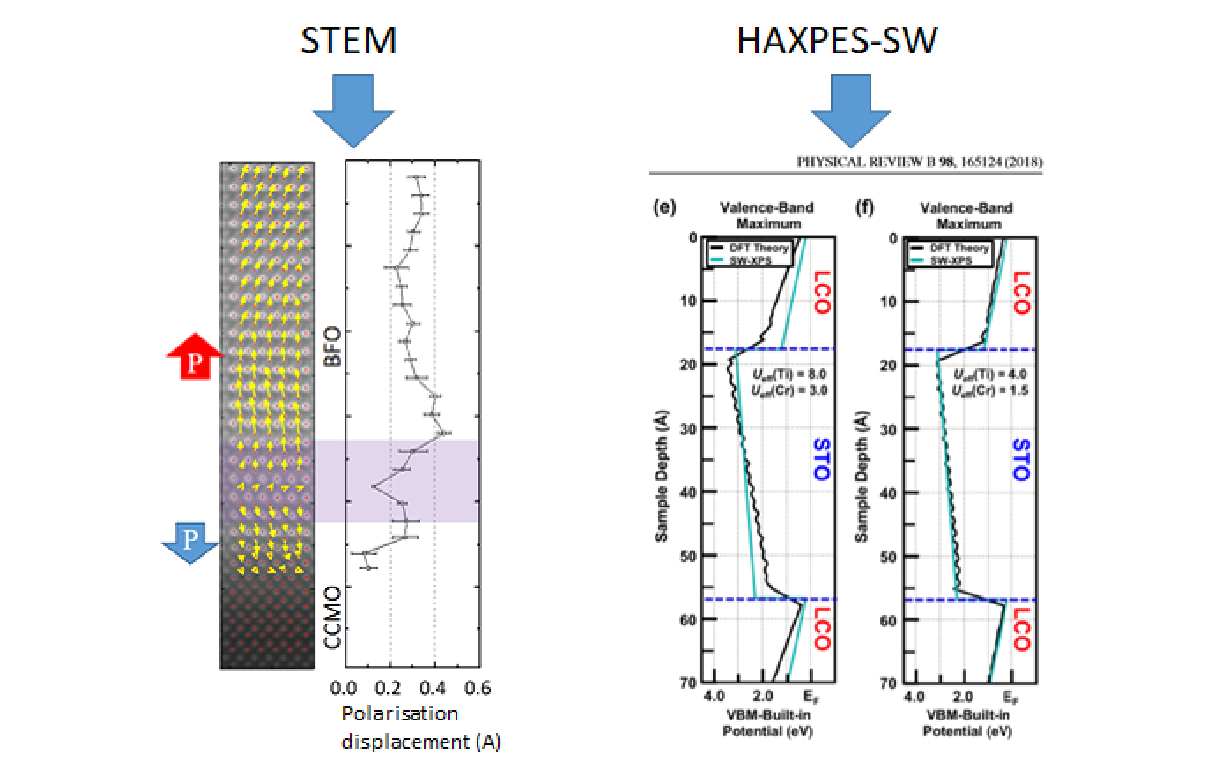

Figure 1. left) STEM reveals the formation of domain walls in a ferroelectric nano-layer [7]. Right) HAXPES reveals the built-in potential within nano-layers [9]. Combining STEM and HAXPES can thus reveal the structural and electronic structure within heterostuctures and devices.

Supervision :

The thesis will be conducted in the STEM group at the Laboratoire de Physiques des Solides @ Université Paris-Sud and at the SOLEIL synchrotron

J.P. Rueff (jean-pascal.rueff@synchrotron-soleil.fr) and A. Gloter (alexandre.gloter@u-psud.fr) will supervise the PhD thesis

More information can be found at:

https://www.synchrotron-soleil.fr/fr/lignes-de-lumiere/galaxies

https://www.stem.lps.u-psud.fr/

The student will be part of a collaborative network involving the research group synthetizing the thin film samples and measuring the transport properties at the Unite Mixte de Physique CNRS-Thales (V. Garcia, M. Bibes, S. Fusil, A. Barthélémy)

http://www.cnrs-thales.fr/

https://oxitronics.wordpress.com/

Applicant:

The candidate holds an MSc or equivalent degree in Physics or related fields (condensed matter physics, applied physics, material science, ...). Students with an interest for experimental physics are welcome to apply. Affinity with spectroscopy, microscopy techniques will be an asset. PhD student will work in an international competitive context requiring a high motivation to learn and a strong intellectual curiosity.