Research Networking Programmes

Science Meeting – Scientific Report

The scientific report (WORD or PDF file - maximum of seven A4 pages) should be submitted online within two months of the event. It will be published on the ESF website.

Proposal Title:

Emergent structural and electronic phenomena at interfaces of nanoscale oxides

Application Reference N°:

Psi-K2 - Science Meeting 5738

1) Summary (up to one page)

Novel phenomena, not found in the bulk constituents, such as interface charge, spin, and orbital reconstructions, have been shown to occur at nanoscale interfaces involving oxide materials. These phenomena have stimulated a flurry of activity aiming at creating and manipulating novel electronic properties of oxide interfaces. Polarity of the oxide component adds an additional level of complexity, which may dramatically impact the interface charge state and electronic characteristics. The reduced thickness of oxide films brings additional features, since interface effects may strongly alter the properties of both film and substrate. This leads to a sub−critical regime at low thickness, where nano−oxides can be stabilized in a polar uncompensated state or/and with a structure and/or stoichiometry different from the corresponding bulk.

The existence of interface electronic states, their nature, charge state, and character of localization are principally driven by the band character and alignment at the interface. However, ab initio computational studies of interfaces suffer from drawbacks of DFT-based methods. Indeed, it is found that (semi−) local exchange correlation functionals (GGA or LDA) fail to reproduce the band−gap and absolute positions of valence and conduction bands of the oxide constituents. It is not yet clear how effective are the improvements in the calculated interface band alignments brought about by the use of non-local (hybrid) functionals.

The atomic structures of low-dimensional oxides and interfaces have been fully established only in a limited number of cases. It is well known that low dimensional systems may adopt structural motifs which differ from the corresponding bulk system. Due to the lack of long range order, it is practically impossible to determine these structures using experimental techniques alone and deep insight and understanding can be achieved only by combining the multitude of different experimental techniques with extensive calculations.

2) Description of the scientific content of and discussions at the event (up to four pages)

With increasing miniaturization of system components in nanotechnology, interfaces between different materials are becoming ever more prominent and can ultimately dominate performance of devices. Oxide materials play a crucial role in numerous technological applications. Research in recent years has therefore focused on oxide nanostructures coupled to various (e.g. metallic and oxide) substrates with the aim to create new low-dimensional hybrid materials with novel physical and chemical properties. The growing importance of these systems stems from the fact that their hybrid character and low dimensionality entail emergent phenomena and novel properties which differ significantly from those of individual constituents. These novel properties open new avenues for materials science and design with the perspective of nanotechnology applications in the fields of heterogeneous catalysis, electronic device technology including magneto-resistive and spintronic devices, gas sensors, (multi)functional coatings or corrosion inhibition, and environmental chemistry.

Theoretical modelling plays a crucial and multifaceted role in this field. First, theory is used to set up a framework of basic principles that govern the emergent phenomena in oxide nanostructures and to provide in-depth analysis of the origins of interactions in these complex systems. Moreover, reliable computational predictions of both energetic parameters (thermodynamics of phase transformations, lattice constants, phonon spectra, chemical bonding and reactivity) and electronic structure (electric potential, charge distributions and transport, local density of states, spin coupling phenomena) can often be achieved by state-of-the-art theoretical approaches. In numerous well-documented cases, theory has helped to resolve experimental ambiguities and to predict new experiments and phenomena. However, in order to further fulfil this important role, some key challenges need to be addressed that are currently hampering theoretical analysis: (1) the accuracy of the present level of theoretical description is often unsatisfactory for this class of hybrid materials, and (2) the interactions and methodological exchanges among the different communities that deal with oxide interfaces with other materials have so far been scarce or even non-existent. For example, the catalysis, fuel cell and microelectronics communities often use the same metal/metal-oxide interfaces but have separate forums for discussions and exchange of ideas.

The aim of the workshop was to make a contribution to the development of the field in two ways. First, by bringing together scientific communities that are dealing with oxides and oxide interfaces from different perspectives, namely: i) electronic structure at oxide/oxide interfaces; ii) surface reactions at ultrathin oxide films; and iii) microelectronic devices. Second, by elucidating limitations and highlighting advances of electronic structure methods for accurately predicting the properties of heterogeneous

multi-component systems, and by identifying strategies for structural optimization of complex interfaces and surface structures.

The workshop was organized in six thematic sessions focussing on different aspects of nano-scaled oxides, namely:

1. Ultrathin oxide films supported on metals
2. Metaloxide nanoparticles
3. Oxide-oxide interfaces
4. Oxide devices
5. 2D electron liquids at oxide interfaces
6. Reactions at oxide surfaces

The sessions were designed to gradually increase the complexity of the systems. Discussions were stimulated by allocating at least ten minutes for questions at each talk and two dedicated round table discussions at the end of both the first and the second day of the workshop. In addition to the oral sessions, there was a lively poster session with ten contributed poster presentations.

The first presentation on ultrathin oxides concerned experimental work on two-dimensional Ni- and Mn-oxides supported on noble metal surfaces. The work focussed on novel oxides phases observed at this length scale and the importance of kinetic effects in the growth of the films. The experimental presentation was followed by a theoretical talk targeting similar systems and highlighting the metallization of the ultrathin oxide films and how electronic states (bound and excited) are modified by the presence of the oxide/metal interface.

The complexity of structure and composition of oxides at the nanoscale was underlined in the second session where structures of, for example, MgO, Fe_2O_3 clusters was discussed. The presented work showed that the clusters may have a different stoichiometry than that of the corresponding bulk, and that the relevant structural motifs might be very different. A part of the discussion on this topic concerned the use of model potentials to predict structural properties of clusters that are too large for exhaustive structural searches with ab initio methods.

The special properties of oxide/oxide interfaces were discussed with examples for perovskites including $SrTiO_3/BaTiO_3$ and $SrTiO_3/LaAlO_3$ where the latter is an example of a superconducting two dimensional electron liquid at the interface. Moreover, the properties of polar/polar interfaces was discussed in one contribution. For various systems, the structure and properties of vacancies was discussed. One example was the aggregation of anion vacancies in oxygen deficient strontium chromite. The importance of vacancies and defects for electron transport properties in oxide devices was also discussed.

The last session concerned reaction at oxide surfaces. Ultrathin oxide films supported on metal surfaces was in this context discussed both as model systems within heterogeneous catalysis and as systems with unique properties. Concerning the theoretical description of reactions at surfaces special attention was given both the need of descriptions beyond the standard DFT-framework based on the generalized gradient approximation and the need for descriptions that include van der Waals interactions.

3) Assessment of the results and impact of the event on the future directions of the field (up to two pages)

Several parallel routes of developments have been clearly evidenced during the workshop.

It is becoming increasingly clear that the semi−local functionals commonly used in DFT are not accurate enough to describe various properties of oxide surfaces and interfaces. Because of this, there most likely will be a change of “standard” calculations to include a part of Hartree−Fock exchange (hybrid functionals). However, there are issues regarding the performance of hybrid functionals for metallic systems which causes problems in describing multi - component systems. One possible route to avoid these problems that most likely will be advanced during the next few years is creating functionals that are space−dependent, i.e. different functionals are used for different parts of the system.

The increased use of hybrid−functionals, will be paralleled by an increased use of functionals that include van der Waals interaction. There is clear evidence that accurate treatment of van der Waals interaction is required for a proper description of metal/oxide interfaces as well as adsorption of molecules on oxide surfaces. It is likely that van der Waals functionals will replace the presently often used semi - empirical corrections.

A computationally more efficient alternative is offered by GGA+U approaches, and numerous examples of their successful application to a variety of oxide materials have been discussed during the presentations. However, as stressed during the discussion, in the case of nano−scale objects, surfaces, and interfaces it may become particularly difficult to take into account the effect of local environment on the value of U. Elaboration of (semi−) empirical rules governing the behavior of U appears as a promising opening for making this efficient approach more robust.

Another growing area concerns powerful tools for structural optimization required for describing the structural and chemical complexity of nano−oxides and their interfaces. Efficient algorithms exist (GA, basin hopping, etc.) and have been successfully applied principally to oxide nano−particles and unsupported thin films. Coming years will see further improvement and extension of these optimization techniques towards supported films and interfaces, with a focus on an efficient handling of strain - induced effects. Also large models for amorphous systems will probably also grow in importance.

Alternatively, application of global optimization methods for a search/optimization of a given property rather than merely for energy minimization has been evoked as an interesting opening towards a more efficient material engineering.

Yet another emerging research area that will certainly receive considerable attention over the next few years is that of the oxide/liquid interfaces.

4) Annexes 4a) and 4b): Programme of the meeting and full list of speakers and participants

Annex 4a: Programme of the meeting

Emergent structural and electronic phenomena at interfaces of nanoscale oxides

April 8-10, 2015

Lausanne, Switzerland

Scientific Program

Wednesday, April 8, 2015

Session I Ultrathin oxide films supported on metals

Chair: Gianfranco Pacchioni

9:00 Falko Netzer
2-D Oxide Layers on Metals: Revealing the Metal-oxide Interface

9.50 Luca Sementa
Structure, Energetics and Electronic Phenomena in Oxide Ultrathin Films

10.30 Stefan Bromley
A plethora of polymorphs: oxide nanofilms and nanoporous oxide phases from structure prediction

11.10 Coffee

Session II Metal oxide nanoparticles

Chair: Falko Netzer

11.40 Marek Sierka
Theory and experiments go hand in hand: nanoparticulate metal oxides

12.20 Sergey Kozlov
Nanostructured Metal Oxides and Transition Metal Nanoparticles Interacting with Oxide Surfaces from Density-Functional Modelling

13.00 Lunch

Session III Oxide-oxide interfaces

Chair: Marek Sierka

14.00 Luca Ghiringhelli
Theoretical evidence of unexpected O-rich phases in MgO clusters and at corners of extended MgO surfaces

14:40 Paola Luches
Atomic scale structure and charge transfer at cerium oxide/metal interfaces

15.20 Karoliina Honkala
Mn and Cu Oxides from First Principles Calculations: Reduction and Oxygen Transport

16.00 Coffee

16.10 **Round Table I: Static and dynamic structure**

Alessandro Furtunelli (Moderator)

17.30 **Poster Session**

Posters

1. **Strain Induced Metal-Insulator Transition in Ultrathin films of $SrRuO_3$**
   B. Mandal, K. Gupta and P. Mahadevan

2. **Rumpling-Controlled Adsorption of NO on Metal-Supported FeO(111) Thin Films**
   C.J. Heard, L.R. Merte, Edvin Lundgren, H. Grönbeck

3. **Mixed-valent perovskite oxides based on $BaBiO_3$ for spintronics**
   G.C. Shan and B. Yan

4. **Defect Density of States of Silicon/Silica and Silicon/Hafnia Interfaces**
   E. Mehes and C. H. Patterson

5. **Density Functional Theory Modeling of Pyrphyrin-Cobalt Adsorption on Rutile(110) Surface**
   Y. Gurdal, S. Luber, M. Iannuzzi, and J. Hutter

6. **Gold assisted oxygen dissociation on Mo doped CaO(001) surface with formation of linear O-Au-O chains**
   J. Nevalaita, K. Honkala, and H. Häkkinen

7. **Cu Adatom Charging on Metal Supported Thin Films: ScN, MgO and NaF on Mo**
   P. A. Žguns, M. Wessel, N. V. Skorodumova

8. **Low dimensional constraints in the phase diagram of magnetite**
   S. Gallego

9. **MoS2/graphene oxide as novel semiconductor/oxide interfaces for electronics**
   T. Musso, P. V. Kumar, A. S. Foster and J. C. Grossman

10. **Water Dissociation at $SrTiO_3$ (110) Surface Promoted by Two-dimensional Electron Gas**
    Z. Wang, X. Hao, S. Gerhold, C. Franchini, M. Schmid, U. Diebold

Thursday, April 9, 2015

Session IV Oxide devices

Chair: Peter Shushko

9:00 Gennadi Bersuker
Charge transfer in multi-component materials stacks

9.50 Stefano Sanvito
Modeling multifunctional oxides devices from first principles

10.30 Tibor Grasser
Capture and Emission of Single Holes in Nanoscale MOS Transistors: Linking DFT to Experiment

11.10 Coffee

Session V 2D electron liquids at oxide interfaces

Chair: Claudine Noguera

11.40 Stefano Gariglio
Study of Superconductivity at $LaAlO_3/SrTiO_3$ Interfaces by Field Effect

12.20 Marc Gabay
Spin Polarized State in the Two-Dimensonal Electron Liquid at the Surface of $SrTiO_3$

13.00 Lunch

Chair: Marc Gabay

14.00 Marco Gibertini
Engineering polar discontinuities in 2D honeycomb lattices

14.40 Julian Velev
Spin-Polarized Two-Dimensional Electron Gas at Oxide Interfaces: Insight from First-Principles Calculations

15.20 Claudine Noguera
Electronic Structure Scenarios at Stoichiometric Polar/Polar Interfaces

16.00 Peter Sushko
From Point Defects to Defect Superstructures in Complex Oxides

16.40 Coffee

16.50 **Round Table II**: **Electronic structure and transport**

Alexander Shluger (Moderator)

19:30 Dinner

Friday, April 10, 2015

Session VI Reactions at oxide surfaces

Chair: Paola Luches

9:00 Hans-Joachim Freund
Model Catalyst Support Design: Oxide Surfaces at the Atomic Level

9.50 Gianfranco Pacchioni
Unusual Adsorption Properties of Two-Dimensional Insulators: Transition Metals on NaCl and MgO Ultrathin Films

10:30 Joachim Paier
C-H Bond Activation by Transition Metal Oxides: Atomistic Understanding of Support Effects

11.10 Coffee

Chair: Hans-Joachim Freund

11.30 Dominique Costa
Atomistic Modeling of Corrosion Resistance: a First Principles Study of O_2 Reduction on the Al(111) Surface Covered with a Thin Hydroxylated Alumina Film

12.10 Matthew Watkins
Characterising Adsorbates at Oxide and Halide Surfaces

12.50 Piero Ugliengo
Can Dispersion Overcome H-bond Interactions? The Case of Drugs Adsorbed on Amorphous Silica Surfaces and in Mesoporous Silica Pores as Modeled by DFT-D

13.30 Lunch

14.30 **Final Discussions**

16:00 End of Workshop

Annex 4b: Full list of speakers and participants

	Name	Role	Affiliation	Country
1	Alessandro FORTUNELLI	Organiser	Consiglio Nazionale delle Ricerche (CNR), Institute for the Chemistry of Organometallic Compounds (ICCOM), Pisa, Italy	Italy
2	Jacek GONIAKOWSKI	Organiser	Institut des Nanosciences de Paris, France	France
3	Henrik GRöNBECK	Organiser	Chalmers University of Technology, Göteberg	Sweden
4	Alex SHLUGER	Organiser	University College London	United Kingdom
5	Gennadi BERSUKER	Speaker	Sematech	USA
6	Stefan T. BROMLEY	Speaker	University of Barcelona	Spain
7	Dominique COSTA	Speaker	CNRS	France
8	Hans-Joachim FREUND	Speaker	Fritz-Haber-Institut, Berlin, Germany	Germany
9	Marc GABAY	Speaker	Université Paris-Sud, Paris	France
10	Silvia GALLEGO	Participant	Instituto de Ciencia de Materiales de	Spain

			Madrid, CSIC	
11	Stefano GARIGLIO	Speaker	DPMC, Université de Genéve	Switzerland
12	Luca M. GHIRINGHELLI	Speaker	Fritz Haber Institute of the Max Planck Society (FHI), Berlin	Germany
13	Marco GIBERTINI	Speaker	EPFL	Switzerland
14	Tibor GRASSER	Speaker	TU Wien	Austria
15	Yeliz GURDAL	Participant	University of Zurich	Switzerland
16	Christopher HEARD	Participant	Chalmers University of Technology	Sweden
17	Karoliina HONKALA	Speaker	University of Jyväskylä	Finland
18	Carolin HüHN	Participant	Otto Schott Institute of Materials Research, Friedrich Schiller University Jena	Germany
19	Sergey KOZLOV	Speaker	University of Barcelona	Spain
20	Hyungjun LEE	Participant	Swiss Federal Institute of Technology Lausanne (EPFL)	Switzerland
21	Paola LUCHES	Speaker	Istituto Nanoscienze, CNR, Modena, Italy	Italy
22	Basudeb MANDAL	Participant	SATYENDRA NATH BOSE NATIONAL	India

			CENTRE FOR BASIC SCIENCES	
23	Eric MEHES	Participant	Trinity College Dublin	Ireland
24	Tiziana MUSSO	Participant	Aalto University	Finland
25	Falko NETZER	Speaker	University of Graz, Austria	Austria
26	Janne NEVALAITA	Participant	University of Jyvaskyla, Department of Physics, Nanoscience Center	Finland
27	Claudine NOGUERA	Speaker	INSP	France
28	Gianfranco PACCHIONI	Speaker	Università degli Studi di Milano Bicocca	Italy
29	Joachim PAIER	Speaker	Humboldt University, Berlin, Germany	Germany
30	Subramanian SANKARANARAYANAN	Participant	Argonne National Laboratory	USA
31	Stefano SANVITO	Speaker	Trinity College Dublin	Ireland
32	Luca SEMENTA	Speaker	UNIVERSITY FEDERICO II OF NAPLES	Italy
33	Guangcun SHAN	Participant	City University of Hong Kong	Hong Kong
34	Marek SIERKA	Speaker	Friedrich-Schiller-Universität Jena	Germany
35	Peter SUSHKO	Speaker	Pacific Northwest National Laboratory	USA

36	Piero UGLIENGO	Speaker	University of Torino	Italy
37	Julian VELEV	Speaker	University of Puerto Rico at Rio Piedras	Puerto Rico
38	Zhiming WANG	Participant	Paul Scherrer Institute	Switzerland
39	Matthew WATKINS	Speaker	University of Lincoln	United Kingdom
40	Pjotrs ZGUNS	Participant	KTH Royal Institute of Technology	Sweden