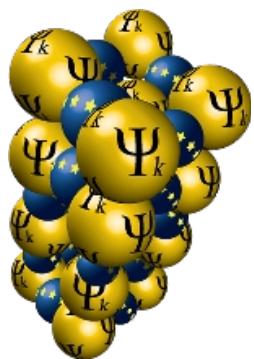


# Workshop on Atomic Scale Materials Microscopy: Theory Meets Experiment

26-28 June 2017  
National Railway Museum, York



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# Psi-k Workshop on Atomic scale materials microscopy: theory meets experiment

Mallard Suite, National Railway Museum, York, 26-28 June 2017  
<http://www.asmm.sciencesconf.org/>

Welcome to this psi-k Workshop on Atomic scale materials microscopy: theory meets experiment.

Atomic scale materials characterization is now one of the major drivers of technological innovation in areas such as nanoelectronics, catalysis, medicine, clean energy generation and energy storage. This can in a large part be attributed to advances in electron and scanning probe microscopies, which are now able to provide atomically resolved structural, chemical and electronic characterization of a wide range of functional materials. However, the types of systems relevant to applications, which include surfaces, interfaces, nanocrystals and two-dimensional materials, are complex and interpreting experimental images and spectra is often extremely challenging. On the other hand, parallel advances in theoretical approaches mean that theory can often offer invaluable guidance. These approaches include first principles methods for structure prediction, simulation of scanning probe and electron microscopy images, and prediction of various spectroscopic signatures (e.g. EELS and STS). Some of the most impressive examples of this kind of research in recent years have combined complementary theoretical and experimental approaches in a synergistic way to unravel the complex structure of materials. This type of integrated approach is increasingly being recognized as critical to advanced materials research and development by both industry and research funders.

The focus of this workshop is on the application and development of first principles methods that, in synergy with advanced microscopy techniques (e.g. TEM, EELS, STM, AFM), help unravel the structure and properties of materials at the atomic scale. It will provide both experts and newcomers with a rounded overview of emerging methods and challenges in the field, and provide an opportunity for in-depth discussion and exchange of ideas.

Workshop organisers:

Keith McKenna, Department of Physics, University of York, UK

Adam Foster, Department of Applied Physics, Aalto University, Finland

Phil Hasnip, Department of Physics, University of York, UK

Workshop sponsors:

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## **General Information**

- The workshop will be held in the Mallard Suite at the National Railway Museum (<http://www.nrm.org.uk>).
- Instructions on how to get to the museum can be found here:  
<http://www.nrm.org.uk/planavisit/visityork/howtogethere>.
- The Mallard Suite should be accessed from the Leeman Road entrance to the National Railway Museum (search for postcode YO26 4XJ to see location). Please note that the museum does not open to the public until 10am and other entrances will be closed.
- You will have easy and free access to the museum during refreshment breaks.
- Streamline Taxis: 01904 656565; York Cars: 01904 765765

**Monday**

**26 June**

**13.00** Registration and coffee/tea

**Session 1 (chair: Adam Foster)**

**13.30** Martin Setvin (*TU Wien, Austria*)

I1. Cleaved  $\text{KTaO}_3$  surfaces studied by combined AFM/STM

**14.20** Matt Watkins (*University of Lincoln, United Kingdom*)

C1. 3D molecular resolution at solvated Fluorite (111) surface: theory meets experiment

**14.45** Julian Gaberle (*University College London, United Kingdom*)

C2. Combining Theory and Experiment to Study Self Assembly of Organic Molecules on an Insulating Surface

**15.10** Coffee/tea break

**15.40** Thomas Frederiksen (*Donostia International Physics Center, Spain*)

I2. First-principles transport methods for nanoelectronics

**16.30** János Daru (*Lehrstuhl für Theoretische Chemie, Ruhr-Universität Bochum, Germany*)

C3. Solvation in 2D: Microsolvated Ions on Inert Surfaces

**16.55** Close of session

**Tuesday**

**27 June**

**Session 2 (chair: Scott Chambers)**

**09.00** Cécile Hébert (*École Polytechnique Fédérale de Lausanne, Switzerland*)

I3. Transmission electron microscopy: new advances and why we need theory

**09.50** Daniel Pingstone (*University of York, United Kingdom*)

C4. Polar MgO(111)/SiC(0001): atomic structure and electronic properties

**10.15** Coffee/tea break

**10.45** Rossitza Pentcheva (*University of Duisburg-Essen, United Kingdom*)

I4. Designing electronic phases at oxide interfaces for electronic, spintronic and energy applications

**11.35** Georg Schusteritsch (*University of Cambridge, United Kingdom*)

C5. Predicting the structure of interfaces using the Ab Initio Random Structure Searching method

**12.00** Lunch and discussion time

**Session 3 (chair: Cécile Hébert)**

**14.00** Rebecca Nicholls (*University of Oxford, United Kingdom*)

I5. Enhancing materials design using microscopy and modelling

**14.50** Edward Tait (*University of Cambridge, United Kingdom*)

C6. Simulation of electron energy loss spectra of nanomaterials with linear-scaling density functional theory

**15.15** Arsham Ghasemi (*University of York, United Kingdom*)

C7. Van der Waals interfaces: TI/superconductor and semiconductor

**15.40** Coffee/tea break

**16.10** Scott Chambers (*Pacific Northwest National Laboratory, United States*)

I6. Understanding complex phenomena at complex oxides interfaces by STEM/EELS/EDS and theoretical modeling

**17.00** Close of session

**Wednesday**

**28 June**

**Session 4 (chair: Rebecca Nicholls)**

**09.00** Vlado Lazarov (*University of York, United Kingdom*)

I7. Structure - Functionality Correlation of Halfmetallic Materials for Spintronics

**09.50** Jonathan Bean (*University of York, United Kingdom*)

C8. Atomic structure and electronic properties of MgO grain boundaries in tunnelling magnetoresistive devices

**10.15** Andrea Floris (*University of Lincoln, United Kingdom*)

C9. Mechanisms of Covalent Dimerization on a Bulk Insulating Surface

**10.40** Coffee/tea break

**11.10** Jamie Warner (*University of Oxford, United Kingdom*)

I8. The atomic structure and dynamics of defects in 2D materials

**12.00** Viktor Zólyomi (*University of Manchester, United Kingdom*)

C10. Anomalous optical response in atomically thin InSe

**12.25** Tim Naginey (*University of Oxford, United Kingdom*)

C11. Including the effects of atomic bonding in (S)TEM image simulation

**12.50** Close of Workshop

## Invited (I) and Contributed (C) Talks



## I1. Cleaved $\text{KTaO}_3$ surfaces studied by combined AFM/STM

Martin Setvin<sup>1</sup>

<sup>1</sup>TU Wien (Austria)

### Abstract

Tantalates are the class of photocatalysts with the highest quantum efficiencies ever reported (above 50% for water splitting [1]).  $\text{KTaO}_3$  is a cubic perovskite, with (001) the most stable surface. This plane is nominally polar, yet it is possible to cleave the sample and obtain a bulk-terminated (001) surface consisting of alternating KO and  $\text{TaO}_2$  terraces 4-10 nm in size. STM does not provide atomic resolution on either of these surfaces, as there is no electronic state associated with atom positions. The atomic resolution can be easily obtained by AFM due to the high reactivity of the surface atoms.

Owing to its uncompensated polarity [2], the as-cleaved surface is energetically unfavorable. It is usually assumed that oxide surfaces compensate their polarity by formation of surface reconstructions, which form during high-temperature annealing. However, nanomaterials prepared by chemical methods typically do not have complex reconstructions. We focus on polarity-compensation mechanisms occurring on the  $\text{KTaO}_3$  (001) surface during annealing to intermediate temperatures or exposure to water. Annealing of the as-cleaved surface results in the rearrangement of the KO and  $\text{TaO}_2$  terraces in a quasi-periodic pattern with  $\sim 2$  nm periodicity, where the atomic structure remains (1x1). Exposing cleaved  $\text{KTaO}_3$  to high doses of water induces a complete restructuring; the surface is terminated by  $\text{KO}_2\text{H}_2$  arranged in a (2x1) pattern. As many perovskite oxides are intrinsically polar along (001), one could assert that the observed compensation mechanisms should be a general occurrence.

### References:

- [1] H. Kato et al., JACS 125, 3082 (2003)
- [2] C. Noguera, J. Phys.: Condens. Matter 12, R367 (2000)

## C1. 3D molecular resolution at solvated Fluorite (111) surface: theory meets experiment

Matt Watkins<sup>1</sup>, Keisuke Miyazawa<sup>2</sup>, Alexander Shluger<sup>3</sup>, Takeshi Fukuma<sup>2</sup>

*University of Lincoln<sup>1</sup>, Kanazawa University<sup>2</sup>, University College London<sup>3</sup>*

### Abstract

Hydration plays important roles in various solid-liquid interfacial phenomena. Very recently, three-dimensional scanning force microscopy (3D-SFM) has been proposed as the tool to visualise solvated surfaces and their hydration structures with lateral and vertical (sub)molecular resolution. However, the relationship between the 3D force map obtained and the equilibrium water density,  $\rho(r)$ , distribution above the surface remains an open question. Here, we investigate this relationship at the interface of an inorganic mineral, fluorite, and water using a combination of refined experimental techniques and computational modelling [1].

Using new developments in 3D-SFM, it is possible obtain quantitative force maps in pure water less than 20 minutes from submersion. This increase in the speed of measurement greatly expands the number of systems the method should be applicable to. Additionally, measurements in pure water can be directly compared to simulated data. Previous measurements [2] were greatly complicated by sample dissolution and the complex electrolyte environment that was needed to maintain stable imaging conditions.

We compare force images generated using the Solvent Tip Approximation (STA) model [3] and from explicit molecular dynamics simulations to the new experimental data. The results show that the simulated STA force map reproduces the major features of the experimentally obtained force image. The agreement between the STA data and experiment strongly implies that the water density used as an input to the STA model is close to the experimental hydration structure and thus provides a tool to bridge between the experimental force data and atomistic solvation structures. At least in this case, the measurements actually reveal the unperturbed water density above the surface.

We can now go further and explore the influence of electrolyte solution on surface structure and nc-AFM imaging. [4]

### References:

- [1] K. Miyazawa et al, *Nanoscale*, 8, 7334 (2016)
- [2] N. Kobayashi et al, *J. Phys. Chem. C*, 117, 24388 (2013)
- [3] M. Watkins, B. Reischl, *J. Chem. Phys.* 138, 154703 (2013)
- [4] K Miyazawa, M Watkins, A L Shluger and T Fukuma, *Nanotechnology*, 28 245701 (2017)

## C2. Combining Theory and Experiment to Study Self Assembly of Organic Molecules on an Insulating Surface

J. Gaberle<sup>1</sup>, D. Z. Gao<sup>1</sup>, M. B. Watkins<sup>2</sup>, L. Nony<sup>3</sup>, Ch. Loppacher<sup>3</sup>, A. Amrous<sup>3</sup>, F. Bocquet<sup>3</sup>, F. Para<sup>3</sup>, S. Lamare<sup>4</sup>, F. Palmino<sup>4</sup>, F. Cherioux<sup>4</sup>, and A. L. Shluger<sup>1</sup>

<sup>1</sup>*Physics and Astronomy, University College London, London (United Kingdom)*, <sup>2</sup>*School of Maths and Physics, University of Lincoln, Lincoln (United Kingdom)*, <sup>3</sup>*Aix-Marseille Université, CNRS, IM2NP UMR 7334, Marseille (France)*, <sup>4</sup>*Institut FEMTO-ST, Université de Franche-Comté, CNRS, ENSMM, Besançon (France)*

### Abstract

We used non-contact atomic force microscopy (NC-AFM) and theoretical simulations to study the adsorption, diffusion, film stability, de-wetting, and desorption of functional organic molecules on bulk insulating surfaces at a range of different temperatures. Our results focus on the importance of molecular mobility and flexibility in order to provide insight into the mechanisms that drive self-assembly in these systems.

Two functionalised molecules, 1,3,5-tri-(4-cyano-4,4 biphenyl)-benzene (TCB) and 1,4-bis(cyanophenyl)-2,5-bis(decyloxy)benzene (CDB), were deposited and annealed on the KCl(001) substrate at temperatures between 300K to 440K and imaged using NC-AFM. CDB self-assembled structures were observed to grow from step edges, while TCB self-assembled structures grew as islands on the terrace and from step edges. Complementary theoretical calculations using van der Waals corrected DFT-D3 were used to study the adsorption of single such molecules on the KCl (001) surface and to investigate the difference in growth mechanism. Using a genetic algorithm an empirical force field was parameterised for each molecule, which were used in conjunction with molecular dynamics (MD) to study the diffusion of individual CDB and TCB molecules on terraces and at step edges. The results demonstrate that the conformational flexibility of the CDB molecule allows it to interact strongly with steps and kinks, where nucleation and subsequently cluster growth occurs. In contrast, the rigid TCB molecule is unable to adapt to step edges and kinks with a significant entropy loss upon adhesion on step edges, leading to different monolayer growth modes. Minimum energy monolayer structures were deduced from NC-AFM data and their stability was investigated in MD simulations. Our results compare well to experimental NC-AFM observations of film stability.

## I2. First-principles transport methods for nanoelectronics

Thomas Frederiksen<sup>1,2</sup>

<sup>1</sup>*Donostia International Physics Center (DIPC), Donostia-San Sebastian (Spain)*, <sup>2</sup>*Ikerbasque, Basque Foundation for Science, Bilbao (Spain)*

### Abstract

Scanning probe microscopies (SPM) allow not only to imagine molecular adsorbates on surfaces but also to characterize, manipulate, and control matter at the atomic scale. In this talk I will describe state-of-the-art methods based on density functional theory (DFT) and nonequilibrium Green's functions (NEGF) to simulate electron transport in realistic nanostructures [1,2]. This machinery can be applied to gain a detailed understanding of the atomistic details and underlying transport mechanisms in SPM experiments, as demonstrated in studies of atomically engineered electrodes for C<sub>60</sub> junctions [3] and operation and control of single-molecule toggle switches [4]. Finally I will discuss some theoretical predictions from our simulations on vibrational excitations [5] and electron beam splitting [6] in graphene nanoribbon devices.

### References:

- [1] M. Brandbyge, J. L. Mozos, P. Ordejón, J. Taylor, and K. Stokbro. Phys. Rev. B 65, 165401 (2002); N. Papir, N. Lorente, T. Frederiksen, A. García, and M. Brandbyge, Comput. Phys. Commun. 212, 8 (2017). Code freely available at <https://launchpad.net/siesta>.
- [2] T. Frederiksen, M. Paulsson, M. Brandbyge, and A.-P. Jauho, Phys. Rev. B 75, 205413 (2007), Code freely available at <https://sourceforge.net/projects/inelasticica/>.
- [3] G. Schull, T. Frederiksen, A. Arnaud, D. Sánchez-Portal, and R. Berndt, Nat. Nanotechnol. 6, 23 (2011); T. Frederiksen, G. Foti, F. Scheurer, V. Speisser, and G. Schull, Nat. Commun. 5, 3659 (2014).
- [4] Y. Kitaguchi, S. Habuka, H. Okuyama, S. Hatta, T. Aruga, T. Frederiksen, M. Paulsson, and H. Ueba, Beilstein J. Nanotechnol. 6, 2088 (2015).
- [5] R. B. Christensen, T. Frederiksen, and M. Brandbyge, Phys. Rev. B 91, 075434 (2015).
- [6] P. Brandimarte, M. Engelund, N. Papir, A. Garcia-Lekue, T. Frederiksen, D. Sánchez-Portal, J. Chem. Phys. 146, 092318 (2017).

### C3. Solvation in 2D: Microsolvated Ions on Inert Surfaces

János Daru, Prashant Gupta, Marx Dominik

*Lehrstuhl für Theoretische Chemie, Ruhr-Universität Bochum, 44780 Bochum (Germany)*

#### Abstract

The present project aims to study the solvation process of alkali cations and halogen anions in the presence of weakly interacting surfaces. This investigation is a step forward toward understanding solvation in restricted environments. We have performed QM/MM simulations on solvatomers deposited on Xe layers on Cu(111) support. The system has been established in collaboration with our experimental partners in order to provide complementary results for STM studies of the same systems. The realistic description of surface polarization is achieved by including the neighboring Xe atoms into the QM subsystem and applying self-consistent image-charge interaction with the metal. In order to reduce finite size effects in our periodic model, the interaction between QM images are decoupled and the QM Xe atoms are embedded into the layers of their classical counterparts. Our computational approach has been thoughtfully tested in a related study of gas-phase ion solvation against high level ab initio benchmarks (with a special focus on treating dispersion interactions in this rather complex system) and converged path integral simulations. Our simulations provided remarkably different solvation structures in comparison with gas-phase solvatomers. The weak interaction with the surface can compensate for loss of water-water and water-ion interactions and therefore stabilize solvatomers that are unlikely or even unstable in gas phase. The sampled configurations of the performed NVT simulations will be used as initial conditions for future NVE trajectories. This ensemble of NVE simulations can be used for rigorous calculation of correlation functions and for obtaining (THz) spectra of the system being a direct probe of the hydrogen bond network dynamics.

## I3. Transmission electron microscopy: new advances and why we need theory

Cécile Hébert

*Centre interdisciplinaire de microscopie électronique (CIME),  
École Polytechnique Fédérale de Lausanne (Switzerland)*

### Abstract

Recent advances in transmission electron microscopy have increased the ability of this technique to obtain quantitative information at the atomic scale, not only on the structure of the sample, but also probing its electronic structure. This calls for the development of new ab-initio techniques for the interpretation of data. Especially, the increased sensitivity of detectors and improved stability of microscopes allows investigating small clusters of atoms or single layers of materials as well as defects like dislocations, grain boundaries etc. On the other hand, the improving ab-initio methods together with the ever increasing computer power makes it possible to tackle larger and larger structures as well as non periodical system.

I will review rapidly the main information that can be gathered by a TEM, and then address cutting edge techniques where theoretical calculation is of particular interest. This comprises high resolution imaging (e.g. for determining the structure of defects or small atomic cluster), as well as electron energy loss spectrometry (which can gather information on the electronic structure of the sample), or chathodoluminescence spectroscopy, an emerging field in TEM.

## C4. Polar MgO(111)/SiC(0001): atomic structure and electronic properties

Daniel Pingstone, Philip Hasnip, Balati Kuerbanjiang, Vlado Lazarov

*University of York (United Kingdom)*

### Abstract

Thin films of MgO are of interest for spintronic and CMOS technologies due to its spin filtering properties and large band gap. Polar MgO(111) is a good crystallographic match to wide band gap semiconductors such as SiC(0001) and GaN(0001), hence understanding polar MgO growth as well as interface atomic structure of these heterostructures is crucial for device application.

In this work we demonstrate successful growth of polar MgO(111) thin films on SiC(0001) by plasma assisted MBE growth. Surface morphology of the grown film (flat vs. faceted surface) can be controlled by the growth conditions. We also show that XPS band offset measurements of the MgO/SiC interface correlate well with the DFT calculated band offsets. The DFT calculations were based on experimentally determined atomic structure of the interface obtained by aberration corrected electron microscopy.

## I4. Designing electronic phases at oxide interfaces for electronic, spintronic and energy applications

Rossitza Pentcheva

*Department of Physics and Center for Nanointegration (CENIDE),  
University of Duisburg-Essen (UDE), Lotharstr. 1 47057 Duisburg (Germany)*

### Abstract

Transition metal oxide interfaces exhibit a broad spectrum of functional properties that are not available in the respective bulk compounds and open possibilities for applications in electronics, spintronics and energy conversion. Based on the insight from first principles calculations including an on-site Hubbard term, I will address the formation of unanticipated charge, spin and orbital reconstructions in honeycomb lattices of perovskite oxides, leading to a rich set of Mott and even topologically nontrivial phases [1-3]. Furthermore, I will address strategies for the optimization of oxide materials for energy conversion as thermoelectrics [4,5] and as anode materials for water splitting [6].

Research in collaboration with D. Doennig, M. E. Gruner, B. Geisler, O. Köksal, H. Hajiyani, S. Baidya and W.E. Pickett; supported by the DFG within SFB/TR80 and SPP1613.

### References:

- [1] D. Doennig, W. E. Pickett, and R. Pentcheva, Phys. Rev. Lett. 111, 126804 (2013).
- [2] D. Doennig, W. E. Pickett, and R. Pentcheva, Phys. Rev. B 89, 121110 (R) (2014).
- [3] D. Doennig, S. Baidya, W. E. Pickett, and R. Pentcheva, Phys. Rev. B 93 165145 (2016).
- [4] M. E. Gruner, U. Eckern and R. Pentcheva, Phys. Rev. B. 92, 235140 (2015).
- [5] B. Geisler, A. Blanca-Romero and R. Pentcheva, Phys. Rev. B 95, 125301 (2017).
- [6] K. Chakrapani, G. Bendt, H. Hajiyani, I. Schwarzrock, T. Lunkenbein, S. Salamon, J. Landers, H. Wende, R. Schlögl, R. Pentcheva, M. Behrens, S. Schulz, Chem Cat. Chem. (2017), DOI: 10.1002/cctc.201700376.

## C5. Predicting the structure of interfaces using the Ab Initio Random Structure Searching method

Georg Schusteritsch<sup>1</sup>, Chris Pickard<sup>1,2</sup>

<sup>1</sup>*Department of Materials Science and Metallurgy [Cambridge University] (DMSM), 27 Charles Babbage Road, Cambridge CB30FS (United Kingdom)*, <sup>2</sup>*The Advanced Institute for Materials Research, Tohoku University (WPI-AIMR) 2-1-1 Katahira, Aoba-ku, Sendai, 980-8577 (Japan)*

### Abstract

First-principles structure prediction of bulk materials is now routinely performed, however the field of predicting the atomic structure of interfaces from first-principles is still in its infancy. A detailed understanding of and ability to predict the atomic structure of interfaces is however of crucial importance for many technologies. Interfaces are very hard to predict due to the complicated geometries, crystal orientations and possible non-stoichiometric conditions involved and provide a major challenge to structure prediction. We present here the ab initio random structure searching (AIRSS) method and how it can be used to predict the structure of interfaces. Our method relies on generating random structures in the vicinity of the interface and relaxing them within the framework of density functional theory. The method is simple, requiring only a small set of parameters, and can be efficiently run on modern parallel computer architectures. We focus here on the prediction of grain boundaries, but application to heterostructure interfaces and surfaces is equally possible. Examples of several grain boundary defects in technologically important materials will be presented, including grain boundaries in 2D materials (graphene), as well as much more complex 3D systems such as grain boundary interfaces in transition metal oxides ( $\text{SrTiO}_3$  and  $\text{TiO}_2$ ). Direct comparison to experimental results will be made.

## I5. Enhancing materials design using microscopy and modelling

Rebecca Nicholls

*University of Oxford (United Kingdom)*

### Abstract

Electron energy loss spectroscopy (EELS) carried out inside a scanning transmission electron microscope (STEM) provides a probe of elemental composition and bonding with atomic resolution. It allows us to map the local chemistry of a material. STEM EELS can tackle a wide variety of materials problems and has been used to identify single atoms, determine crystal phases, map dopants at grain boundaries and visualise plasmon modes. Combining experimental EELS with modelling can play an invaluable role in both the interpretation of experimental data and the design of experiments. Crucially, it can allow us to solve problems which experiment or modelling alone cannot. Examples include using EELS to identify the presence of a C-N bond in nitrogen-doped graphene [1] and to count nitrogen-vacancies in nanodiamond [2]. Simulation of an EELS spectrum using first-principles techniques starts from an atomistic model. But what happens if the atomistic structure of the materials is not known? We have used a combination of first principles structure prediction, EELS and diffraction to solve the structure of an unknown crystal phase at the interface of a metal and an oxide [3]. I will discuss the approach used and the resulting crystal structure.

### References:

- [1] RJ Nicholls et al., ACS Nano 7 (2013) 7145-7150
- [2] SLY Chang et al., Nanoscale 8 (2016) 10548-10552
- [3] RJ Nicholls et al., Adv Eng Mater 17 (2015) 211-215

## C6. Simulation of electron energy loss spectra of nanomaterials with linear-scaling density functional theory

Edward Tait<sup>1</sup>, Laura Ratcliff<sup>2</sup>, Mike Payne<sup>1</sup>, Peter Haynes<sup>3</sup>, Nicholas Hine<sup>4</sup>

<sup>1</sup>*Cavendish Laboratory - University of Cambridge, Theory of Condensed Matter Group, Department of Physics, Cavendish Laboratory, 19 JJ Thomson Ave, Cambridge, CB3 0HE (United Kingdom)*, <sup>2</sup>*Argonne Leadership Computing Facility*, <sup>3</sup>*Imperial College London, Faculty of Engineering, Department of Materials*, <sup>4</sup>*Department of Physics [Warwick], University of Warwick Gibbet Hill Road Coventry CV4 7AL (United Kingdom)*

### Abstract

Electron Energy Loss Spectroscopy provides a powerful tool for investigating the local electronic structure of complex systems such as nanostructures, interfaces, surfaces and even individual defects. Interpretation of experimental electron energy loss spectra is often challenging and can require theoretical modelling of candidate structures, which themselves may be large and complex, beyond the capabilities of traditional cubic-scaling density functional theory. Here, functionality is presented to compute electron energy loss spectra within the ONETEP linear scaling density functional theory code. Simulated spectra are shown to agree with those computed using conventional plane wave methods to a high degree of precision. The ability of ONETEP to tackle large problems is then exploited to investigate convergence of spectra with respect to supercell size. Finally, a study of the electron energy loss spectra of defects on the (101) surface of an anatase slab is presented and the concentrations of defects which might be experimentally detectable is discussed.

## C7. Van der Waals interfaces: TI/superconductor and semiconductor

Arsham Ghasemi<sup>1</sup>, Demie Kepaptsoglou<sup>2</sup>, Kenji Nawa <sup>3</sup>, Susannah Speller<sup>4</sup>, Pedro Galindo<sup>5</sup>, Quentin Ramasse<sup>2</sup>, Kohji Nakamura<sup>3</sup>, Thorsten Hesjedal<sup>4</sup>, Vlado Lazarov<sup>1</sup>

<sup>1</sup> Department of Physics, University of York, <sup>2</sup> SuperSTEM Laboratory, SciTech Daresbury Campus, <sup>3</sup> Division of Materials Science, Mie University, <sup>4</sup> Department of Physics, Clarendon Laboratory, University of Oxford, <sup>5</sup> Department of Computer Science and Engineering, Universidad de Cádiz

### Abstract

Heterostructured materials are the basis of modern logic and data storage technologies. One of the main criteria for realising new interface enabled heterostructure functionality is the ability to control their atomic and electronic properties on an atomic level. Lattice mismatch between the single crystal layers significantly influences the crystallography and the structure of the heterostructured interfaces. While small lattice mismatch in strongly bonded heterointerfaces is prerequisite for well-defined epitaxy, in this work we show that well defined epitaxial heterostructures can be realised via weak van der Waals (vdW) interactions in spite of the large lattices mismatch and dissimilar crystallographic layer structures.

In this work we demonstrate this on the case of superconducting  $\text{Fe}_x\text{Cu}_{1-x}\text{Se}$  and  $\text{Bi}_2\text{Te}_3$  topological insulator (TI) with lattice mismatch of  $\sim 9\%$ . By using aberration-corrected scanning transmission electron microscopy and electron energy loss spectroscopy we show that the interface is determined by Se-Te van der Waals-like bond. The DFT calculations show that this particular interface bonding is very weakly dependent of the atomic registry position between the interface-layers, but it is sufficiently strong to enable the epitaxial relation between the layers. Finally, in case of TI ( $\text{Bi}_2\text{Te}_3$ )/semiconductor (Ge) interfaces we show that a monolayer of Te can drastically change the bonding of  $\text{Bi}_2\text{Te}_3/\text{Ge}$  at the interface which is beneficial for TI thin film defects control [1].

### References:

- [1] Ghasemi, A., et al., Van der Waals epitaxy between the highly lattice mismatched Cu doped FeSe and  $\text{Bi}_2\text{Te}_3$ . Accepted at Nature Asia Materials, 2017.

## I6. Understanding complex phenomena at complex oxides interfaces by STEM/EELS/EDS and theoretical modeling

Scott Chambers, Steven Spurgeon, Yingge Du, Peter Sushko

*Pacific Northwest National Laboratory (United States)*

### Abstract

Heteroepitaxial film growth of multi-component materials involves the intricate interplay between several kinds of physical interactions. Adatom arrival rates, surface diffusion coefficients and local chemistry constitute one level of complexity resulting from interactions of the film constituents as they arrive at the substrate. Point defect concentrations, step densities and the presence of surface dipoles add a second level of complexity as the incoming atoms interact with the substrate. The plethora of interactions that take place dictates the nucleation and growth process in ways that are not easily anticipated. Monitoring these processes, and the resulting material structures, requires a range of characterization tools spanning several length scales. On the nanoscale, one of the most powerful sets of methods is scanning transmission electron microscopy (STEM) and related spectroscopies, electron energy loss spectroscopy (EELS) and energy dispersive spectroscopy (EDS). When combined with classical and quantum mechanical modeling, these techniques yield information and insight relevant to the behavior of actual heterostructures at an atomistic level. In this talk, I will present illustrative results from our work using these methods to track and understand what happens during the MBE growth of  $\text{Sr}_x\text{La}_{1-x}\text{CrO}_3$ ,  $\text{LaFeO}_3$ , and  $\text{La}_2\text{MnNiO}_6$  on  $\text{SrTiO}_3(001)$  as well as  $\text{SrZr}_x\text{Ti}_{1-x}\text{CrO}_3$  on  $\text{Ge}(001)$ .

## I7. Structure - Functionality Correlation of Halfmetallic Materials for Spintronics

Vlado Lazarov

*University of York (United Kingdom)*

### **Abstract**

Half metal ferromagnetic (HMF) materials are crucial for spintronics since they are predicted to be to be 100% spin polarised at the Fermi level. One of the challenges in the field of spintronics is the control of the defects and atomic structure of the heterostructured interfaces when HMFs are incorporated in the nanometre scale devices. In this talk we will present the experimental and theoretical methods to assess the spin polarisation of thin films HMF materials and their interfaces as well as a direct correlation between the atomic structure and the performance of real spintronic devices.

## C8. Atomic structure and electronic properties of MgO grain boundaries in tunnelling magnetoresistive devices

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### Abstract

Polycrystalline metal oxides find diverse applications in areas such as nanoelectronics, photovoltaics and catalysis. Although grain boundary defects are ubiquitous their structure and electronic properties are very poorly understood since it is extremely challenging to probe the structure of buried interfaces directly. In this paper we combine novel plan-view high-resolution transmission electron microscopy and first principles calculations to provide atomic level understanding of the structure and properties of grain boundaries in the barrier layer of a magnetic tunnel junction. We show that the highly [001] textured MgO films contain numerous tilt grain boundaries. First principles calculations reveal how these grain boundaries are associated with locally reduced band gaps (by up to 3 eV). Using a simple model we show how shunting a proportion of the tunnelling current through grain boundaries imposes limits on the maximum magnetoresistance that can be achieved in devices.

## C9. Mechanisms of Covalent Dimerization on a Bulk Insulating Surface

Andrea Floris<sup>1</sup>, Chunyan Guo<sup>2</sup>, Lev Kantorovich<sup>3</sup>, Angelika Kühnle<sup>4</sup>

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### Abstract

We study the reaction mechanisms of a covalent dimerization between organic molecules on a bulk insulating surface [4-iodobenzoic acid molecules on calcite (10.4)] [1]. NC-AFM experiments [1,2] reveal that at 580K the molecules assemble in one-dimensional chains of covalent dimers. These structures result from a complex set of processes, including a nominally rather costly double de-halogenation reaction. Via density functional theory and nudge elastic band, we identify some key features making the dimerization possible on calcite, in the absence of a conventional (e.g. metallic) catalytic agent. We show that the insulating substrate plays an active role as a catalyst by identifying two relevant processes [1]: one exhibiting an intermediate state of chemisorbed molecules after the de-halogenations and a second, non-trivial reaction channel where two iodine atoms “cooperate” to minimize the cost of their detachment from the molecules. The knowledge of covalent assembly mechanisms on bulk insulators is an important step to realize (and, ultimately, control) molecular structures that combine the robustness of covalent architectures with their electronic decoupling from the substrate. This step has potentially important technological applications in nano- and molecular electronics.

### References:

- [1] Guo, C; Wang, Y.; Kittelmann, M.; Kantorovitch, L; Kuehnle, A; Floris, A. Mechanisms of covalent dimerization on a bulk insulating surface. *J. Phys. Chem. C*, 2017, 121, 10053–10062.
- [2] Kittelmann, M; Rahe, P.; Nimmrich, M; Hauke, C. M.; Gourdon, A; Kuehnle, A. On-surface covalent linking of organic building blocks on a bulk insulator. *ACS Nano* 2011, 5, 8420–8425.

## I8. The atomic structure and dynamics of defects in 2D materials

Jamie Warner

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### Abstract

Defects in 2D materials influence the chemical, electronic, magnetic, mechanical and optical properties. Understanding how defects cause bond rearrangement in 2D materials is critical for building better understanding of their properties. Aberration corrected transmission electron microscopy is able to directly image atomic structure of 2D materials and enables the measurements of bond lengths and strain. Using annular dark field scanning transmission electron microscopy, I will show how we identify dopants by their contrast increase and use atomically resolved electron energy loss spectroscopy to confirm elemental identification. I will discuss vacancies, grain boundaries, dislocations, and dopants in graphene, MoS<sub>2</sub> and WS<sub>2</sub> 2D materials. Image simulations are performed using atomic models based on DFT calculations, which confirms the experimentally observed structures and enables the prediction of band structure and charge transfer within the non-periodic regions of the sample.

## C10. Anomalous optical response in atomically thin InSe

Viktor Zólyomi

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### Abstract

Indium selenide (InSe) is a layered post-transition metal chalcogenide van der Waals crystal exhibiting a honeycomb in-plane structure that can be exfoliated into a 2D semiconducting crystal of varying thickness. We demonstrate through photoluminescence (PL) measurements that the optical gap of few-layer InSe increases with the reduction of the thickness of the material, and that the principal optical transition vanishes in the monolayer. (See *Nature Nanotechnology* vol. 12, 223-227 (2017) and *Scientific Reports* vol. 6, 39619 (2016).) We reveal the origin of this anomalous optical response using first principles density functional theory (DFT), in particular, we identify the mirror symmetry of the monolayer as the cause for the vanishing of the principal PL peak. We reproduce the measured PL peak energies with good accuracy by applying a scissor correction to the excitation energies predicted by DFT. We discuss the limitations of this scissor correction and the options for improving upon them using many-body GW theory. We also present a tight-binding model parametrized from the scissor-corrected DFT calculations which enables the prediction of the optical transition energies and strengths of multilayer InSe at any thickness. (See *Physical Review B* vol. 94, 245431 (2016).)

## C11. Including the effects of atomic bonding in (S)TEM image simulation

Tim Naginey

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### Abstract

Most of the software used to simulate TEM/STEM images completely neglects interatomic interactions in the sample and thus leaves out the effects of charge transfer and chemical bonding. The effect of these interactions on the image is generally small compared to the total charge density, but essential to understanding many important properties of materials. These interactions are especially important for fully quantitative interpretations of TEM/STEM images of certain sample types such as bulk oxides because of the strong ionic bonds, and 2D materials composed of light elements since most of the electrons are involved in bonding. In order to accurately simulate TEM/STEM phase images of these and other such materials, we have employed the CASTEP code to generate accurate projected potentials which take into account both intra- and interatomic electron interactions. CASTEP uses density functional theory (DFT) to calculate electron densities, which are directly related to the electrostatic potential via Poisson's equation. These potentials are then used to calculate the projected potentials for use in multi-slice algorithms to simulate TEM/STEM images. We have added to the functionality of CASTEP so that these projected potentials can be obtained directly from the software, thus allowing us easy and accurate simulation of images with bonding effects included which enables accurate interpretation of experimental images of materials, such as h-BN.

## List of Participants

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# Visit York

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# Summary Schedule

26/06/17            13:00 Registration and coffee/tea

## **Session 1**

13:30 I1. Setvin  
14:20 C1. Watkins  
14:45 C2. Gaberle  
15:10 Coffee/tea break  
15:40 I2. Frederiksen  
16:30 C3. Daru  
17:00 Close of session

27/06/17            **Session 2**

09:00 I3. Hébert  
09:50 C4. Pingstone  
10:15 Coffee/tea break  
10:45 I4. Pentcheva  
11:35 C5. Schusteritsch

12:00 Lunch / discussion time

## **Session 3**

14:00 I5. Nicholls  
14:50 C6. Tait  
15:15 C7. Ghasemi  
15:40 Coffee/tea break  
16:10 I6. Chambers  
17:00 Close of session

28/06/17            **Session 4**

09:00 I7. Lazarov  
09:50 C8. Bean  
10:15 C9. Floris  
10:40 Coffee/tea break  
11:10 I8. Warner  
12:00 C10. Zólyomi  
12:25 C11. Naginay  
12:50 Close of workshop