Report on Workshop Computer Simulation of Oxides: Dopants, Defects and Surfaces

Trinity College Dublin

9th - 11th September 2009

Science Foundation Ireland, Atlantic Centre for Atomistic Modelling, Psi-k Network and CECAM

Charles H. Patterson, School of Physics, Trinity College

Graeme Watson, School of Chemistry, Trinity College

Simon Elliott, Tyndall National Institute, Cork

Michael Nolan, Tyndall National Institute, Cork

www.tyndall.ie/research/theory-and-modelling/oxides-workshop/

www.cecam.org/workshop-347.html

WORKSHOP SUMMARY

Computer simulation of oxides is a broad topic. This workshop had invited contributions on the role of oxides in catalysis, methods for electronic and atomic structures of oxides, defects and dopants in oxides and complex oxides such as cuprates. It consisted of 6 sessions under the headings: Surfaces and Catalysis, Electronic Structure Methods, Structure, Surfaces and Defects, Oxides and Dopants and Complex Oxides. It brought together around 70 researchers. There were ten invited speakers, 16 participants gave contributed talks and 24 posters were presented.

In the session on Surfaces and Catalysis, Horia Metiu (Santa Barbara) spoke on mechanisms of catalysed oxidation reactions investigated using density functional methods. Jörg Libuda (Erlangen) spoke on experimental spectroscopic studies of oxide storage catalysts aimed at improving the selectivity and activity of heterogeneous catalysts.

In the session on Electronic Structure Methods, Georg Kresse (Wien) spoke on application of hybrid functionals in the VASP code to oxygen vacancies in ZnO and formation of polarons in K doped $BaBiO_3$. He emphasised that these functionals predict lattice polarons in materials such as $BaBiO_3$, which conventional functionals do not. Hong Jiang (Beijing) spoke on application application of the GW approximation to lanthanide oxides beginning from an LDA+U state rather than a more conventional LDA state. In particular, he showed that GW calculations beginning from the LDA+U states give quantitative agreement with experimental band gaps of the series Ln_2O_3.

In the session on Structure, Alan Chadwick (Kent) gave an overview of application of X-ray absorption spectroscopy as a probe of structure of oxides, using microscopy and XAS to identify the surface morphology of oxide nanoparticles.

In the session on Surfaces and Defects, Richard Catlow (London) gave an overview of properties of ZnO predicted using DFT methods, including structure and properties of ZnO nano-particles, reactions catalysed at ZnO surfaces, and the structures of defects in ZnO. David Look (Ohio) gave an overview of optical spectroscopies of defects in ZnO formed by electron irradiation.

In the session on Oxides and Dopants, Su-Huai Wei (Colorado) covered properties of a wide range of oxides and their properties, including ZnO, In_2O_3, and TiO_2. Chris van de Walle (Santa Barbara) described recent work on calculating formation energies of defects in oxides. He described calculations of defect transition levels using conventional and hybrid density functional methods.

In the session on Complex Oxides, Francesc Illas (Barcelona) made a comparison between the electronic structures and exchange coupling constants in cuprate and pnictide superconductors and showed that the pnictides have a strongly frustrated interwoven network of exchange couplings between Fe ions.

One of the trends that has emerged in computer simulation of oxides is that hybrid density functionals such as the HSE functional give significantly improved predictions of oxide properties compared to density functionals which do not include Hartree-Fock exchange. These functionals are available in several codes and are now being fairly widely adopted for oxide simulation.

WORKSHOP PROGRAMME

9th September

12:00 - 14:00 **Registration**
14:00 - 14:10 **Welcome**

Surfaces and Catalysis

14:10 15:00 **H. Metiu** Catalysis by Atomic Sized Centres
15:00 15:20 **J. Graciani** Cu, Au and Ce Nanoparticles Supported on $TiO_2(110)$
15:20 15:40 **G. Novell-Leruth** Selectivity in Oxidation Processes on $RuO_2(110)$

15:40 16:10 **Break**

16:10 17:00 **J. Libuda** Modelling Oxide Based Storage Catalysts
17:00 17:20 **R. Bennett** Non-Stoichiometric Titanium Dioxide: Experimental Insights and Challenges in Charge Transfer and Surface Reactions
17:20 17:40 **D. Costa** Realistic Ab Initio Model of the Passive Film Formed on Stainless Steels
17:40 18:00 **U. Wdowik** Lattice Dynamics of Co-Deficient and Fe-Doped CoO

18:00 20:00 **Poster Session and Reception**

10th September

Electronic Structure Methods

09:00 - 09:50 **G. Kresse** Hybrid Functionals and GW Applied to Simple and Complex Oxides
09:50 10:40 **H. Jiang** Localised and Itinerant States in d and f Electron Oxides united by $GW@LDA+U$
10:40 11:00 **H. Dixit** Quasiparticle Band Gap of IIB-VI Transparent Oxides within the GW Approximation

11:00 11:20 **Break**

Structure

11:20 12:10 **A. Chadwick** X-ray Absorption Spectroscopy: a Probe of Local Structure and Oxidation State
12:10 12:30 **K. P. McKenna** Electronic Properties of Defects in Polycrystalline Dielectric Materials
12:30 12:50 **R. Tétot** Multi Scale Modelling of Low Index Rutile TiO_2 Surfaces

12:50 15:00 **Lunch**

Surfaces and Defects

15:00 15:50 **R. Catlow** Modelling of Defects, Surface Properties and Nano Clusters of Zinc Oxide
15:50 16:10 **P. A. Mulheran** The Reduced Rutile (110) Surface: Energetics and Diffusion of Ti Point Defects in the Selvedge
16:10 16:30 **M. M. Islam** Electronic Properties of Oxygen Deficient and Metal Doped TiO_2

16:30 16:50 **Break**

16:50 17:40 **D. Look** Electrical and Optical Activity of Point Defects in ZnO
17:40 18:00 **S. Datta** Photoelectrolysis of Water for Hydrogen Production

19:30 **Dinner**

11th September

Oxides and Dopants

09:00 09:50 **S.-H. Wei** First-Principles Investigation of Unusual Materials Properties of Oxides
09:50 10:10 **A. Droghetti** Defect-Induced Magnetism in Oxides
10:10 10:30 **D. Scanlon** Intrinsic Ferromagnetism in CeO_2: Dispelling the Myth of Vacancy-Site-Localisation Mediated Superexchange

10:30 11:10 **Break**

11:10 12:00 **C. Van de Walle** Sources of Conductivity in Transparent Oxides
12:00 12:20 **A. Walsh** Band Alignment and Defect Physics of Functional Oxides

12:20 14:30 **Lunch**

Complex Oxides

14:30 15:20 **F. Illas** Similarities and Differences between Pnictides and Cuprate Superconducting Parent Compounds
15:20 15:40 **V. Fiorentini** Electronic Structure of Doped Cuprates by Self-Interaction-Corrected DFT
15:40 16:00 **P. Alippi** Role of Native Defects in the Dielectric and Conductivity Behaviour of $CaCu_3Ti_4O_{12}$

16:00 **Close**

LIST OF POSTER TITLES AND FIRST AUTHORS

Titanocene Adsorption Studies on $TiO_2(110)$ Rutile Surface Using Ab-Initio and Molecular Dynamics Approaches, **S. Agrawal**

Density Functional Theory of Doping in Both Bulk and Surface State Titania, Classical Simulation of TiO_2-Water Interface, **N. J. English**

Ab-Initio and Atomistic Simulation of Cu Doping in the Lead-Free Ferroelectric, **R. S. Kavathekar**

Perovskite Potassium Sodium Niobate, **S. Koerbel**

Small Polarons in Nb- and Ta-Doped Rutile and Anatase TiO_2, **B. J. Morgan**

Ferromagnetism in ZnO Induced by Complex Defects, **A. Chakrabarty**

Reconstruction of the Polar ZnO(0001) Surface, **H. Meskine**

Simulation of the Oxygen K edge Resonant X-ray Emission Spectroscopy of Rutile Titanium Dioxide, **C. McGuinness**

Energetics of Al Doping and Intrinsic Defects in Monoclinic and Cubic Zirconia: First Principles Calculations, **C. Århammar**

Self-Consistent First-Principles Method for Complex Disordered Materials, **A. Marmodoro**

Water Gas Shift Reaction on a Highly Active Inverse CeOx/Cu(111) Catalyst: Unique Role of Ceria Nanoparticles, **J. Graciani**

Transparent Conducting Oxides (TCO): Tin Oxides as a Case Study, **A. Miglio**

Origin of Ferromagnetism in Molybdenum Dioxide (MoO2) from Ab-Initio Calculation, **J. Nisar**

Simultaneous Multi-Parameter Scanning Probe Microscopy of $TiO_2(110)$-(1x1), **S. J. OBrien**

Competing Mechanisms in Atomic Layer Deposition of La_2O_3 versus Er_2O_3 from Cyclopentadienyl Precursors, **M. Nolan**

Role of the Substrate Surface on the Atomic Layer Deposition of Alumina on Silicon Nitride, **M. E. Grillo**

Correlation Effects in p-Electron Magnets: the case of RbO_2, **R. Kovacik**

Electronic Structure of Striped Phase of $Ca_{1.875}Na_{0.125}CuO_2Cl_2$, **C. H. Patterson**

Atomic Scale Modelling of Deposition Processes for High-k Dielectrics, **M. Shirazi and S. Klejna**

TCOs in the UV: a First-Principles Investigation of InOOH, $In(OH)_3$, ZnO_2, $Zn(OH)_2$, CdO_2, $Cd(OH)_2$, **M. P. Jigato**

Defects and Diffusion in Cr_2O_3: a DFT+U Study, **F. Lebreau**

Electronic Structure of Amorphous Silica using Extrapolar Method and PAW Formalism, **D. Waroquiers**

Defect States in Titanium Dioxide, **J. Stausholm-Möller**

Electronic Structure Calculations on the Oxygen Conductivity in $Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_3$, **M.-W. Lumey**

ABSTRACTS OF INVITED TALKS

CATALYSIS BY ATOMIC SIZED CENTRES

Horia Metiu*
Department of Chemistry and Biochemistry,
University of California Santa Barbara, California 93106-9510 USA.

We perform density functional calculations to explore the properties of two new classes of catalysts, both consisting of atomic-size active centers. In one class the cation at the surface of an oxide is replaced with another cation which we call a dopant. By an appropriate choice of the dopant-oxide pair we can weaken the bond of the oxygen atoms at the surface of the oxide and make the system a better oxidant and a better oxidation catalyst. Other choices of dopant-oxide pairs will cause the dopant to adsorb oxygen and weaken the O-O bond to activate oxygen for oxidation reactions. A second class of catalysts with atomic-size active center consists of small oxide clusters supported on a different oxide (for example, a VO_3 cluster supported on TiO_2). Some of the oxygen atoms in the cluster end up bridging two different cations (for example, V-O-Ti) and if the two cations are well chosen, the bridging oxygen becomes active in oxidation reactions. We study the mechanism of methanol oxidation to formaldehyde by VO_3 supported on TiO_2 and plan to screen a large set of oxide clusters on an oxide for hydrocarbon activation.

MODELLING OXIDE BASED STORAGE CATALYSTS

Jorg Libuda
Lehrstuhl fur Physikalische Chemie 2 and Erlangen Catalysis Resource Center,
Friedrich-Alexander-Universitat Erlangen-Nrnberg, Egerlandstr. 3, 91058 Erlangen, Germany.

The integration of storage functionalities into catalytic materials represents an intriguing and versatile tool to improve the selectivity and activity of heterogeneous catalysts under non-stationary reaction conditions. Several prominent examples can be found in environmental catalysis: Among the classical examples are ceria-based supports which act as oxygen-storage catalysts (OSC). Another more recent example are NO_x storage and reduction catalysts (NSR), which have recently been introduced into automobile exhaust gas after treatment systems. Also, regenerable catalytic sulfur traps (CST) have been discussed. Due to the complexity of the resulting oxide-based materials, however, the underlying surface chemistry on these systems remains poorly understood at the microscopic level. Towards a better insight into mechanistic and kinetic details, we follow a surface-science-type approach using single-crystal-based model systems. NSR model systems are prepared using thin Al_2O_3 films grown on NiAl(110) on which BaO nanoparticles are grown. By means of synchrotron-based high resolution photoelectron spectroscopy (HR-PES) it is shown that there is a strong tendency to form mixed oxides particles ($BaAl_2O_4$). The reactivity of these systems with respect to NO_2, NO and CO_2 is probed using molecular beam (MB) techniques and time-resolved IR reflection absorption spectroscopy (TR-IRAS). Pd nanoparticles are co-deposited by physical vapor deposition (PVD), controlling the metal oxide (MO) interaction. The nature of the adsorbate species, their stability, and the reaction mechanism is discussed based on a comparison of the experimental data with density function theory (DFT) calculations. In addition, the mechanism of sulfur poisoning is probed in SO_2/NO_2 multi MB experiments. Finally, the reactivity under ideal ultrahigh-vacuum (UHV) conditions is compared to realistic reaction conditions by performing TR-IRAS in a high pressure cell (HPC). In a second part we report on the development of a OSC model system, prepared by using a well ordered $CeO_2(111)$ grown on Cu(111). Growth and structure of the film is investigated by scanning tunneling microscopy (STM). Atomically flat and ordered films can be prepared by applying suitable growth methods. Pt nanoparticles are deposited by means of PVD. We investigate the activation of CH_4 on this system using supersonic MB experiments and follow the individual steps of the reaction by means of X-ray photoelectron spectroscopy (XPS). The MO interaction, spillover and reverse spillover of hydrogen and oxygen, the dehydrogenation kinetics of methane and the oxidative self cleaning of the $Pt/CeO_2/Cu(111)$ model system are compared with DFT calculations and single crystal data. Finally, we investigate the interaction of CO_2 with oxidized and reduced CeO_2 films. Both carbonate formation and reoxidation of CeO_{2-x} is observed. Finally, we investigate the effect of MgO doping of CeO_2 films, with the aim of tuning the interaction with respect to CO_2.

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[3] A. Desikusumastuti, M. Happel, M. Laurin, T. Staudt, Z. Qin, S. Shaikhutdinov, J. Libuda, PCCP 11, 2514 (2009).
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[11] A. Desikusumastuti, M. Happel, Z. Qin, T. Staudt, Y. Lykhach, M. Laurin, S. Shaikhutdinov, F. Rohr, J. Libuda, J. Phys. Chem. C 113, 9755 (2009).
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[13] T. Staudt, Y. Lykhach, L. Hammer, M. A. Schneider, V. Matoln and J. Libuda, submitted.
[14] Y. Lykhach, T. Staudt, M. P. A. Lorenz, R. Streber, A. Bayer, H.-P. Steinrck, J. Libuda, submitted.

HYBRID FUNCTIONALS AND GW APPLIED TO SIMPLE AND COMPLEX OXIDES

G. Kresse*, C. Franchini, M. Shishkin, M. Marsman, and J. Paier
Computational Materials Physics, Faculty of Physics,
University of Vienna, Sensengasse 8/12, Austria

A major shortcoming of density functional theory is that the predicted band gaps are usually significantly too small. It is generally argued that this shortcoming is related to the fact that density functional theory is a ground state theory, and as such, it is not possible to relate the one electron energies to the experimentally observed quasi particle energies. Although true to some extent, the modeling of the position of donor and acceptor levels in semiconductors is seriously hampered by the band gap error. Several cures to this problem have been suggested. A particular attractive and fairly simple one is the inclusion of a small fraction of the non-local exchange in the Hamiltonian (hybrid functionals) [1], but a more rigorous approach is via many-electron Green's function techniques, which allow to predict band gaps within few percent of experiment, when performed self-consistently with vertex corrections [2]. Here we present results for two applications, the oxygen vacancy in ZnO [3] and a study of polaronic hole trapping in K doped $BaBiO_3$ [4] using hybrid functionals. For $BaBiO_3$, hybrid functionals predict that Bi^{3+} sites can trap two holes from the valence band to form Bi^{5+} cations. The trapping is accompanied by large local lattice distortions. The composite particle consisting of the electronic hole and the local lattice phonon field shows all properties of a polaron, despite possessing a rather dispersed electronic hole [4].

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[2] M. Shishkin, M. Marsman, and G. Kresse, Phys. Rev. Lett. 99, 246403 (2007).
[3] F. Oba, A. Togo, I. Tanaka, J. Paier, and G. Kresse, Phys. Rev. B 77, 245202 (2008).
[4] C. Franchini, G. Kresse, and R. Podloucky, Phys. Rev. Lett. 102, 256402 (2009).

LOCALISED AND ITINERANT STATES IN d AND f ELECTRON OXIDES UNITED BY GW@LDA+U

Hong Jiang
College of Chemistry, Peking University,
Beijing, China

The accurate first-principles description of d- and f-electron systems is currently regarded as one of the great challenges in condensed matter physics. These systems are characterized by the simultaneous presence of itinerant (delocalized) and highly localized states and interactions between them. Density-functional theory (DFT) in the local-density or generalized gradient approximation (LDA or GGA, respectively) proves to be inadequate for d/f-electron systems due to the severe delocalization (or self-interaction) error, leading to qualitatively incorrect metallic ground states for many wide-gap insulating systems. This difficulty can be partly overcome by introducing a local Hubbard-like correction (LDA+U), but itinerant states are still treated on the LDA level. Many-body perturbation theory in the GW approach offers both a quasi-particle perspective (appropriate for itinerant states) and an exact treatment of exchange (appropriate for localized states). The combination of GW with LDA+U (GW@LDA+U) is therefore promising for d/f-electron systems. In this talk, we first apply the GW@LDA+U method to lanthanide oxides (CeO_2 and Ln_2O_3 (Ln=lanthanide series)) [1]. These compounds have important technological applications, in particular in catalysis and microelectronics. Good agreement between the GW density of states and experimental spectra is observed for CeO_2 and Ce_2O_3. Unlike the LDA+U method GW@LDA+U exhibits only a weak dependence on U in a physically meaningful range of U values. Our GW@LDA+U calculations provide a quantitative and qualitative understanding of the general trend observed for the band gaps of the Ln_2O_3 series in terms of the relative positions of the occupied and unoccupied f-states and reproduce the characteristic features of the series. We further investigate the GW@LDA+U method in a set of prototypical d-electron systems including 1) ZnS with semicore d-states, 2) ScN and TiO_2 with empty d-states and 3) late transition metal oxides (MnO, FeO, CoO and NiO) with partially occupied d-states. It is found that for ZnS, ScN and TiO_2, the GW band gap only weakly depends on U, but for the late transition metal oxides the dependence on U is as strong as in LDA+U. These different trends can be understood in terms of changes in the hybridization and screening. Our work demonstrates that GW@LDA+U with physical values of U provides a balanced and accurate description of both localized and itinerant states in d/f-electron systems.

[1] H. Jiang, R. I. Gomez-Abal, P. Rinke and M. Scheffler, Phys. Rev. Lett. 102, 126403 (2009).

X-RAY ABSORPTION SPECTROSCOPY: A PROBE OF LOCAL STRUCTURE AND OXIDATION STATE

Alan Chadwick
Functional Materials Group,
School of Physical Sciences, University of Kent,
Canterbury, Kent CT2 7NH, UK

X-ray absorption spectroscopy (XAS) is now a well-established technique for determining local structure and has unique features when compared to other methods. This contribution will briefly review the basis of the technique and then focus on its applications in the characterisation of functional oxides. To illustrate these applications a number of systems that are being studied at Kent will be considered. The materials that will be highlighted are oxides with potential technological uses; namely in energy storage (fuel cells and batteries), as sensors, catalysts and optical devices. The examples are chosen to highlight investigations of bulk and nanocrystalline materials, in situ measurements and the combination of XAS with other techniques. The talk will conclude with a forward look to some of the new facilities and techniques that are developing in XAS.

MODELLING OF DEFECTS, SURFACE PROPERTIES AND NANO CLUSTERS OF ZINC OXIDE

Richard Catlow*, Alexei Sokol, Scott Woodley,
Department of Chemistry, University College London, UK

Zinc Oxide is a highly versatile material with wide ranging applications in electronics and ceramics. This talk will review recent computational studies [1] aimed at elucidating:

(1)The fundamental defect structure of the material, which remains controversial.

(2)The complex surface structure of the material.

(3)The nature of catalytic reactions on the ZnO surface.

(4)The structures and properties of nano-particulate ZnO.

The calculations we report employ both interatomic potentials and Density Functional Theory and represent a case study of the applications of contemporary computational methods to oxide materials.

[1] Catlow C.R.A., French S.A, Sokol A.A., Al-Sunaidi A.A. and Woodley S.M., J. Comp. Chem., 29, 2234 (2008)

ELECTRICAL AND OPTICAL ACTIVITY OF POINT DEFECTS IN ZnO

David C. Look
Semiconductor Research Center, Wright State University,
3640 Col. Glenn Hwy., Dayton, Ohio 45435, USA.

Point defects play important roles in many semiconductor materials and devices, and this is certainly the case for semiconducting ZnO. For example, in pure, as-grown, n-type ZnO, the Zn vacancy V$_{Zn}$ is sometimes the dominant acceptor, and in p-type material, the O vacancy is one of the chief compensating donors. Also, in ion-implanted ZnO, used in some device applications, large concentrations of point defects, including clusters, are generated. Electron irradiation (EI) will also produce point defects, and since EI-generated defects are usually just simple vacancies and interstitials this is the method of choice for detailed studies. Indeed, 1-MeV electron irradiation leads to clear electrical and optical signatures of several defects in ZnO, most notably an acceptor related to V$_{Zn}$, and a shallow donor related to the Zn interstitial Zn$_I$. Since V$_{Zn}$ has been studied extensively by positron annihilation, we will concentrate on Zn$_I$. Temperature-dependent Hall-effect (T-Hall) analysis establishes the energy of this donor as about 30 meV, and its production rate at 1 MeV as about 0.7 cm^{-1}, which is within a factor-two or so of the predicted Zn$_I$ production rate of about 0.3 cm^{-1}. However, since Zn$_I$ is likely mobile at room temperature, it can complex with acceptors, and we believe that the observed 30-meV donor is Zn$_I$-N$_O$, which is found by density-functional theory (DFT) to be bound with about 0.9 eV and to have a (0/+) transition in the conduction band. Although DFT is not accurate for energies as shallow as 30 meV, still it predicts that the energy of the complex will be shallower than that of isolated Zn$_I$. Low-temperature (4-K) photoluminescence (PL) of the same irradiated sample finds a strong new line at 3.36070 eV, and a much weaker triplet at 3.33711, 3.33793, and 3.33840 eV, and we assign these four lines to neutral-donor-bound-exciton D0X transitions in which the donor final state is n = 1s, 2s, 2px,y, and 2pz, respectively. A simple hydrogenic analysis gives ED = 4/3(E1s E2s) = 31 meV, nearly the same as that found by T-Hall analysis. The irradiation also produces a broad PL line at 1.8 eV. Another group, performing EPR experiments on irradiated ZnO, has assigned this line to a donor-acceptor pair recombination involving the singly-ionized Zn vacancy. This group also saw the new 3.3607 line and thought it probably represented Group-III donors in a perturbed environment. Ion implantation of In produces a 1.8-meV-wide band of overlapping D0X lines centered near 3.361 eV and likely including our 3.3607-eV defect-related transition. Indeed, there is a clear 3.338-eV line (n = 2) in the implanted sample, suggesting that the implantation process produces stable Zn$_I$-related defects. Furthermore, modified TRIM calculations predict nearly equal Zn interstitial and vacancy concentrations of mid-1020-cm^{-3} after implantation, and T-Hall modeling confirms this number of donors and acceptors. Other implantation-produced PL lines appear in the range 3.33 3.35-eV (the defect region), and they include a strong 3.333-eV transition, often seen in as-grown material and usually assigned to an exciton bound to an extended defect, such as a stacking fault (SF). Since all of our defect lines anneal out at the low temperature of 400 C, the SF assignment is open to question and must be further investigated. We will discuss several defect-related transitions in as-grown ZnO, including those at 1.8-eV, 3.333-eV, and 3.338-eV.

FIRST-PRINCIPLES INVESTIGATION OF UNUSUAL MATERIALS PROPERTIES OF OXIDES

Su-Huai Wei
National Renewable Energy Laboratory, Golden CO 80401, USA

Post-transition metal oxides (ZnO, In_2O_3, SnO_2, etc.) and their alloys comprise a group of materials that have many unique physical properties such as simultaneously high electron conductivity and optical transmission, high catalytic efficiency, and chemical stability. Therefore, they are widely used in optoelectronic applications such as photovoltaic and photoelectrochemical devices, LEDs, display panels, and chemical sensors. They have also been proposed as ideal hosts for high TC spintronic materials. In this talk, I will discuss our recent first-principles theoretical study of the oxides, demonstrating that the properties of the binary and multinary oxides are more complex than previously thought. We find that (i) many oxides (In_2O_3, Cd_2SnO_4, etc.) have non-equivalent fundamental and optical band gaps, arising from parity forbidden band edge transitions; a good transparent conducting oxide should have small fundamental band gap but a large optical band gap [1]. (ii) The band gap renormalization in degenerate n-type doped oxides arises from the non-parabolic nature of the conduction band (i.e., not a rigid shift as previous thought), and is highly sensitive to the electronic states of the dopants [2]. (iii) The ground state crystal structure of the non-isostructural $(InMO_3)_m(ZnO)_n$ (M = In, Ga, Al) alloy should satisfy several fundamental rules such as the octahedron rule and the octet rule [3]. The formation of the layer quaternary structure or amorphous structure also results in some interesting changes in the electronic and optical properties of the alloy [4]. (iv) The origin of the electron and hole induced ferromagnetism in oxides are investigated [5, 6]. For example, we show that the spontaneous magnetization in d0 oxides with sufficient holes is intrinsic properties of the oxides and can be enhanced by anion site doping or through quantum confinement [6]. (v) We have proposed a designing principle for the band edge modification of the oxide materials. For example, we demonstrate that TiO_2 co-doped with Mo and C is suitable for photoelectrochemical water splitting applications [7]. (vi) Finally, we have analyzed the doping asymmetry problem in the wide-gap oxides and proposed several approaches to overcome the p-type and bipolar doping bottlenecks in these materials [8].

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[2] Origin of band-gap renormalization in degenerately doped semiconductors, A. Walsh, J. L. F. Da Silva, S.-H. Wei, Phys. Rev. B 78, 075211 (2008).
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Al-Jassim, and S.-H. Wei, Phys. Rev. B 79, 073105 (2009). A. Walsh, J. L. F. Da Silva, and S.-H. Wei (submitted).
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[8] Approach to overcome the doping asymmetry in wideband gap semiconductors, Y. Yan, J. Li, S.-H. Wei et al., Phys. Rev. Lett. 98, 135506 (2007); phys. status solidi (b) 245, 641 (2008).

SOURCES OF CONDUCTIVITY IN TRANSPARENT OXIDES

Chris G. Van de Walle
Materials Department, University of California, Santa Barbara, USA

Oxides are used in a wide range of devices, ranging from gas sensors to varistors. Recent advances in bulk and single-crystal growth open up the prospect of exciting new applications. Transparent conducting oxides (TCOs) provide metallic conductivity while absorbing little or no visible light; they are essential for devices such as solar cells, light-emitting diodes, and flat-panel displays. Improvements in carrier concentrations and mobilities have enabled fabrication of transparent transistors. Furthermore, controllable p-type doping would allow for optoelectronic devices such as light emitting diodes and detectors. Recent efforts to enhance the performance of these oxides have highlighted the fact that the causes and mechanisms of conduction are poorly understood.

First-principles calculations can be used to elucidate these issues, but the band-gap problem inherent in density functional theory (DFT) affects defect levels in the band gap as well as formation energies [1]. Another limitation is due to the supercell approach, in which properties of isolated defects are modeled using periodic boundary conditions [2]. Interactions between periodic images can lead to errors in formation energies, particularly for charged defects. I will give a brief overview of various approaches that have recently been successfully applied to overcome these problems. Areas in which improvements are still needed will be identified.

I will use ZnO [3] as a prototype to illustrate how accurate calculations can elucidate sources of conductivity in ZnO, and also mention applications to SnO_2 [4], MgO, Al_2O_3 [5], In_2O_3, and TiO_2. Oxygen vacancies are widely accepted as the source of n-type conductivity, but first-principles calculations have established that this cannot be true in ZnO [3]. We have suggested that hydrogen is a plausible cause of unintentional doping, a prediction that has been confirmed by numerous experimental studies. Both interstitial [6] and substitutional [7] hydrogen act as shallow donors, with the latter forming an unusual multicenter bond. Links to experiment will be discussed.

Work performed in collaboration with Anderson Janotti, Sukit Limpijumnong, Pakpoom Reunchan, Patrick Rinke, Matthias Scheffler, Abhishek Singh, and Joel Varley.

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SIMILARITIES AND DIFFERENCES BETWEEN PNICTIDES AND CUPRATE SUPERCONDUCTING PARENT COMPOUNDS

Francesc Illas
Departament de Qumica Fsica and Institut de Qumica Terica i Computacional (IQTCUB),
Universitat de Barcelona, C/ Mart i Franqus 1, E-08028 Barcelona, Spain

After almost ten years of relative stagnation, the search for superconductors with high critical temperature is experiencing revitalization due to recent discovery of superconductivity in iron-arsenide layered materials [1]. The new superconducting materials involve iron as transition metal rather than copper as in well-known superconducting cuprates. The parent material LaOFeAs exhibits an intriguing magnetic behaviour and become superconducting after (electron) doping with F or (hole) doping with Sr leading to a phase diagram closely related to that of superconducting cuprates. Neutron scattering experiments show that undoped LaOFeAs exhibits a complex magnetic behaviour with an evident change in both χ versus T curve and conductivity, and undergoes a structural distortion from tetragonal to monoclinic symmetry at 155 K [2]. This relationship poses intriguing questions about similarities, differences, and ultimately on the underlying mechanisms of the superconductivity in both types of materials. These are questions that can be answered by first principles electronic structure methods. However, it is now well established that standard LDA and GGA incorrectly predict a strong d character of the bands above and below Fermi level and a too small band-gap for cuprates indicating either a metallic or, in the most favourable cases, a semiconducting behaviour. These predictions are in a clear contradiction with the experimentally measured properties such as the charge transfer insulating gap of 1-2 eV, antiferromagnetic ordering derived from the leading J1 = -140 meV nearest neighbour exchange interaction or the strong mixing between Cu d and O p states for most of the valence bands. Clearly, proper description of the electronic structure of LaOFeAs requires as well going beyond the LDA and GGA methods thus avoiding the erroneous interpretations one can find in the literature dealing with the theoretical description of cuprates [3].

In this work we show that the magnetic structure of LaOFeAs and superconducting cuprates parent compounds are more similar than imagined. In fact, accurate hybrid-DF and GGA+U periodic density functional calculations consistently describe the ground state of LaOFeAs as a complex insulator/semiconductor with a physical nature intermediate between Mott-Hubbard and charge-transfer limiting situations and a band gap at finite T perturbed by spin excitations [4]. The electronic structure involves Fe^{2+} cations in a distorted tetrahedral environment which can be effectively considered as particles with S=2 spin moments localized at Fe^{2+} sites with a local $3d^6$ electronic configuration in a quasi-tetragonal FeAs4 structural unit. The calculations that the electronic ground state involves an intricate magnetic structure with two nearly equal antiferromagnetic nearest-neighbours and next nearest-neighbours magnetic coupling constants which gives rise to a highly frustrated magnetic ground state which cannot be easily anticipated from the crystal structure. Hence, the present study provides unbiased, independent confirmation of the magnetic order suggested by de la Cruz et al. [2] from neutron diffraction experiments on polycrystalline LaOFeAs samples and has is in agreement with subsequent studies using similar theoretical techiques [5].

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ABSTRACTS OF CONTRIBUTED TALKS

Cu, Au AND Ce NANOPARTICLES SUPPORTED ON TIO$_2$(110) AS HIGHLY EFFICIENT CATALYSTS FOR WATER-GAS SHIFT REACTIONS

Javier Fdez. Sanz, Jess Graciani* and Jos A. Rodrguez
Dpto de Qumica Fsica, Universidad de Sevilla,
E-41012, Sevilla, Spain
and
Chemistry Department, Brookhaven National Laboratory,
Upton, NY 11973, USA.

Although bulk metallic gold is not active as a WGS catalyst, Au nanoparticles supported on TiO$_2$ (110) have an activity comparable to that of Cu/ZnO(000). Cu/TiO$_2$ (110) is clearly a better catalysts than Cu/ZnO(000) or Au/TiO$_2$(110). The catalysts that have the highest activity for the WGS have also the lowest apparent activation energy. On Cu(111) and Cu(100) the apparent activation energies are 18.1 and 15.2 kcal/mol, respectively. The apparent activation energy decreases to 12.4 kcal/mol on Cu/ZnO(000), 10.2 on Au/TiO$_2$(110) and 8.3 kcal/mol on Cu/TiO$_2$ (110). The Cutitania interactions are substantially stronger than the Autitania interactions. In STM images the average particle size in Cu/TiO$_2$ (110) is smaller than in Au/TiO$_2$ (110). The Cu particles are dispersed on the terraces and steps of the oxide surface, while the Au particles concentrate on the steps. The morphology of Cu/TiO$_2$(110) favors high catalytic activity. The results of density-functional calculations indicate that the metal-oxide interface plays an essential role in the catalysis, helping in the dissociation of water and in the formation of an OCOH intermediate whichdecomposes to yield CO$_2$ and hydrogen.

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RULES FOR SELECTIVITY IN OXIDATION PROCESSES ON $RuO_2(110)$

Gerard Novell-Leruth* and Núria López
Institute of Chemical Research of Catalonia, ICIQ
Avgda. Països Catalans, 16, 43007 Tarragona, SPAIN.

RuO_2 has been studied as a powerful material in oxidation processes, e.g. the CO oxidation,[1] hydrochloride oxidation to chlorine,[2] and hydrogen-water related processes.[3] RuO_2 has been tested as a mild oxidation agent to perform selective oxidations of alcohols to aldehydes and ketones or even in ethylene to epoxide. Following the activity model devised by Nørskov and co.[4] the activity of oxygen atom of Ag and RuO_2 shall be rather close. We have demonstrated that the reactivity of $RuO_2(110)$ for methanol is close to that of Ag but in ethylene partial oxidation it is very different. For methanol oxidation the RuO_2 and Ag show a similar pathway: partial dehydrogenation of methanol to obtain formaldehyde and water. Ethylene oxidation is initially similar on two catalysts, both produce an OMME intermediate, but the selectivity to epoxidation of Ag and RuO_2 is completely different (50To understand this different selectivity, we have performed extensive calculations on the methanol oxidation and ethylene partial oxidation on $RuO_2(110)$ with DFT methods. With this methodology we can analyse each step of the process and dissect the results to clarify these differences. We have studied the different pathways that take place for these oxidation processes and analysed in detail the differences. Also we have compared our results with the experimental ones and they are in agreement.

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NON-STOICHIOMETRIC TITANIUM DIOXIDE: EXPERIMENTAL INSIGHTS AND CHALLENGES IN CHARGE TRANSFER AND SURFACE REACTIONS

R.A. Bennett*, J.S. Mulley and N.D. McCavish
School of Chemistry, University of Reading, Reading, RG6 6AF, UK.

Reducible transition metal oxides play a key role as active materials in the development of electronic, optical and energy harvesting devices. In spintronics, where magnetic properties of the material are harnessed to manipulate spin polarised electron currents, doped TiO_2 is a candidate host for dilute magnetic semiconductor; in gas sensors surface chemical reactions induce changes in electronic structure which are picked up by external instruments through changes in electrical conductivity or depletion depths in gate structures. In both these examples the subtle interplay between electronic and geometric structure at surfaces and interfaces dictates the material behaviour. This balance depends upon the surface environment and treatment history. Rutile titanium dioxide (TiO_2) has become the prototypical reducible system for scientific study due to its relatively simple electronic structure and accessibility in single crystalline form [1]. The material properties are sensitive to the nature of its free surfaces and the presence of oxide-metal interfaces. Non-stoichiometry is often intentionally induced experimentally as it tends to lead to a semi-conducting bulk. These semiconducting crystals display a fascinating surface chemistry with regard to their degree of reduction and re-oxidation [2-4]. Here we describe scanning tunnelling microscopy images of the surface phases along with STM movies of surface oxidation and reduction chemistry happening at elevated temperatures [5]. We elucidate the behaviour of the bulk and selvedge defects interacting with the surface through high resolution photoemission spectroscopy [6,7] and allied first principles calculations [8-10]The surface dynamics and charge transfer pose significant, and industrially relevant, problems in understanding the behaviour of TiO_2 for both modelling and experimental communities.

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A REALISTIC AB INITIO MODEL OF THE PASSIVE FILM FORMED ON STAINLESS STEELS

Dominique Costa,* Kamal Sharkas, Mazharul M. Islam and Philippe Marcus
Laboratoire de Physico-Chimie des Surfaces,
CNRS-ENSCP (UMR 7045),
Ecole Nationale Suprieure de Chimie de Paris,
11 rue P. et M. Curie, 75005 Paris, France.

Stainless steels are widely used for their good corrosion resistance, due to the formation of a protective passive film. The passive film is composed of a thin (some atomic layers) oxide film, mainly a Cr_2O_3 film, which may contain some Fe^{3+}. This oxide film is hydroxylated at the surface. The aim of this study was to elaborate a realistic ab initio model of this passive film. [1] Following the seminal work of Kresse et al on chromia surfaces [2], the reactivity of the (0001)-Cr-Cr_2O_3 surface towards water was studied by means of periodic DFT+U. Several water coverages were studied, from 1.2 H_2O/nm^2 to 14.1 H_2O/nm^2, corresponding to 1, 2 and 3 water/Cr at the (0001)-Cr_2O_3 surface, respectively. With increasing coverage, water gradually completes the coordination sphere of the surface Cr atoms from 3 (dry surface) to 4 (1.2 and 4.7 H_2O/nm^2), 5 (9.4 H_2O/nm2) and 6 (14.1 H_2O/nm^2). For all studied coverages, water replaces an O atom from the missing above plane. At coverages 1.2 and 4.7 H_2O/nm^2, the Cr-Os (surface Oxygen) acid-base character and bond directionality govern the water adsorption. The adsorption is molecular at the lowest coverage. At 4.7 H_2O/nm^2, molecular and dissociative states are isoenergetic. The activation energy barrier between the two states is low, 12 kJ/mol, allowing proton exchange between the OH groups, as evidenced by ab inito molecular dynamics performed at room temperature. At coverages of 9.4 and 14.1 H_2O/nm^2, 1D- (respectively 2D-) water networks are formed. The resulting surface terminations are -$Cr(OH)_2$ and -$Cr(OH)_3$-like respectively. The increased stability of those terminations as compared to the previous ones are due to the stabilization of the adsorbed phase through a H-bond network, water forming a flat hexagonal ice layer, and to the increase in the Cr coordination number, stabilizing the Cr (t_{2g}) orbitals in the valence band. An atomistic thermodynamic approach allows us to specify the temperature and water pressure domains of prevalence for each surface termination. It is found that the -$Cr(OH)_3$-like, -$Cr(OH)_2$ and anhydrous surfaces may be stabilized depending on (T,P) conditions. Calculated energies of adsorption, OH coverages at saturation and OH frequencies are in good agreement with published experimental data [3-4] and support the full hydroxylation model, where Cr achieves a 6-fold coordination, at saturation. Finally, the presence of Fe^{3+} ions in the passive film, is also investigated. We thus propose a representative model to be used in further theoretical investigation of the reactivity of passive films formed at the surface of stainless steels.

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LATTICE DYNAMICS OF Co-DEFICIENT AND Fe-DOPED CoO

U. D. Wdowik* and K. Parlinski
Institute of Technology, Pedagogical University,
Podchorazych 2, 30-04 Cracow, Poland.

Ab initio calculated Hellmann-Feynman forces [1] were used to investigate an influence of vacancies and impurities on the lattice dynamics of a charge-transfer insulator CoO. Corrections for the strong on-site interactions have been taken into account via the Hubbard potential U and the local exchange interaction J. A supercell approach was used to model CoO crystal containing vacancies and impurities. Vacancies of concentrations of 3% and 6% were introduced into the cobalt sublattice. Calculations for Fe-doped system were performed with constant U on Co and variable U on Fe. For structures with defects the phonon density of states and the dispersion relations of phonons were calculated using a direct method [2] and the harmonic approximation. To analyze the numerous of phonon dispersion curves, a filter which enables to remove the fake phonon branches was applied [3, 4]. It allowed us to present the phonon dispersion curves to be more close to the dispersion relations of a real defected sample. Cobalt vacancies and Fe impurities affect the optical phonon vibrations, while the long wavelength acoustic phonons do not experience significant changes upon the doping of defects. For system with vacancies the increasing nonstoichiometry decreases the TO frequencies and increases the LO frequencies. Defects modify the effective force constants of its local surrounding and give rise to an appearance of additional modes. It was found that the vibrational properties of Fe impurity in the CoO crystal are essentially different from the vibrational properties of the host cations. Differences in the vibrational dynamics of dopant and host atoms are due to the force constant defect between Fe and Co. The mean-squared vibrational amplitudes (MSD) of cations and anions in the ideal and defected CoO are compared to the existing experimental data. The MSD of cations and anions in Co-deficient CoO increase with the increasing concentration of vacancies. The calculated MSD of Fe remain in very good agreement with those measured by Moessbauer spectroscopy [5].

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QUASIPARTICLE BAND GAP OF IIB-VI TRANSPARENT OXIDES WITHIN THE GW APPROXIMATION

Hemant Dixit* , Rolando Saniz, Bart Partoens and Dirk Lamoen
CMT-group and EMAT,
Departement Fysica, Universiteit Antwerpen,
Groenenborgerlaan 171, B-2020 Antwerpen, Belgium.

The GW approximation [1] to many body perturbation theory represents the state of the art technique to calculate the quasiparticle correction to the band gap of solids and has been successfully applied to many materials. Although the GW approximation often works well with pseudopotentials (PP's) and plane wave basis sets used within Density Functional Theory Local density approximation (DFT-LDA), the II-VI materials are particularly challenging due to the strong p-d hybridization between the cation 'd' and anion 'p' states [2,3]. Recently, the self-consistent GW scheme [4] and quasiparticle corrections based on the generalized Kohn-Sham schemes [5,6] have been used to improve the GW band gap for II-VI semiconductors and insulators. Although these schemes make closer estimate of the band gap with the GW approximation, there is still need of an elaborate theory and it is a topic of current research. We present the GW band gap calculated with the ABINIT [7] code, using the PP and plane wave basis set, for II-VI transparent oxides namely ZnO and CdO. The quasiparticle corrections are calculated systematically with different number of valence electrons in the cation-pseudopotential. We find that the 20-electron cation pseudopotential yields the best quasiparticle correction. The dependence of self-energy on the exchange interaction between the atomic orbitals is discussed. The positioning of the cation 'd' energy level in the quasiparticle bandstructure is addressed. The correlation between the p-d overhybridization and the underestimation of the non-self-consistent GW band gap is made through a comparison of zincblende (ZB) and rocksalt (RS) ZnO. In ZB-ZnO the p and d state cam mix anywhere in the Brillouin zone and leads to the p-d hybridization, while the RS phase includes the inversion symmetry at the Gamma point in the Brillouin zone, hence the p and d states do not mix at the Gamma point and remain unhybridized. Thus the GW correction at the Gamma point is better for the RS-ZnO compared to the ZB counterpart. We also present the self-consistent GW band gap for these materials.

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ELECTRONIC PROPERTIES OF DEFECTS IN POLYCRYSTALLINE DIELECTRIC MATERIALS

K P McKenna* and A L Shluger
London Centre for Nanotechnology, University College London,
Gower Street, London, WC1E 6BT, UK
and
World Premier International Research Center,
Advanced Institute for Materials Research,
Tohoku University, Japan.

Insulating films in electronic devices, such as magnetic tunnel junctions and MOSFETs, are often polycrystalline and defects near grain boundaries (GBs) can play important roles in processes such as electron tunnelling [1], charge trapping and dielectric breakdown [2,3]. Understanding the electronic properties of GBs and of their associated defects is a challenging experimental problem because it is difficult to separate interface related properties from those associated with the bulk. It is also a difficult theoretical problem because accurate modelling of charged defects in complex GB structures is difficult using standard quantum mechanical methods. To model these complex systems we have developed a multi-scale methodology, combining atomistic models, periodic DFT and embedded cluster methods [4,5]. In this talk, these methods will be described and results will be presented for GBs in MgO and HfO_2. Our results show that even pristine (i.e. defect free) GBs in MgO and HfO_2 can act as both electron and hole traps [5-7]. We also find that defects favourably segregate to grain boundaries, in various charge states, and that their electronic properties are different from their counterparts in the bulk [4,5]. The implications of the results for technological applications such as catalysts and MOSFETs will be discussed.

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MULTI SCALE MODELLING OF LOW INDEX RUTILE TiO2 SURFACES BY A TIGHT-BINDING VARIABLE-CHARGE MODEL AND AB INITIO CALCULATIONS

R. Tétot*, A. Hallil, E. Amzallag
Institut de Chimie Molculaire et des Matriaux d'ORSAY (ICMMO),
UMR 8182 CNRS-Universit Paris-Sud 11,
Laboratoire d'Etude des Matriaux Hors- Equilibre (LEMHE),
Orsay, F-91405, France.

Performing realistic large-scale atomistic simulations of oxide surfaces as well as of interfaces formed upon various deposits (oxide, metal, nanoclusters), using interatomic potentials, is currently a topic of great interest in materials sciences. To this aim, a number of variable-charge models have been developed since two decades ([1,2] and references therein). However, all these models poorly account for the iono-covalent metal-oxygen bond in oxides what makes them poorly transferable. In this work, we shall present a new transferable variable-charge model [3] based on the charge equilibrium (QEq) scheme [4], in which the so-called Alternating Lattice Model (ALM) from Goniakowski and Noguera [5] has been implemented. The ALM allows describing at the electronic level, using a tight-binding approach, the iono-covalent character of the metal-oxygen bond in insulating oxides. The main result is that the covalent energy becomes a square root function of both the coordinance and the atomic charges and, consequently, takes part in the QEq optimization. We shall present results obtained with this SMTB-Q (Second-Moment-Tight-Binding QEq) model on the energetic, the atomic relaxations and the charge transfer for the three more stable surfaces of rutile TiO_2 ((110), (100), (001)). We shall compare these results with new DFT calculations performed with the last release of Crystal code [6] both with GGA and hybrid B3LYP functionals. Finally, we shall present results obtained for oxygen vacancies on and near the TiO_2(110) surface.

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THE REDUCED RUTILE (110) SURFACE ENERGETICS AND DIFFUSION OF Ti POINT DEFECTS IN THE SELVEDGE

***P.A. Mulheran, C.S. Browne and M. Nolan**
University of Strathclyde, UK
and
University of Reading, UK
and
Tyndall National Institute, Cork, Ireland.

The surface chemistry and reactivity of the reduced $TiO_2(110)$ surface is known to be dominated by the presence of Ti surface interstitials [1,2]. Here we study the energetics and diffusion of Ti interstitials and adatoms in the selvedge with a combined computational approach using density function theory and an empirical potential scheme. We start by characterising Ti adatoms through their binding sites and associated electronic properties using the DFT+U methodology. The parameter U is set by comparing the electronic density of states to UPS and XPS data taken from self-doped thin rutile films [3]. With GGA (PW91) we find that a value of U=3eV provides a good description of the reduced Ti states induced by the adatom. We then use this same value of U to calculate the energies and electronic structure of Ti interstitials in the selvedge. In order to investigate the diffusion pathways of the Ti species, we employ the charge equilibration (QEq) empirical potential parameterised for rutile surfaces and oxygen vacancies [4]. Whilst this potential does provide a good description of the adatom and interstitial adsorption sites, we find that it over-binds the interstitials by 2eV or so with respect to the adatom. Consequently, the potential as presented in [4] is not suitable for studying the dynamics of the Ti point defects in the selvedge. A Bader analysis [5] of the DFT+U results indicates that the primary failing of the QEq potential is its propensity to transfer charge to and from under- or over-coordinated oxygen. Surprisingly, when charge transfer to oxygen is prohibited in the QEq scheme, we find that the defect energy landscape is brought into line with the DFT+U results. This allows us to employ this modified QEq potential in our exploration of the Ti diffusion pathways. Using the Nudged Elastic Band method, we investigate a variety of possible pathways, and find that an interstitialcy mechanism dominates [6]. In particular, diffusion from the most stable adatom site (neighbouring 2 bridging oxygen and one in-plane oxygen) to a 1st-layer interstitial involves exchange with a 6-fold coordinated Ti underneath the bridging oxygen. To confirm our result, we return to the DFT+U calculations and perform constrained relaxation along the diffusion pathway, and confirm it as a minimum energy pathway whose activation energy is in good agreement with the empirical result. Our empirical potential scheme thus provides a good model for the reduced rutile surface, and can be further employed in dynamic simulations. In combination with the DFT+U calculations, we are therefore starting to obtain a good understanding of the surface reactivity of the reduced rutile (110) surface.

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ELECTRONIC PROPERTIES OF OXYGEN DEFICIENT AND METAL DOPED TiO2: A FIRST PRINCIPLES INVESTIGATION

Mazharul M Islam*[a,b], T. Bredow[c] and A. Gerson[b]
[a] Laboratoire de Physico-Chimie des Surfaces,
CNRS-ENSCP (UMR No. 7045), Universit Pierre et Marie Curie,
11 rue Pierre et Marie Curie, 75231 Paris Cedex 05, France.
[b] Applied Centre for Structural and Synchrotron Studies,
University of South Australia, Mawson Lakes Campus,
Mawson Lakes, Adelaide, South Australia 5095, Australia.
[c] Institut fr Physikalische und Theoretische Chemie,
Universitat Bonn,
Wegelerstrasse 12, 53115 Bonn, Germany.
rana-islam@enscp.fr

The electronic properties of stoichiometric, defective, and metal-doped rutile TiO_2 have been investigated theoretically with periodic quantum-chemical calculations. Theoretical results obtained with the Perdew-Wang density functional method and with a density functional-Hartree-Fock hybrid method are compared. The defective systems were simulated by creating a neutral oxygen vacancy. Doping of rutile with several metals such as Al, V, Cr, Mn, Fe, Co, Ni, Cu, Zn are investigated to elucidate their effect in the electronic properties of rutile. Occupied defect states are observed in the band gap of rutile due to the presence of oxygen vacancies, which is in accord with previous theoretical studies and the experimentally observed colouring. For the investigation of aluminum doping, three different situations have been considered: substitution of a single Ti atom by an Al atom, co-substitution of Ti by Al and O by Cl, and substitution of two Ti by two Al combined with the formation of an O vacancy. In the last two cases, aluminum doping does not introduce band gap states, and the band gap is even increased compared to undoped rutile. We conclude that stoichiometric Al doping reduces pigment colouring induced by oxygen vacancies in rutile and also suppresses the photocatalytic activity of titania pigments [1]. All possible spin states are investigated systematically for the substitutional doping with transition elements with and without oxygen vacancy. It is observed that rutile doping with transition elements introduces states in the band gap of rutile. This will enhance the photocatalytic activity of TiO_2 which is in agreement with experimental observations.

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PHOTOELECTROLYSIS OF WATER FOR HYDROGEN PRODUCTION: A DFT-BASED SCREENING PROCEDURE FOR EFFICIENT MATERIAL SEARCH

Soumendu Datta*, Juan M. Garcia Lastra, Kristian S. Thygesen,
Karsten W. Jacobsen
Centre for Atomic-scale Material Design (CAMD),
Dept. of Physics, Technical University of Denmark,
Lyngby, Denmark.

The world is rapidly running out of fossil fuels. As a mater of considerable urgency, technologies for the generation of new types of energy must be developed. There is a growing concensus that hydrogen has the potential to suplement and ultimately replace fossil-fuels for the future need. One of the most promising methods of hydrogen generation using a source of renewable energy is that based on photoelectrochemical water decomposition using solar energy. The energy conversion efficiency of water photoelectrolysis is determined mainly by the properties of the materials used for photoelectrodes. The structural stability of photoelectrodes in aqueous medium and under direct solar radiation, their low cost, proper band gap for utilizing the visible range of solar spectrum, proper alignment of valence band and conduction band edges with respect to water oxidation and reduction potentials, high catalytic activity towards water splitting reaction are the essentioal requirements for good photoelectrode materials. It is primarily for their stability that metal oxide semiconductors arguably hold the most promise for constructing a stable photoelectrolysis system. We would like to develop a density functional theory (DFT) based screening procedure to look for best possible metal oxides semiconductors, considering primarilly the three key properties: stability, band gap and band edge alignment. Our stability analysis is based on electro-chemical study which includes calculation of formation energy of the metal oxides in the aqueous environment. To get correct band gap estimate, we use GW corrections on top of self-consistent DFT calculation, which includes quasi-particle effect by calculation of self-energy. On the other hand, the consideration of band edge positions requires a series of slab models to allign them with respect to a valid reference energy (vacuum level or normal hydrogen electrode). In this presentation, we will discuss about all these steps by implementing them on a range of metal oxides.

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DEFECT-INDUCED MAGNETISM IN OXIDES

Andrea Droghetti*, Chaitanya Das Pemmaraju and Stefano Sanvito
School of Physics and CRANN,
Trinity College Dublin, Ireland.

Dilute magnetic semiconductors (DMS) represent a novel class of materials widely studied for spintronic applications. DMS are usually produced by doping a semiconductor with transition metal (TM) impurities, thus combining the semiconducting properties of the host with the magnetic ones of the guest [1]. The research on DMS has recently revealed new and unexpected features. Indeed a number of oxide materials, either rich in intrinsic defects or intentionally doped with non-magnetic impurities, were found to exhibit room temperature ferromagnetism, or at least a SQUID signal interpreted as ferromagnetism. A notable case is that of HfO2 [2]. Although the formation of the magnetic moments in these, so called, d^0 magnets is usually explained in terms of spin-polarized localized holes, at present there is not a clear understanding of the experimental observations. From a theoretical point of view, most of the calculations to date, which aim at explaining this new kind of defect-related magnetism, are based on density functional theory (DFT) using local approximations to the exchange correlation potential (LSDA or GGA). These notoriously underestimate Coulomb repulsion and tend to over-delocalize the charge density. Most of these calculations therefore return a spurious metallic (half-metallic) ground state with large magnetic interaction. However, it is well established that, in oxides, holes are often localized around the defect by lattice distortion forming small bound polarons [3]. We demonstrate [4, 5, 6] through a few examples that, when strong correlations are introduced at the level of self-interaction correction (SIC) implemented using the atomic SIC scheme (ASIC) [7], the correct hole localization is recovered and even the formation of a local moment becomes a delicate issue. Magnetism in d^0 materials hence depends on the subtle interplay between covalency, Hund's coupling and polaronic distortions around the impurities. We also report the results of some preliminary studies on these d^0 systems using Exact Exchange DFT.

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INTRINSIC FERROMAGNETISM IN CeO_2: DISPELLING THE MYTH OF VACANCY-SITE-LOCALIZATION MEDIATED SUPEREXCHANGE

David O. Scanlon*, Patrick, R. L. Keating and Graeme W. Watson
School of Chemistry,
Trinity College Dublin, Dublin 2, Ireland.

Intrinsic ferromagnetism in CeO_2 is a source of controversy in the literature[1, 2] and has been linked to the excess electrons left over upon oxygen vacancy formation on Ce sites neighbouring the vacancy.[2, 3] A recent theoretical study[4] concluded that increased vacancy concentration changes the localization behaviour of CeO_2, resulting in some degree of charge localization in the vacancy site itself, which leads to superexchange and polarization effects that enhance the stability of ferromagnetism. In this study, we show conclusively that oxygen vacancy concentrations in the bulk of up to 12.5% do not cause localization in the vacancy site, and that this is not responsible for any enhanced ferromagnetism.[5] Investigation of oxygen vacancies on the (111), (110) and (100) low index surfaces also show no evidence for ferromagnetic preference. It is concluded that oxygen vacancies are not the cause of the ferromagnetism reported in samples of undoped CeO_2. In light of this, other possible ferromagnetic intrinsic defects will be discussed.

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BAND ALIGNMENT AND DEFECT PHYSICS OF FUNCTIONAL OXIDES

Aron Walsh*
Department of Chemistry, Materials Chemistry,
University College London, UK.

The natural band alignment between different materials has proved an enigmatic issue in both experimental and theoretical semiconductor physics. The problem becomes more intense with the study of metal oxides owing to the large variation in both crystal structure and oxygen stoichiometry. A solution would be highly desirable for many applications, in particular, for assessing material suitability for energy related devices such as photoelectrochemical hydrogen production and photovoltaics. I will present a critical overview of existing approaches to calculate the intrinsic offsets of insulators, and the highlight their implications for defect formation and charge carrier generation.

ELECTRONIC STRUCTURE OF DOPED CUPRATES BY SELF-INTERACTION-CORRECTED DFT

A. Filippetti, D. Puggioni, G. M. Lopez, G. Peralta, and V. Fiorentini*
CNR-INFM SLACS and Physics Dept.,
University of Cagliari, Italy.

Doped magnetic cuprates are a highly relevant materials family,including many different complex systems such as high-Tc superconductors, low-dimensional Heisenberg magnets, etc. Most of these systems in their undoped state are described incorrectly as non-magnetic metals by standard DFT approaches such as GGA and LDA,precluding a meaningful study of the electronic structure of their defected and doped variants. The pseudo-self-interaction-corrected DFT method has been shown in recent years to be able to circumvent the problem, opening up the possibility of applications to doped magnetic cuprates. Here we will review some of these applications, possibly including: effectively 3D cuprates such as CuO in its monoclinic (pure and Mn- doped) and epitaxial-tetragonal variants [1]; effectively 2D cuprates such as $YBa_2Cu_3O_{(6+x)}$ and $Y_{(1-y)}Ca_yBa_2Cu_3O_6$ [2], discussing the distinct physics of chains and planes; effectively 1D cuprates such as Ca-doped yttrium cuprate [3] and $GeCuO_3$ [4], exhibiting, respectively, spin-compensated magnetic polarons and spin-Peierls distortions. Time permitting, we will mention rare-earth titanates, where the method is also successful. All these systems, and more, are described in a comprehensive review [5] of the method and applications, to appear shortly.

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THE ROLE OF NATIVE DEFECTS IN THE DIELECTRIC AND CONDUCTIVITY BEHAVIOR OF $CaCu_3Ti_4O_{12}$

Pietro Delugas [a] **and Paola Alippi*** [b]
[a] **CNR-IMM, Istituto per la Microelettronica e Microsistemi, Catania, Italy.**
[b] **CNR-Istituto di Struttura della Materia, Rome, Italy.**

The colossal (10^4) static dieletric constant of $CaCu_3Ti_4O_{12}$ (CCTO) has motivated intense research in recent years. Many studies have suggested that this property is not intrinsic property,but rather due to atomic-scale defective alteration. Ab initio computations are a natural tool to investigate this kind of issues. Here we report and discuss structure, electronic properties, and thermodynamics of native point defects in CCTO, studied by means of local and gradient-corrected DFT calculations using the VASP code. A first point of interest is the identification of native defects determining the high intrinsic conductivity of CCTO. As in many ionic materials, vacancies are all liable to act as dopants. V_O is the natural candidate n-type defect: its level within the CCTO band gap is 0.1 eV below the conduction, similar to the 0.08 eV activation energy of the measured bulk conductivity [1]. In O-lean conditions, the V_O concentration at 500 K is a sizable $10^{16}/cm^3$. Cation vacancies (V_{Cu} and V_{Ca}) in turn behave as acceptor-like defects. V_{Cu}, with a concentration of $10^{18}/cm^3$ in O-rich conditions, may be a source of significant p-type conditions. A second important issue is how defects contribute to the anomalous dielectric response. In this context, a most interesting indication of our calculations is that the antisite Cu_{Ca} is highly orientable electrical dipole. Its off-center geometry has a sizable dipole of 1.2 e*Å, and the barrier for Cu_{Ca} reorientation is 0.1 eV, quite compatible with the thermal behavior of CCTO dipoles. Calculated Cu_{Ca} concentrations reach $10^{20}/cm^3$ in Cu-rich condition (indeed large concentration of Cu_{Ca} have been reported in single crystal samples [2]). The existence of a high density of orientable dipoles and their mutual interaction could be a key ingredient to explain the dielectric behavior of CCTO.

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ABSTRACTS OF POSTERS

TITANOCENE ADSORPTION STUDIES ON TIO2 (110) RUTILE SURFACE USING AB-INITIO AND MOLECULAR DYNAMICS APPROACHES

Saurabh Agrawal,* Niall J English, Damian A Mooney and JMD MacElroy
Solar Energy Conversion Strategic Research Cluster,
UCD School of Chemical and Bioprocess Engineering,
University College Dublin, Belfield, Dublin 4, Ireland.

Ab-initio calculation and classical molecular dynamics simulations are carried out on three titanocene derivatives and TiO_2 (110) rutile surface to study the adsorption and conformational properties due to complex formation. The TiO_2 (110) surface, titanocene dyes and their complexes are studied using force field parameters derived from experimental reports, the GAFF forcefield and by utilizing quantum mechanical approaches. Here we have performed UV/Vis spectrum calculations for the titanocene dyes using B3LYP computation. Further, the adsorption of titanocene derivatives on TiO_2 (110) rutile surface has been studied using a QM approach employing pseudo potentials (PAW) with plane-wave periodic DFT. The Density of state (DOS) is also determined for surface and titanocene-surface complexes using the same periodic DFT approach.

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DENSITY FUNCTIONAL THEORY STUDIES OF DOPING IN BOTH BULK- AND SURFACE-STATE TIIANIA

Run Long and Niall J. English*
School of Chemical and Bioprocess Engineering,
University College Dublin, Ireland.

The structural, energetic and electronic properties of substitutional Ge, N/W, Bi/S (co)doped bulk anatase-titania systems have been investigated, along with those of a range of adsorptive and substitutional S- and P-doped rutile-titania (110) surfaces, by first- principles density functional theory (DFT) calculations. The stability of the various doping configurations was compared on the basis of their calculated formation/adsorption energies, and preferred dopant states were identified and characterised in terms of structural features. In many cases, red-shifts in optical absorption edge and reductions in photon transition energy were observed, along with synergistic effects between electronic states introduced by co-dopants. These observations have been used to rationalise various recent experimental observations under these dopant conditions.

CLASSICAL SIMULATION OF TiO_2-WATER INTERFACE

Ritwik S. Kavathekar*, Niall J. English, Damian A. Mooney, JMD MacElroy
SEC Strategic Research Cluster, School of Chemical and Bioprocess Engineering,
University College Dublin, Dublin, Ireland.

Titanium-dioxide (TiO_2) is a promising candidate for photo-electro-chemical (PEC) conversion of water into molecular hydrogen. Considerable work on band gap engineering of TiO_2 using dopinghas been done and the metal oxide-water interface probed by many experimental techniques. We discuss the nature/geometry of water at the titania-water interface, at different crystal faces, as seen by classical molecular modelling using the Matsui-Akaogi [1] force field and a flexible SPC [2] water model. MD runs show that water molecules in the vicinity of the interface are distinctly arranged, while the ordering is broken away from the surface. We find there is a shift of 5 to 8 deg of the H-O-H bond angle from the equilibrium bulk water value leading to compression of water at the first and second monolayers (ML). Similar deviations from the bulk water values are noted for O-H bond distances, dipoles and density. The relaxation time of the molecular dipole auto-correlation function, is large as compared to pure water. The angle the dipole vectors make with the surface normal is indicative of the orientation of the water molecules and is found to be very small for the nearest monolayers.

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AB INITIO AND ATOMISTIC SIMULATION OF CU DOPING IN THE LEAD-FREE FERROELECTRIC PEROVSKITE POTASSIUM SODIUM NIOBATE

Sabine Koerbel*, Pavel Marton, and Christian Elsaesser
Fraunhofer Institute for Mechanics of Materials IWM,
Woehlerstrasse 11, 79108 Freiburg, Germany.

Lead-free ferroelectric materials, one of them potassium sodium niobate (KNN) system, are currently considered as possible candidates that could replace lead zirconate titanate (PZT) in piezoelectric devices. Adding CuO during the fabrication process improves the sintering behaviour of the KNN ceramics, rising the question how copper doping influences the ferroelectric properties of KNN. We have applied density functional theory and empirical interatomic potentials to determine the preferred lattice site of Cu impurities in KNN for different thermodynamic conditions, the electronic defect structure, and the influence of the Cu impurities on the energy barriers associated with switching the ferroelectric polarisation.

SMALL POLARONS IN Nb- AND Ta-DOPED RUTILE AND ANATASE TIO2

Benjamin J. Morgan*, David O. Scanlon, Graeme, W. Watson
School of Chemistry,
Trinity College Dublin, Dublin 2, Ireland.

Experimental studies of thin-film Nb- and Ta-doped TiO_2 have reported that doped anatase is highly conductive, yet doped rutile is semiconducting [1-5]. Standard DFT functionals (LDA, GGA) predict that for doped anatase TiO_2 the excess charge occupies the bottom of the conduction band, and is delocalised over all the Ti atoms [6-9]. This has previously been proposed as the source of the experimentally observed high conductivity [6]. GGA predicts a similar metallic system for Nb-doped rutile, however, in contradiction with experimental data that characterise doped rutile as a semiconductor with a localised gap state [10]. This demonstrates that standard DFT functionals cannot explain the difference in experimental behaviour between polymorphs. Supplementing GGA with a +U on-site Coulomb correction recovers an electronic structure for Nb-doped rutile TiO_2 that is in agreement with the experimental data; a localised gap state is seen, corresponding to a small polaron on a single Ti site. GGA + U also predicts a small-polaronic Ti^{3+} gap state within a semiconducting system for Nb, Ta-doped anatase. On this basis we suggest the experimental variance between polymorphs in doped thin films is not an inherent property of the bulk crystals, but is due to other factors, e.g. additional defects or sample morphology, dependent on the synthesis history. For both anatase and rutile the defect feature is found to be insensitive to the identity of the dopant, and similar Ti^{3+} polarons are expected generally for doping where electrons are donated to the Ti lattice.

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FERROMAGNETISM IN ZnO INDUCED BY COMPLEX DEFECTS

Aurab Chakrabarty, Robert C. Barklie and Charles H. Patterson
School of Physics,
Trinity College Dublin, Dublin 2, Ireland.

Room temperature ferromagnetism (FM) in transition metal doped ZnO has been extensively investigated in past few years, yet the mechanism of ferromagnetic exchange remains controversial. Recent observations of FM in undoped oxide thin films and the apparent strong correlation between oxygen vacancies and FM motivated a model for the exchange mechanism based on a shallow spin-split donor level [1]. Here we present an alternative explanation for FM exchange coupling in ZnO with vacancy defects. The Hubbard model exhibits FM phases for certain fillings and for U/t ratios above a threshold value; predicted Curie temperatures can exceed 300K [3]. We therefore seek vacancy defects which have large Hubbard U parameters and can trap two electrons. Electron paramagnetic resonance (EPR) spectroscopy of ZnO powder heated in vacuum shows a very sharp resonance. It appears on heating and is reduced on exposure to air. It is attributed to trapped single electrons in void-like vacancies near surfaces of grains in the powder, which are formed by heating. Hybrid DFT calculations are performed on a range of void-like defects in order to identify defects which can trap one or two electrons. Transition metal ions doped in ZnO thin films enhance FM moment by short range s-d coupling with trapped electrons but are not essential for FM.

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RECONSTRUCTION OF THE POLAR ZnO(0001) SURFACE

Hakim Meskine* and Paul Mulheran
Department of Chemical Engineering,
University of Strathclyde, UK.

There has been renewed interest in recent years in the polar ZnO (0001) surface due in part to its technological applications, for example its use in multilayer optical coatings where it supports a thin Ag film. The long-standing controversy over the stabilization mechanism of this polar surface has recently been resolved in STM experiments [1], where equilateral triangular reconstructions with a wide range of sizes are clearly observed. DFT calculations [2] show that under these experimental UHV conditions, with low hydrogen and water availability in the gas phase, these reconstructions are indeed favoured over charge transfer from an unreconstructed bulk lattice termination. The surface-layer triangles are formed from single ZnO-bilayer steps terminated by oxygen, so the surface layer is non-stoichiometric with an excess of Zn over O vacancies. Electrostatic arguments show that an optimal excess of 0.25ML will (almost) completely remove the dipole moment normal to the surface, and that the organisation of vacancies into the regular triangles further reduces the electrostatic energy [2,3]. In this work we expand on this theme, and develop formal-charge atomistic models to capture these effects. This allows large system sizes and their evolution to be modelled. Using lattice-based Monte Carlo simulations, we show that a wide range of triangle sizes will evolve in the system in agreement with experimental observations. We further develop this model to include charge transfer so that the alternative stabilisation mechanisms can be assessed, and the growth of ad-layers modelled.

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SIMULATION OF the Oxygen K edge Resonant X-ray emission spectroscopy of rutile TITANIUM DIOXIDE

Cormac McGuinness*[1], Brian Kennedy[1], Declan Cockburn[1],
Brendan Arnold[1], Al Grogan[1], Tanel Kaambre[2,3], Russell G. Egdell[4]
and P. Blaha[5]
[1] School of Physics, Trinity College Dublin, Dublin 2, Ireland.
[2] MAXLAB, Lund University, P.O. Box 118, S-22100, Sweden.
[3] Institute of Physics, Tartu University,
Riga 142, EE-51014, Tartu, Estonia.
[4] Department of Chemistry, University of Oxford,
Oxford, OX1 3QR, UK.
[5] Technische Universitt Wien, Institut für Materialchemie,
Getreidemarkt 9, 1060 Vienna, Austria.

Resonant x-ray emission spectroscopy (RXES) is a sensitive element-specific and symmetry-selective probe of the occupied electronic bandstructure of a material, as illustrated in the example of graphite [1]. Momentum conservation in RXES results in the resonant spectra being k-selective measures of the occupied density of states arising from restricted portions of the Brillouin zone as determined by the unoccupied bandstructure. Further, the symmetry selectivity inherent in RXES (and resonant inelastic x-ray scattering) is a probe of the spatial symmetry of the local molecular orbital, i.e. σ and π bonding, where excitation to σ^* states leads to x-ray emission from states in a 90^o scattering geometry [2]. This can be exploited in the class of transition metal oxides with rutile-like tetragonal crystal structure. Rutile titanium dioxide is the prototype of this structure and though not a layered compound such as graphite, it exhibits planar coordination in the case of the oxygen anion which undergoes sp^2 hybridisation in Ti_3O [3]. X-ray absorption spectra at the oxygen K edge thus exhibits linear dichroism due to these Ti_3O planes all being parallel to the tetragonal c-axis. We present here measurements of the RXES spectra at the oxygen K edge, obtained in geometries where the exciting linearly polarised light is parallel to the c- or the a-axes and emission spectra are recorded outgoing along both the c- and a-axes for each initial orientation. Each RXES spectrum then reflects the projected oxygen 2p partial density of states arising from the orbital projections perpendicular to the direction of the outgoing emission, where the contributing parts of the valence band are determined by the k-points selected from the projection of the unoccupied bandstructure along the axis determined by the polarisation vector of the exciting synchrotron radiation. This geometry, symmetry selective, and polarisation dependent RXES can be modelled completely through density functional theory methods, here specifically through the Wien2k code [4]. Simulations of the RXES spectra take into account the occupied densities of states arising from the selection of appropriately weighted defined ranges of k-points arising from the polarisation, orbital projection, symmetry and the specific excitation energy used in the experiment. Excellent agreement is found between the simulated RXES spectra and the measured spectra obtained from a bulk single crystal of TiO_2. Measurements from nanostructured TiO_2 will also be presented.

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ENERGETICS OF AL DOPING AND INTRINSIC DEFECTS IN MONOCLINIC AND CUBIC ZIRCONIA: FIRST-PRINCIPLES CALCULATIONS

Cecilia Århammar*[1,2], C. Moyses Araujo[2] and Rajeev Ahuja[1,2]
[1] Applied Materials Physics,
Department of Materials and Engineering, Royal Institute of Technology (KTH),
S-100 44 Stockholm, Sweden.
[2] Condensed Matter Theory Group, Department of Physics and Materials Science,
Box 530, Uppsala University, S-751 21 Uppsala, Sweden.

In this work, we try to find ways of increasing the solubility of aluminum in zirconia by tuning parameters which can be calculated by first principles methods. These parameters are closely related to the variables of an experiment, such as the control of oxygen gas pressure in a Chemical Vapor Deposition (CVD) reactor or the choice of substrate or growth layer when a coating is deposited. For this, first-principles theory within the supercell approach has been employed to investigate Al doping and intrinsic defects in monoclinic and cubic zirconia. The effect of oxygen chemical potential and Fermi level on the formation energy and on the defect concentration have been taken into account. The formation of oxygen vacancies is found to be energetically more favorable in the cubic than in the monoclinic phase, under the same oxygen chemical potential and Fermi energy. In both phases, substitutional aluminum decays from the neutral charge state into the charge state -1, with the transition energy just above to the top of the valence band. Our findings indicate that by confining the Fermi energy to the region between the middle of the band gap and the bottom of the conduction band, high aluminum solubility could be achieved, although formation of aluminum is likely followed by the formation of interstitial oxygen. Furthermore, the concentration of aluminum with charge state -1, along with the equilibrium Fermi energy have been calculated in a self-consistent procedure. Here, the possible compensating defects with the relevant charge states have been considered. The obtained concentrations of aluminum and oxygen vacancies follow the experimental trend but underestimates experimental data. When the formation of defect clusters, composed by two substitutional aluminum and one oxygen vacancy, are considered, good quantitative agreement with experimental values of both aluminum and the oxygen vacancy concentration is achieved. The results suggest that, defect clusters will be formed as a result of Al doping in cubic phase of zirconia, whereas the concentration of defect clusters is negligible in the monoclinic phase, both in accordance with experiment.

A SELF-CONSISTENT FIRST-PRINCIPLES METHOD FOR COMPLEX DISORDERED MATERIALS

Alberto Marmodoro* and Julie B. Staunton
Department of Physics, University of Warwick,
CV4 7AL, Coventry, UK.

Realistic materials are always affected by some degree of symmetry-breaking disorder. The Coherent Potential Approximation (CPA) provides a general method to self-consistently determine an effective medium, where translational invariance is restored and first-principle calculations schemes can be deployed to describe averaged properties. Its main limitations emerge from a single site formalism. This has been generalised by the Dynamic Cluster Approximation (DCA) / Non-Local CPA (NLCPA) to account for short range ordering effects (SRO), and by the Multi Sublattice CPA (MSCPA) for materials with complex unit cells.Here we illustrate an unification of the two developments into a single scheme, which should provide all the flexibility required for describing compounds where both site-specificity and short-range ordering are important.The theory is illustrated through a simple tight-binding model for clarity. A rephrasing within a multiple scattering formalism is also offered.

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WATER GAS SHIFT REACTION ON A HIGHLY ACTIVE INVERSE $CeO_x/Cu(111)$ CATALYST: UNIQUE ROLE OF CERIA NANOPARTICLES

Jesus Graciani*[1,2], Jose A. Rodriguez[2], Jaime Evans[3], Fan Yang[2], Javier Fdez. Sanz[1]
[1] Department of Physical Chemistry, University of Seville, Profesor García González, 1. E-41012-Sevilla, Spain.
[2] Chemistry Department, Brookhaven National Laboratory, Upton, NY 11973, USA.
[3] Facultad de Ciencias, Universidad Central de Venezuela, Caracas 1020 A, Venezuela.

The water-gas shift (WGS, $CO + H_2O \rightarrow CO_2 + H_2$) is an important reaction frequently used in the chemical industry for the production of clean H_2. Oxide supported copper catalysts show significant water-gas shift activity but their performance is not fully understood and is highly dependent on the synthesis conditions or the nature of the oxide support. Either metallic Cu or Cu^{+1} cations have been proposed as active sites for the WGS. In addition, the oxide support may not be a simple spectator and may play a direct role in the catalytic process. Extended surfaces and nanoparticles of metallic copper are able to catalyze the WGS and Cu(111) has become a benchmark surface for studying the WGS. Specific rates, activation energies, and reaction orders are consistent with data reported for ZnO-supported Cu catalysts. The rate limiting step for the WGS on Cu(111) seems to be the dissociation of water, and it is affected by the presence of surface modifiers such as S, O or Cs.

In this article, we investigate the WGS reaction on Cu(111) surfaces partially covered with ceria nanoparticles experimentally and theoretically (DFT). Bulk ceria is a well known oxide support for WGS catalysts. The $CeO_x/Cu(111)$ system allows us to study in detail the role of the oxide in the catalytic process and, furthermore, catalysts with an inverse oxide/metal configuration have some advantages for practical applications.

$CeO_x/Cu(111)$ system illustrates the important role that an oxide can play in the water-gas shift reaction. When optimizing the performance of copper-based WGS catalysts, the major emphasis is usually in controlling the oxidation state and morphology of the copper within the catalytic system. The oxide is frequently seen as a simple support for copper or as a secondary player in the catalysis. This is certainly valid in the case of Cu/ZnO a common catalyst for industrial applications.

However, as a support for catalysts, ceria is more active than zinc oxide. A comparison of the WGS activities of CeOx/Cu(111) and $Cu/CeO_2(111)$ shows that an optimization of the physical and chemical properties of the oxide component is as important as the optimization of the properties for the metal component. The key to the high catalytic activity of $CeO_x/Cu(111)$ is in the nano size of the ceria particles and the effects of the metal oxide interface.

TRANSPARENT CONDUCTING OXIDES (TCO): TIN OXIDES AS A CASE STUDY

Anna Miglio, Martin Stankovski, Matteo Giantomassi, Xavier Gonze and Gian-Marco Rignanese
Uniti de Physico-Chimie et de Physique des Matiriaux (PCPM)
Universiti Catholique de Louvain, Belgium.

TCOs are a class of oxides with increasing importance in many technological applications like solar cells and flat panel displays. They are optically transparent, wide gap semiconductors or insulators which also display good electrical conductivity, due to doping or intrinsic defects. Among the TCOs most widely used, we have focused on tin oxides (SnO_2 and the less stable SnO) as a case study.In order to explore their electronic bulk properties, we first performed DFT ground state ab-initio calculations within a PAW implementation as well as standard norm conserving pseudopotential approach, employing both LDA and GGA exchange-correlation functionals. The Sn semi-core s, p and d states, relevant especially in SnO_2, are explicitly taken into account as valence states in the PAW atomic data sets. To improve the description of the band gap, we have subsequently applied one-shot GW corrections.

ORIGINATION OF FERROMAGNETISM IN MOLYBDENUM DIOXIDE (MoO2) FROM AB-INITIO CALCULATION

J. Nisar*[1], X. Peng[1] and R. Ahuja[1,2],
[1] Condensed Matter Theory Group, Department of Physics and Materials Science,
Box 530, Uppsala University, S-751 21 Uppsala, Sweden.
[2] Applied Materials Physics,
Department of Materials and Engineering,
Royal Institute of Technology (KTH),
S-100 44 Stockholm, Sweden.

We have performed spin polarized calculations of the unexpected ferromagnetism in ultrathin films of molybdenum dioxide (MoO_2) within the framework of density functional theory. It is found that the ideal bulk MoO_2 is metallic and non-magnetic. The defective bulk with Mo vacancy, O vacancy, Mo interstitial or O interstitial remains to be non-magnetic. Using slab model, we observed ferromagnetism in both oxygen rich and deficient MoO_2 (100) surfaces with average surface magnetic moment 1.53 and 0.69 μB per surface Mo atom, respectively. Partial density of states of surface Mo atom at Fermi level (EF) is much larger than that of the Mo atom in the center of the slab and in bulk Mo atom, which indicates that ferromagnetism in surface (100) is due to Stoner instability. Enrichment of oxygen at the surface is found to be more favorable for ferromagnetism in MoO_2 (100). The 2p-states of surface oxygen atoms are significantly hybridized with the 4d states of Mo atoms and are appreciably spin-polarized.

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SIMULTANEOUS MULTI-PARAMETER SCANNING PROBE MICROSCOPY OF TiO2(110)-(1X1)

Simon J. O'Brien *, H. Ozgur Ozer and John B. Pethica
Centre for Research on Nanostructures and Nanodevices (CRANN)
and School of Physics,
Trinity College Dublin, Ireland.

Scanning tunneling microscopy (STM) and atomic force microscopy (AFM) are widely used tools for surface science [1]. Their ability to provide direct real-space images of local surface structure is particularly useful for the study of atomic-scale defects and adsorbates [2]. Recently it has been shown that it is possible to chemically identify atomic species on a surface using a combination of atomic force spectroscopy and detailed atomistic modeling of the tip and surface [3]. This demonstrated the potential of the technique for providing atomic scale chemical information but also highlighted the one of the major challenges i.e. the influence of the tip. Providing complimentary information using the same tip would help narrow down the number of possible tip models [4]. Now, using a novel low-amplitude off-resonance technique, we can obtain simultaneous quantitative STM and force gradient information using the same tip [5]. We can also extend this to include images of the variation in the local apparent barrier height as well as dissipation. We have applied this technique to the study of the TiO_2(110)-(1x1) surface. Our images show inversions of contrast in STM imaging with atomic scale defects appearing as either depressions or protrusions depending on the tip. This would indicate that the bridging O rows can also be imaged rather than simply the Ti rows as is often stated in the literature. In images of force gradient and barrier height the contrast appears much less sensitive to tip changes with defects generally appearing less attractive in force gradient and as areas of lowered apparent barrier height.

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COMPETING MECHANISMS IN ATOMIC LAYER DEPOSITION OF La2O3 VERSUS Er2O3 CYCLOPENTADIENYL PRECURSORS

Michael Nolan* and Simon D. Elliott
Tyndall National Institute,
Lee Maltings, Prospect Row, Cork.
michael.nolan@tyndall.ie

Thin films of rare earth metal oxides are interesting materials for many technology applications, which require a method for controlled growth of such films. If suitable precursors are available, atomic layer deposition (ALD) is the method of choice for nanoscale thin film deposition. One of our goals is the rational design of ALD precursors. Of the many desirable properties of an ALD precursor, reactivity with respect to ligand elimination is important for the efficiency and rate of the growth process. We therefore formulate a model reaction for ligand elimination, which allows us to use cheap quantum chemical calculations to carry out in silico screening of many different metal-ligand combinations. Here, we present results on potential lanthanum precursors with ligands such as alkoxides, amides, cyclopentadienyls and -diketonates. Cyclopentadienyls are found to strike a good balance between reactivity on the surface, volatility and stability against auto-decomposition. Despite cyclopentadienyl-based showing great promise, little is known about the reactions that take place during growth. We present the results of first principles periodic density functional theory (DFT) computations of key reactions in ALD growth of La_2O_3 and Er_2O_3. We study the (001) surface of the hexagonal phase of each oxide, and start with the precursor adsorbed at a hydroxylated surface. We analyse the interaction of the precursor molecule with the oxide surface, the energetics of successive ligand eliminations and the resulting surface structures to predict the most stable adsorbate once the metal precursor pulse is finished. We find contrasting behaviour for each oxide. On La_2O_3, transfer of hydrogen from the surface to a C_p ligand has a barrier of 0.8 eV, whereas on Er_2O_3 hydrogen transfer proceeds spontaneously. On La_2O_3, non-ALD desorption of precursor fragments is favoured, but on Er_2O_3, reactive adsorption is thermodynamically favoured over desorption. We thus predict that ligand elimination is significantly more favourable on surfaces of Er_2O_3 relative to La_2O_3, and so that Er_2O_3 ALD is a better process. These studies provide new insights into the key reactions occurring during ALD of rare earth oxides and new understanding of experimental findings that better quality films can be grown using C_p precursors of later rare earths, but not of early rare earths.

THE ROLE OF THE SUBSTRATE SURFACE ON THE ATOMIC LAYER DEPOSITION OF ALUMINA ON SILICON NITRIDE

Maria-Elena Grillo*[1], Simon Elliott[1], Claudia Wiemer[2], Luca Lamagna[2], Sabina Spiga[2]
[1] Tyndall National Institute,
Lee Maltings, Prospect Row, Cork, Ireland.
[2] CNR-INFM MDM National Laboratory,
Via C. Olivetti 2, 20041 Agrate Brianza, Italy.
maria.grillo@tyndall.ie

The need to improve performance and scaling of the floating-gate NAND Flash technology, a TANOS stack comprising TaN metal gate, Al_2O3 top dielectric, Si_3N_4 trapping layer, and SiO_2 bottom oxide, has been proposed. One of the key issues of integrating materials in the stack is achieving a good electrical passivation of their interface. Therefore, we investigate the effect of the surfaces of silicon oxide (SiO_2), oxynitride (Si_2N_2O), and of silicon nitride (Si_3N_4) substrates on the initial growth rates on the atomic layer deposition (ALD) of Al_2O_3 for the trimethylaluminium (TMA)/H_2O and ozone (O_3) processes at different temperatures within the framework of the GOSSAMER project [1]. The growth of Al_2O_3 has been investigated in the early stages of the ALD process by in-situ Spectroscopic Ellipsometry (SE) in order to evaluate the growth rate of the first few oxide monolayers. Moreover, thickness, normalized growth rates and electronic density values have been extracted with ex-situ SE and X-ray Reflectometry (XRR), and then compared with density functional theory calculations (DFT). At low temperatures, the initial growth rate is larger for oxides grown using the water process. In contrast, at high temperatures, the growth rate is independent of the substrate. This is explained in terms of the hydroxylation extent of the exposed surface similarly to that found for the growth of HfO_2 films using $HfCl_4/H_2O_2$. The degree of surface hydroxylation is determined from the calculated temperature (T) dependence of the H_2O coverage for the studied surfaces. Evaluation of the surface energies of the wet oxides and of Si_3N_4 (0001) surfaces yields the thermodynamically preferred H_2O depending on the H_2O partial pressure and T. The obtained H_2O is in good agreement with the slow desorption of H_2O during the purge, as inferred from rate studies [3]. The adsorption of water is dissociative on all the studied substrates. On Si_3N_4, the surface hydroxyls (OH) adsorb on silicon dangling bonds, and the H-atoms on twofold coordinated nitrogen sites. On the oxides, the water dissociation products OH and H bind on the threefold coordinated Si- and surface oxygen atoms, respectively. The rate estimates of Al_2O_3 growth per cycle using the theoretically determined H_2O agree well with those estimated using experimental values [4].

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CORRELATION EFFECTS IN P-ELECTRON MAGNETS: THE CASE OF RBO2

Roman Kovacik* and Claude Ederer
School of Physics,
Trinity College Dublin, Ireland.

The development of spintronics in the recent years has triggered a need for new materials such as half metallic ferromagnets. Half-metals with 2p-magnetism were proposed from electronic structure calculations, e.g. Rb_4O_6 [1]. However, recent measurements indicate that Rb_4O_6 is a magnetically frustrated system that exhibits spin-glass-like behavior in a magnetic field [2]. The discrepancy between theory and experiment was attributed to inadequate treatment of the molecular states within the local spin density approximation (LSDA). This assumption was supported by LSDA calculations for rubidium superoxide (RbO_2), experimentally known to be an insulating antiferromagnet, which turns out to be half-metallic in LSDA as well. According to [2], this outcome could not be corrected within LDA+U even for values of U as large as 13.6 eV. Our results of GGA+U calculations for the RbO_2 show that, when allowing the system to reduce its symmetry, on-site interactions on the oxygen sites lead to a strong tendency towards the formation of an orbitally polarized insulating state for U greater than 2 eV, in contrast to the half-metallic behavior predicted for this class of compounds within pure LDA/GGA. The obtained energy differences between different orbitally ordered configurations are sizeable, indicating an orbital ordering temperature higher than the antiferromagnetic Neel temperature of 15 K. Our results demonstrate the importance of correlation effects in p-electron magnets such as RbO_2, which can serve as an important benchmark system to study correlation effects in a "clean" system where unoccupied p-states are not defect-induced. Furthermore, we discuss the effect of orbital correlations in RbO_2, using an effective tight-binding model corresponding to a molecular orbital basis, which is constructed via maximally localized Wannier functions [3]. The basis-set dependence of U is analyzed, and the effect of the Hartree interaction on the orbital ordering is highlighted.

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ELECTRONIC STRUCTURE OF STRIPED PHASE OF $Ca_{1.875}Na_{0.125}CuO_2Cl_2$

C. H. Patterson*
School of Physics,
Trinity College Dublin, Dublin2, Ireland.

Stripes are modulations of charge and spin density and are commonly seen in doped magnetic oxides on a length scale of several lattice constants. They are mostly commensurate with the crystal lattice. They occur in cuprates [1], nickelates, manganites [2,3], etc. and have been observed by a range of experimental probes including electron microscopy, neutron scattering, x-ray diffraction and scanning tunneling microscopy (STM). The phenomenon of stripe formation may be caused by localisation and ordering of holes, which have been introduced by doping. It may be associated with significant lattice distortion and spin reordering, compared to undoped parent compounds. We present hybrid DFT calculations on stripe formation in hole doped $Ca_2CuO_2Cl_2$ (CCOC) [4]. Stripes have been extensively studied by STM in sodium-doped CCOC with hole concentrations, x, in the range x = 0.05 to x = 0.15 per Cu ion [1]. Similar stripes are observed in several other cuprates in the same hole concentration range. CCOC is chosen for study as it cleaves easily to expose layers of Cl ions. Around x = 0.125, when there is one hole per eight Cu ions, 1-D stripes are observed with a spacing of four lattice constants. STM imaging in constant current (topographic) mode allows positions of Cl ions (and Cu ions directly beneath) to be observed. Stripes were then imaged in scanning tunneling conductance mode, which reveals that stripes are centred on O ions in rows running perpendicular to the stripe direction, i.e. they are bond centred stripes (on O ions) rather than site centred (on Cu ions). O ions between transition metal ions with a magnetic moment commonly induce anti-ferromagnetic coupling between the metal ion magnetic moments, a phenomenon known as super-exchange. However, when a hole is localized on the O ion between two transition metal magnetic moments, it induces ferromagnetic coupling between the metal ion magnetic moments by a double-exchange mechanism. We propose a magnetic order for Cu ion spins and hole localisation on O ions in the CuO_2 layers of CCOC with x = 0.125. Holes are localised in rows on O ions, separated by four lattice constants; each pair of Cu magnetic moments on either side of an O ion with a localized hole are parallel and each pair of Cu magnetic moments on either side of an ordinary O ion are anti-parallel, satisfying the rules for super- and double-exchange.

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ATOMIC SCALE MODELLING OF DEPOSITION PROCESSES FOR HIGH-K DIELECTRICS

Mahdi Shirazi*, Sylwia Klejna and Simon D. Elliott
Tyndall National Institute,
Lee Maltings, Prospect Row, Cork, Ireland.
simon.elliott@tyndall.ie

Atomic layer deposition (ALD) is a technique for growing thin films of a material from precursor chemicals. An optimum ALD process can coat any nanostructure with unrivalled control of stoichiometry and thickness. For these reasons, ALD is now used in semiconductor fabrication lines to deposit nanometre-thin oxide films, and has thus enabled the introduction of HfO_2-based high-permittivity dielectrics into the CMOS gate stack. ALD is thus set to be one of the leading techniques for industrially-scalable nanomanufacturing. Because of this, the field is undergoing rapid expansion and there is a proliferation of new precursor chemicals and growth processes, supposedl achieving ALD in new materials systems. However, the basic growth reactions have been properly characterised for only a few processes to date, via careful in situ experiments and ab initio theory. Of the many open questions that remain, we are addressing some in the FORME cluster by using atomic scale modelling, in collaboration with in situ XPS and FTIR applied to ALD experiments. Incubation periods are frequently observed when depositing oxides onto semiconductor substrates, but there is little control of these early cycles of growth. With interest increasing in transistors based on high mobility substrates, such as GaAs, we are investigating the surface reactions that are responsible, with a view to proposing surface treatments that may improve the interface characteristics. As a first example, we are modelling the cleanup effect, by which trimethylaluminium cleans arsenic oxides off the GaAs surface before ALD growth of Al_2O_3 commences. Our primary tool is first principles Density Functional Theory (DFT), but we are also developing a tool for multi-scale simulation of the growth process. There is a lack of understanding of how the ALD mechanism affects the microstructure of the film. Growth reactions are comparatively rare events, and so Kinetic Monte Carlo (KMC) is an appropriate simulation tool, enabling us to go beyond a separate study of each microscopic event and to extrapolate to the growth of films on long time-scales (100 s) and length-scales (100 nm). KMC depends on a good description of the reaction intermediates, pathways and energetics. As the first step therefore, we model surface reactions such as precursor adsorption and proton diffusion, determining the free energies via ab initio thermodynamics. Here, we present the results of such reaction modelling for $Hf(NMe_2)_4 + H_2O$ on a slab of monoclinic HfO_2 (100) by plane wave DFT (VASP code), which is a suitable model for the chemical reactions of the precursor at the growing surface. This work is supported by the SFI-funded strategic research cluster Functional Oxides and Related Materials for Electronics (FORME).

TCOs IN THE UV: A FIRST-PRINCIPLES INVESTIGATION OF InOOH, $In(OH)_3$, ZnO_2, $Zn(OH)_2$, CdO_2, $Cd(OH)_2$

Manuel Perez Jigato*
KU Leuven,
IKS, Celestijnenlaan 200D, 3000-Leuven, Belgium.

Peroxides, hydroxides, and oxyhydroxides are routinely used as precursors in the preparation of conventional n-type transparent conducting oxides ($Sn{:}In_2O_3$, $F{:}SnO_2$, Al:ZnO) [1]. On the other hand, there exist experimental measurements suggesting that the precursors themselves have optical gaps in the UV region of the spectrum [2], but very few reports exist in the literature regarding the electronic structure of this type of compounds [3]. Furthermore, in contrast to more conventional ZnO, In_2O_3, CdO, different intrinsic defect phenomena could be expected from the presence of peroxide ions $(O_2)^{2-}$, or from the presence of OH groups - with or without hydrogen bonds [4]. First-principles calculations are presented on a series of compounds, ie, InOOH, $In(OH)_3$, ZnO_2, $Zn(OH)_2$, CdO_2, $Cd(OH)_2$ in order to determine their possible role as n-type transparent-conducting oxides. Band structures are discussed in order to determine their semiconducting character. The planewave-pseudopotential methods, as implemented in ABINIT [5] is being used for LDA calculations of the compound series. Norm-conserving pseudopotentials of the HGH type [6] are used. Since GW band structure calculations are to be carried out and, in relation to the presence of d-electrons, the full shell semi-core electrons are present in the pseudopotential [7]. Future work on dielectric and optical properties of the basis compounds, on intrinsic defect formation and on carrier introduction and will be discussed.

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DEFECTS AND DIFFUSION IN Cr2O3: A DFT+U STUDY

F. Lebreau*, Mazharul M Islam , B. Diawara, P. Marcus
Laboratoire de Physico-Chimie des Surfaces,
CNRS-ENSCP (UMR No. 7045), Universiti Pierre et Marie Curie,
11 rue Pierre et Marie Curie, 75231 Paris Cedex 05, France.

Chromia protective layers are formed on many industrial alloys to prevent corrosion by oxidation. The role of such layers is to limit the inward diffusion of oxygen and the outward diffusion of cations. As a consequence, it is very important to study the growth mechanism of Cr_2O_3 scales. The experimental investigations suggest that Cr_2O_3 scale growth is controlled by diffusion of elements (cations and anions). However, the ionic transport inside such material is disputed due to its strong dependence on the synthesis conditions. In this study, different types of point defects, ranging from chromium defects (interstitial or vacancy) to oxygen vacancy, are investigated theoretically with periodic quantum-chemical calculations. Diffusions of Cr and O are studied in the bulk Cr_2O_3. Bulk Cr_2O_3 is an antiferromagnetic insulator with calculated band gap (Eg) 2.8 eV (exp Eg = 3.4 eV). The optimized bulk lattice vectors are calculated to be a = 5.07 and c = 13.85 , very close to experimental values, a = 4.95 and c = 13.57 . Experimental investigation suggests that the predominant defects in Cr_2O_3 are single vacancies as cationic or anionic. The structural, energetic, electronic and magnetic properties inside defective supercells are investigated. Here we have calculated vacancy formation energy (E) for both defect types by employing supercells with increasing size. It is observed that defect formation energy is converged for a supercell with 2x2x1 dimensions. Relative stabilities of such defects are in concordance with experiments: n-conductor Cr_2O_3 contains oxygen vacancies and chromium interstitials, and p-conductor Cr_2O_3 normally contains chromium vacancies. Magnetic properties show a compensation of the lost charge removed by the creation of a vacancy, inducing a polaronic distortion. The diffusions of Cr and O are investigated via Cr and O vacancy respectively using climbing NEB calculations. For Cr diffusion, two possible migration paths are investigated. The first type is the migration of Cr through the vertex of coordination polyhedra which occurs on same Cr bi-layer. The second type consists of the migration of Cr through the facet of coordination polyhedra. The smallest activation energy EM (2.57 eV) was obtained for the migration of second type, which is in good agreement with the experimental EM (2.46 eV). Two possible pathways are also observed for the migration of oxygen. The first type consists of the migration of oxygen in the vacancy plane and the second type of oxygen migration occurs through an unoccupied octahedral (Cr) site. The calculated EM ranges from 2.50 eV to 3.4 eV, which is in agreement with experiment.

ELECTRONIC STRUCTURE OF AMORPHOUS SILICA USING EXTRAPOLAR METHOD AND PAW FORMALISM

David Waroquiers[1,2], Xavier Gonze[1,2], Gian-Marco Rignanese[1,2] and Matteo Giantomassi[1,2]
[1] Unité de Physico-Chimie et de Physique des Matériaux (PCPM),
Universite-Catholique de Louvain,
B-1348 Louvain-la-Neuve, Belgium.
[2] European Theoretical Spectroscopy Facility (ETSF).

Amorphous silica is of particular technology interest for its electronic and optical properties. It is commonly used in a lot of devices such as optical fibers, lenses, filters, gate dielectrics in MOS transistors, ... The electronic and optical properties can be computed within density functional theory combined with many-body pertubation theory (GW approximation and BS equation). In the present work, we investigate the electronic structure and in particular the bandgap of amorphous silica. With the version 6 of ABINIT (using the latest developments: band-FFT parallelism, extrapolar method to reduce the number of empty states needed in GW calculations and PAW formalism), it is possible to study the electronic properties of supercells with more than 50 atoms per unit cell with a reasonable amount of CPU time in the GW framework. We report the results obtained for several 72-atom cells with slightly varying structural arrangements. For each model, the atomic positions have been fully relaxed using a fixed density (constrained volume).

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DEFECT STATES IN TITANIUM DIOXIDE

Jess Stausholm-Møller*[1], Berit Hinnemann[2], Georg K.H. Madsen[2], Bjørk Hammer[1]
[1] Interdisciplinary Nanoscience Center (iNANO),
The Faculty of Science, Aarhus University, Denmark.
[2] Haldor Topsoe A/S, Nymoellevej 55, 2800 Kgs. Lyngby Denmark.

Experimental studies of Rutile Titania reveal defect states lying about 0.85 eV below the conduction band, which has been assigned to Ti 3d states. In it's stoichiometric form, Titania is a wide band gap semiconductor with an indirect band gap of 3.0 eV and is thus mostly considered inert. But Titania has proven to be of great technological interest, as it has found its way into a wide range of areas, spanning from photonics and catalysis to white pigments in paint and cosmetics. In order to improve Titania based technologies, an understanding of the electronic properties (and thus also electronic defect states) is absolutely essential. From a theoretical point of view this poses a great challenge as the strongly correlated nature of Titania, and other transition metal oxides, is something which Density Functional Theory (DFT) noticeably fails to describe correctly. In light of this failure it is generally accepted that one needs to go beyond standard DFT in order to better describe this kind of strongly correlated systems. We present a DFT+U analysis of defects which may give rise to this observed defect state. All of the defects properly exist in bulk Rutile Titania to some degree. The DFT code used is the real space GPAW code in which we have implemented the rotational invariant representation of DFT+U, as it is proposed by Dudarev et. al. in their article from 1998. The motivation behind our work is twofold: One: We wish to prove our implementation of DFT+U in GPAW fully functional. Two: to study the nature of defect states originating from possible defects.

Ms Saurabh Agrawal
University College Dublin, Ireland
saurabh.agarwal@ucdconnect.ie

Mr Jeremy Allen
Trinity College Dublin, Ireland
allenje@tcd.ie

Ms Paola Alippi
CNR-ISM, Italy
paola.alippi@ism.cnr.it

Dr Emilie Amzallag
CNRS-Univ. Paris Sud 11, France
emilie.amzallag@u-psud.fr

Ms Cecilia Århammar
RIT, Stockholm, Sweden
arhammar@kth.se

Dr Corrine Arrouvel
University of Bath, UK
C.Arrouvel@bath.ac.uk

Dr Roger Bennett
University of Reading, UK
r.a.bennett@reading.ac.uk

Mr Mario Burbano
Trinity College Dublin, Ireland
burbanom@tcd.ie

Mr Aurab Chakrabarty
Trinity College Dublin, Ireland
chakraa@tcd.ie

Prof. Richard Catlow
University College London, UK
c.r.a.catlow@ucl.ac.uk

Prof. Alan Chadwick
University of Kent, UK
A.V.Chadwick@kent.ac.uk

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Mr Declan Cockburn
Trinity College Dublin, Ireland
cockburd@tcd.ie

Ms Dominique Costa
LPCS Chimie Paris Tech, France
dominique-costa@enscp.fr

Dr Soumendu Datta
Technical University of Denmark
sdatta@fysik.dtu.dk

Ms Hemant Dixit
University of Antwerp, Belgium
hemant.dixit@student.ua.ac.be

Mr Andrea Droghetti
Trinity College Dublin, Ireland
drogheta@tcd.ie

Dr Claude Ederer
Trinity College Dublin, Ireland
edererc@tcd.ie

Dr Simon Elliott
Tyndall National Institute, Ireland
simon.elliott@tyndall.ie

Dr Niall English
University College Dublin, Ireland
Niall.English@ucd.ie

Prof Vincenzo Fiorentini
Universita' di Cagliari, Italy
vincenzo.fiorentini@dsf.unica.it

Dr Daniel Fritsch
Trinity College Dublin, Ireland
fritschd@tcd.ie

Ms Natasha Galea
Trinity College Dublin, Ireland
galean@tcd.ie

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Dr Jose RB Gomes
University of Aveiro, Portugal
jrgomes@ua.pt

Dr Jesus Graciani
University of Seville, Spain
graciani@us.es

Ms Maria-Elena Grillo
Tyndall National Institute, Ireland
Maria.grillo@tyndall.ie

Mr Morad El-Hendawy
University College Dublin, Ireland
Morad.elhendawy@ucd.ie

Dr Mohammad Mazharul Islam
Université P. et M. Curie, France
rana-islam@enscp.fr

Prof. Francesc Illas
University of Barcelona, Spain
francesc.illas@ub.edu

Dr Satoshi Itoh
Toshiba R and D Center, Japan
satoshi.itoh@toshiba.co.jp

Prof. Hong Jiang
Peking University, China
h.jiang@pku.edu.cn

Dr Maneul Perez Jigato
KU Leuven, Belgium
manuel.perezjigato@fys.kuleuven.be

Mr Ritwik Kavathekar
University College Dublin, Ireland
ritwik.kavathekar@ucdconnect.ie

Mr Patrick Keating
Trinity College Dublin, Ireland
keatinpr@tcd.ie

.
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Mr Brian Kennedy
Trinity College Dublin, Ireland
bkennedy@tcd.ie

Ms Sylwia Klejna
Tyndall National Institute, Ireland
sylwia.klejna@gmail.com

Ms Sabine Koerbel
Fraunhofer IWM, Germany
sabine.koerbel@iwm.fraunhofer.de

Ms Kalle Korpela
Trinity College Dublin, Ireland
korpelak@tcd.ie

Dr Roman Kovacik
Trinity College Dublin, Ireland
kovacikr@tcd.ie

Prof. Georg Kresse
University of Vienna, Austria
Georg.kresse@univie.ac.at

Prof Joerg Libuda
University of Erlangen, Germany
Joerg.libuda@chemie.uni-relangen.de

Mr Francois Lebreau
ENSCP, France
francois-lebreau@enscp.fr

Prof. David Look
Wright State University, USA
David.Look@WPAFB.AF.MIL

Dr Marck Lumey
RWTH Aachen University, Germany
marck.lumey@ac.rwth-aachen.de

Mr Alberto Marmodoro
University of Warwick, UK
a.marmodoro@warwick.ac.uk

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Dr Cormac McGuinness
Trinity College Dublin, Ireland
Cormac.McGuinness@tcd.ie

Dr Keith McKenna
University College London, UK
k.mckenna@ucl.ac.uk

Dr Hakim Meskine
University of Strathclyde, UK
hakim.meskine@strath.ac.uk

Prof. Horia Metiu
Univ. California Santa Barbara, USA
metiu@chem.ucsb.edu

Ms Anna Miglio
Univ. Catholique de Louvain, Belgium
anna.miglio@uclouvain.be

Dr Benjamin Morgan
Trinity College Dublin, Ireland
benmorgan2@gmail.com

Dr Paul Mulheran
University of Strathclyde, UK
paul.mulheran@strath.ac.uk

Ms Jawad Nisar
Uppsala University, Sweden
jawad.nisar@fysik.uu.se

Dr Michael Nolan
Tyndall National Institute, Ireland
michael.nolan@tyndall.ie

Dr Gerard Novell-Leruth
Inst. Chem. Res. Catalonia, Spain
gnovell@iciq.es

Dr Simon O'Brien
Trinity College Dublin, Ireland
sjobrien@tcd.ie

.
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Ms Marita O'Sullivan
Trinity College Dublin, Ireland
osullim6@tcd.ie

Dr Charles Patterson
Trinity College Dublin, Ireland
Charles.Patterson@tcd.ie

Dr Chaitanya Das Pemmaraju
Trinity College Dublin, Ireland
pemmaras@tcd.ie

Prof Stefano Sanvito
Trinity College Dublin, Ireland
sanvitos@tcd.ie

Mr David Scanlon
Trinity College Dublin, Ireland
scanloda@tcd.ie

Mr Mahdi Shirazi
Tyndall National Institute, Ireland
mahdi.shirazi@tyndall.ie

Mr Jess Stausholm-Møller
Aarhus University, Denmark
jsm@phys.au.dk

Dr Robert Tétot
CNRS-Univ. Paris Sud 11, France
robert.tetot@u-psud.fr

Prof. Chris van de Walle
Univ. California Santa Barbara, USA
vandewalle@mrl.ucsb.edu

Dr Aron Walsh
University College London, UK
aronjwalsh@gmail.com

Mr David Waroquiers
Univ. Catholique de Louvain, Belgium
david.waroquiers@uclouvain.be

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Prof. Graeme Watson
Trinity College Dublin, Ireland
watsong@tcd.ie

Dr Urszula D. Wdowik
Pedagogical University, Cracow, Poland
sfwdowik@cyf-kr.edu.pl

Dr. Su-Huai Wei
NREL, USA
Suhuai.Wei@nrel.gov

Psi-k Network : Towards Atomistic Materials Design

Psi-k
Daresbury Science & Innovation Campus
Daresbury, Warrington
WA4 4AD
UK

Tel: +44 (0)1925 603227
Fax: +44 (0)1925 603634

PSI-K WORKSHOP FINANCE REPORT

Title of the Workshop	Computer Simulation of Oxides: Dopants, Defects and Surfaces
Workshop Organisers	Charles Patterson, Graeme Watson, Simon Elliott and Michael Nolan
Location of the Workshop	Trinity College Dublin, Ireland
Dates of the Workshop	9th to 11th September 2009
Total Grant from Psi-k	€2700.00

EXPENDITURE

WORKSHOP DELEGATES / SPEAKERS			
Name and Country of Claimant	**Travel**	**Accommodation**	**Total (€'s)**
R Catlow/UK	€133.00	€74.50	€207.50
A Chadwick/UK	105.49	298.00	403.49
F. Illas/Spain	120.00	298.00	418.00
H. Jiang/China*	375.00	372.50	747.50
J. Libuda/Germany	123.24	298.00	421.24
G. Kresse/Germany	250.28	149.00	399.28
D. Look/USA	700.00	372.50	1072.50
H. Metiu/USA	700.00	372.50	1072.50
S-H. Wei/USA	700.00	298.00	998.00
C van de Walle/USA	900.50	223.50	1124.00
M. Nolan/Ireland	53.40	0.00	53.40
C. Arhammer/Sweden	0.00	150.00	150.00
S. Elliott/Ireland	0.00	223.50	223.50
		Total Travel & Accommodation	**€7290.91**

*50% of 750.00 Euro travel cost shared with M. Scheffler, Berlin

WORKSHOP REFRESHMENTS / CONFERENCE DINNERS			
Date	**Tea / Coffee**	**Lunch / Dinner**	**Total (€'s)**
Coffee/biscuits in breaks	€386.52	€	€386.52
Reception at poster session	1573.04		1573.04
Subsidy to dinner	1537.85		1537.85
		Total Refreshments	**€3497.41**

MISCELLANEOUS EXPENDITURE	
Details	**Total (€'s)**
Poster Prize	€35.00
Folders/blutack	88.39
Total Miscellaneous	**€123.39**

Total Travel & Accommodation	**€7290.91**
Total Refreshments	**€3497.41**
Total Miscellaneous	**€123.39**

TOTAL EXPENDITURE	**€10911.71**