

O 81: Oxides and Insulator Surfaces I

Time: Thursday 10:30–13:30

Location: H4

Invited Talk

O 81.1 Thu 10:30 H4

Imaging orbitals and defects in superconducting FeSe/SrTiO₃ — ●JENNIFER HOFFMAN^{1,2}, DENNIS HUANG¹, TATIANA WEBB¹, SHIANG FENG¹, CAN-LI SONG^{1,3}, CUI-ZU CHANG⁴, JAGADEESH MOODERA⁴, and EFTHIMIOS KAXIRAS¹ — ¹Harvard University, Cambridge, MA, USA — ²University of British Columbia, Vancouver, Canada — ³Tsinghua University, Beijing, China — ⁴Massachusetts Institute of Technology, Cambridge, MA, USA

Single-layer FeSe grown epitaxially on SrTiO₃ has been shown to superconduct with T_c as high as 100 K, more than a factor of 10 higher than bulk FeSe. This dramatic enhancement motivates intense efforts to understand the superconducting mechanism and to design and fabricate devices. Nematic order, breaking the 4-fold rotational symmetry of the crystal, has been proposed as an important factor in the superconducting phase diagram. Meanwhile, atomic defects, which may pin nematic fluctuations or otherwise perturb superconductivity, can provide important clues into the superconducting mechanism as well as practical routes to superconducting devices. Here we use scanning tunneling microscopy (STM) to search for orbital nematicity in single-layer FeSe/SrTiO₃, and to investigate atomic-scale defects which locally influence superconductivity. From quasiparticle interference (QPI) images, we disentangle scattering intensities from the orthogonal Fe $3d_{xz}$ and $3d_{yz}$ bands, and quantitatively exclude pinned nematic orbital order with domain size larger than $\delta r \sim 20$ nm. Furthermore, we identify a prevalent “dumbbell”-shaped atomic-scale defect whose placement could be harnessed to define two-dimensional superconducting devices.

O 81.2 Thu 11:00 H4

Surface structure of Fe₃O₄(110) investigated by Scanning Tunneling Microscopy and Density Functional Theory. — ●BRIAN WALLS, OLAF LÜBBEN, and IGOR V. SHVETS — School of Physics and Centre for Research on Adaptive Nanostructures and Nanodevices (CRANN), Trinity College Dublin, Dublin 2, Ireland

We have performed a combined Scanning Tunneling Microscopy (STM) and Density Functional Theory (DFT) study of the (110) surface of single crystalline magnetite (Fe₃O₄). The (110)-terminated surface consists of two alternating planes, namely the A and B planes. Previous STM studies of the Fe₃O₄(110) surface have shown an A-plane terminated row reconstruction [1,2]. However, in this work STM measurements reveal not just the row reconstruction, but also an atomically flat surface structure which is present when the rows break. Interestingly, this flat structure lies just $\sim 3\text{\AA}$ below the adjacent rows.

DFT calculations were performed in order to gain an understanding of the flat structure. The calculations indicate that the presence of vacancies leads to an energetically favourable model and a good match between simulated STM images (Tersoff-Hamann scheme) and experimental images.

References:

1. R. Jansen *et al.*, *Surf. Sci.* **328**, 237-247 (1995).
2. G. Maris *et al.*, *Surf. Sci.* **600**, 5084-5091 (2006).

O 81.3 Thu 11:15 H4

Simulating atomic-scale phenomena on surfaces of unconventional superconductors — ●ANDREAS KREISEL¹, PEAYUSH CHOUBEY², TOM BERLIJN³, BRIAN ANDERSEN¹, and PETER HIRSCHFELD² — ¹Niels Bohr Institute, Denmark — ²Univ. of Florida, USA — ³CNMS & CSMD, Oak Ridge Nat. Lab., USA

Interest in atomic scale effects in superconductors has increased because of two general developments: First, the discovery of new materials as the cuprate superconductors, heavy fermion and Fe-based superconductors where the coherence length of the cooper pairs is as small to be comparable to the lattice constant, rendering small scale effects important. Second, the experimental ability to image sub-atomic features using scanning-tunneling microscopy which allows to unravel numerous physical properties of the homogeneous system such as the quasi particle excitation spectra or various types of competing order as well as properties of local disorder. On the theoretical side, the available methods are based on lattice models restricting the spatial resolution of such calculations. In the present project we combine lattice calculations using the Bogoliubov-de Gennes equations describing the superconductor with wave function information containing sub-atomic

resolution obtained from *ab initio* approaches. This allows us to calculate phenomena on surfaces of superconductors as directly measured in scanning tunneling experiments and therefore opens the possibility to identify underlying properties of these materials and explain observed features of disorder. It will be shown how this method applies to the cuprate material Bi₂Sr₂CaCu₂O₈ and a Fe based superconductor.

O 81.4 Thu 11:30 H4

Decomposition of the model perovskite SrTiO₃ under electrochemical stress — ●CHRISTIAN RODENBÜCHER, GUSTAV BIHLMAYER, PAUL MEUFFELS, RAINER WASER, and KRISTOF SZOT — Peter-Grünberg-Institut, Forschungszentrum Jülich, 52425 Jülich

Transition metal oxides are the key materials for future energy-efficient electronics in particular for logic and memory devices based on the resistive switching effect. Since the switching effect is related to a local reaction of the oxide to an external gradient of the electrical and chemical potential, we investigate the influence of electrochemical stress on the prototype perovskite SrTiO₃. We demonstrate that upon application of a DC voltage under UHV conditions, the surface region of alkaline earth titanates transforms into lower binary oxides with nanoporous structure. By means of IRT, XPS, EDX, HR-TEM, and LC-AFM we present that this transformation takes place at relatively low temperatures and is related to a fundamental macroscopic decomposition of the oxide changing the physical properties of the surface region up to depths of several tens of micrometers. Our results demonstrate that in ternary oxides phase transformations can be induced by gradients of the electrochemical potential using a technologically simple method, which not only opens up a new way for tailoring micro layers of functional transition metal oxides with bespoke properties for optical, electronic and chemical applications but also demonstrates the mutability of metal oxides under electrical stress being relevant for the understanding of the electroforming and switching process in novel memristive devices.

O 81.5 Thu 11:45 H4

Electronic structure of CeTiO₄ — ●LUKAS SOJKA¹ and DOMINIK LEGUT² — ¹FMMI, VSB-TU Ostrava, CZ 708 33 Ostrava, Czech Republic — ²IT4Innovations Center, VSB-TU Ostrava, CZ 708 33 Ostrava, Czech Republic

Cerium titanate structures offer broad range of technological applications because of their optical and catalytic properties. Cerium titanate can form various phases, which depend on the oxidation state of cerium. Using the first-principle calculations, we identified the ground-state structure of a new found phase, CeTiO₄. In analogy with LaTaO₄, the calculated enthalpy of formation indicates that the most stable structure is the monoclinic one over the orthorhombic structure, and its stability is by factor four higher than in LaTaO₄. Based on the calculated electronic structure we determined optical properties, mechanical properties (elastic constants) and thermodynamical properties of both structures of CeTiO₄. The results were obtained using single-electron framework of density functional theory calculations employing the VASP code. our results also indicate that cerium is in the oxidation state of Ce⁴⁺.

O 81.6 Thu 12:00 H4

DFT calculations of the electronic and atomic structure of metal-oxide nanowires formed on Ir(100) — FLORIAN MITTENDORFER¹, PASCAL FERSTL², MATTHIAS GUBO², KLAUS HEINZ², M.ALEXANDER SCHNEIDER², LUTZ HAMMER², and ●JOSEF REDINGER¹ — ¹Inst. of Applied Physics, TU Wien, Vienna, Austria — ²Lehrstuhl für Festkörperphysik, Univ. Erlangen-Nürnberg, Erlangen, Germany

Recently, a self-organized growth of quasi one-dimensional ordered cobalt oxide nanowires on the Ir(100) surface has been witnessed. By deposition of 1/3 ML Co in oxygen rich conditions nanowires of either CoO₂ or CoO₃ stoichiometry are formed, which bind via oxygen to the Ir substrate and leave the Co chains almost completely decoupled from the substrate. We report on DFT calculations for nanowires of CoO₂ and CoO₃ type as well as their Ni, Fe and Mn analogues. We find a very good agreement with experimental data concerning structural details and predict an electronic structure which is not strictly one-dimensional, despite the structural decoupling of the metal atoms

from the substrate. First results of collinear calculations indicate a change of magnetism proceeding from nonmagnetic NiO₂, via ferromagnetic CoO₂ and FeO₂ to antiferromagnetic MnO₂.

O 81.7 Thu 12:15 H4

Two-Dimensional Iron Tungstate Honeycomb Layers on Pt(111) — ●SASCHA POMP¹, DAVID KUHNESS¹, GIOVANNI BARCARO², LUCA SEMENTA², ALESSANDRO FORTUNELLI², MARTIN STERRER¹, FALKO P. NETZER¹, and SVETLOZAR SURNEV¹ — ¹Institute of Physics, University of Graz, A-8010 Graz, Austria — ²CNR-ICCOM & IPCF, Consiglio Nazionale delle Ricerche, I-56124 Pisa, Italy

We report the first example of a 2D ternary oxide layer with a honeycomb geometry identified as FeWO₃, which has no bulk analogue. The 2D iron tungstate phase described here has been synthesized in UHV via a solid state reaction of (WO₃)₃ clusters with a FeO monolayer on a Pt(111) surface. It has been characterized by a variety of surface analytical techniques, involving x-ray photoelectron spectroscopy (XPS), scanning tunneling microscopy (STM), low-energy electron diffraction (LEED) and temperature programmed desorption (TPD), combined with density functional theory (DFT) calculations. Consistent with the experimental results, the DFT calculations show that the FeWO₃ layer consists of a mixed layer of Fe and W atoms, formally Fe²⁺ and W⁴⁺ species, sitting in fcc and hcp Pt hollow sites, respectively, and arranged in a (2x2) superstructure. This layer is terminated by oxygen atoms in Fe-W bridging positions, forming a buckled honeycomb lattice. In addition the DFT calculations predict that the 2D FeWO₃ layer exhibits ferromagnetic order with a Curie temperature of 95 K, as opposed to the antiferromagnetic behavior in the bulk FeWO₄ phase.

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In-situ electron microscopy studies of praseodymia on Ru(0001) — ●JON-OLAF KRISPONEIT¹, JAN HÖCKER¹, ANDREAS SCHÄFER², JULIAN CAMBEIS¹, ALEXEI ZAKHAROV², YURAN NIU², JENS FALTA¹, and JAN INGO FLEGE¹ — ¹University of Bremen, Bremen, Germany — ²Lund University, Lund, Sweden

Due to the multiple valence states of rare earth elements, their oxides (REOs) play an important role in catalysis applications. A prominent example is ceria, which is well known for its oxygen storage capacity. Grown as microparticles on Ru(0001), ceria shows an excellent crystalline quality and thermal stability, making it well suited for catalytic model studies. We extend these efforts to the less studied praseodymia, which exhibits an intriguingly complex phase diagram with many stable mixed-valence compounds between Pr₂O₃ and the fully-oxidized PrO₂. Furthermore, praseodymia shows the highest oxygen mobility among the REOs, rendering PrO_x/Ru(0001) an attractive inverse catalyst model system.

We have prepared ultra-thin films of PrO_x/Ru(0001) by reactive molecular beam epitaxy. Here, we present in-situ investigations on local morphology and structure by low energy electron microscopy and micro-illumination diffraction (LEEM/ μ -LEED), revealing the nucleation of triangular islands and the formation of rotational domains. Furthermore, we studied the local chemical composition by x-ray absorption spectroscopy in imaging mode (XAS-PEEM) and discuss post-oxidation and reduction processes as identified by x-ray photoelectron spectroscopy (XPS).

O 81.9 Thu 12:45 H4

Electronic structure of ultra-thin ZnO on Metal substrates — ●BJOERN BIENIEK¹, PATRICK RINKE², OLIVER T. HOFMANN³, and MATTHIAS SCHEFFLER¹ — ¹Fritz-Haber-Institut der MPG, Berlin, Germany — ²Aalto University, Helsinki, Finland — ³TU Graz, Austria

ZnO is a promising candidate for applications in opto-electronics. For a successful application stable *n*-type and *p*-type ZnO would be needed.

As for many wide band gap semi-conductors, *p*-type conductivity is difficult to achieve in ZnO. We propose ZnO ultra-thin films on metal substrates as model systems for investigating *p*-type conductivity in ZnO. In our investigation of the electronic structure of ultra-thin ZnO films (1 to 4 layers) on the (111) surfaces of Ag, Cu, Pd, Pt, Ni, and Rh by means of DFT with the PBE and HSE06 exchange-correlation functionals we find a novel mechanism to achieve *p*-type conductivity at the surfaces of ZnO thin films on metal substrates. This mechanism is based on the intrinsic polar nature of ZnO (000 $\bar{1}$) films. With increasing thickness the polar character of wurtzite ZnO emerges as the films structurally transform from α -BN to wurtzite. electrons are transferred from the Zn-terminated interface to adjacent layers. The resulting field shifts the electronic states upwards until the Fermi energy, provided by the metal, is reached and the film becomes effectively *p*-type doped at its surface by pinning the electronic states of the top most layer(s) at the Fermi level. The number of layers necessary to achieve effective *p*-type doping depends on the metallic substrate. We also discuss intrinsic defects in the ZnO films on metal substrates.

O 81.10 Thu 13:00 H4

Role of dopants on the performance of metal oxide surfaces for the water oxidation: a DFT+*U* approach — ●HAMIDREZA HAJIYANI and ROSSITZA PENTCHEVA — Fakultät für Physik and Center of Nanointegration (CENIDE), Universität Duisburg-Essen, 47057, Duisburg

Based on density functional theory calculations including an on-site Coulomb repulsion term, we explore the oxygen evolution reaction (OER) at transition metal oxide surfaces. We address strategies how to reduce the overpotential during OER as well as modification of the band edge positions through dopants. A systematic variation of dopands throughout the 3*d*, 4*d* and 5*d* series in α -Fe₂O₃ (0001) surface unravels trends concerning the role of *d*-band occupation and orbital polarization. Consistent with previous results, the overpotentials correlate with the binding energy of chemisorbed species within a volcano plot. The underlying mechanisms are discussed by monitoring changes of valence and spin state of the surface cations throughout the intermediate steps of OER. We further generalize our results to other oxide structures such as the spinel. Support by the DFG within priority program SPP1613, project PE883/9-2 and a computational grant at the Leibniz Rechenzentrum are gratefully acknowledged.

O 81.11 Thu 13:15 H4

DFT study of metallic adsorbates on bulk and thin films of Zirconia — ●WERNFRIED MAYR-SCHMÖLZER, FLORIAN MITTENDORFER, and JOSEF REDINGER — Inst. of Applied Physics, TU Wien, Vienna, Austria

Zirconia (ZrO₂) is a material with many interesting properties, making it useful for various technological applications, such as a solid electrolyte in solid-oxide fuel-cells or as an oxygen gas sensor. Therefore, a detailed understanding of adsorption and interface properties of Zirconia is very useful. We present results of DFT calculations for the adsorption of metal adatoms and clusters on bulk surfaces and on thin Zirconia films grown by oxidation of a Pt₃Zr substrate. The calculations were performed using the Vienna Ab-Initio Simulation Package (VASP) employing van-der-Waals density functionals. The bonding and adsorption mechanism was studied for various metal adatoms such as noble Au and Ag as well as reactive Ni and Pd. On bulk surfaces we only find a weak physisorption for noble Au and even weaker for Ag (\approx 0.5eV), while reactive Ni and Pd show significantly higher adsorption energies ($>$ 2.0 eV). On a thin supported ZrO₂ film a general increase of the adsorption energies by more than 0.5 eV is predicted, resulting a chemisorbed state for Ag, whereas Au remains more weakly bound. To investigate mobility and cluster formation of these noble adsorbates we report on the surface diffusion barriers for silver and gold where we find values below 0.5 eV. We also report on the interface energy of silver and gold films of varying thickness on the thin oxide film.