

O 66: Oxide Surfaces 2

Time: Thursday 10:30–13:00

Location: S053

Topical Talk

Charge-ordered states on incipient ferroelectric polar surfaces — ●CESARE FRANCHINI — University of Vienna — University of Bologna

The precise atomic-scale knowledge of surface properties is mandatory for interpreting experimental data, optimizing (photo)catalytic processes, or predicting novel electronic phases. This is particularly challenging for perovskite materials, which typically show a variety of surface structural reconstructions that prevent a generally valid and transferable understanding of surface properties. However, recent experiments have shown that a novel cleavage protocol based on controlled exploitation of ferroelectric instabilities can generate well-defined bulk-terminated (001) surfaces, paving the way for a precise characterization of the surface electronic structure. This talk shall report first principles electronic structure calculations on polar $\text{KTaO}_3(001)$, focusing on the dichotomy between charge localized/delocalized phases and their impact on surface reactivity. Our data, supported by experimental observations, show that polarity-induced uncompensated carriers in $\text{KTaO}_3(001)$ exhibit charge-order patterns rather than common 2DEGs, manifested by charge-density wave and (bi)polaron states. Eventually, the trapped charge suppresses ferroelectric surface distortions, resulting in a binary CO adsorption process.

[1] M. Setvin et al. *Science* **359**, 572 (2018). [2] M. Reticcioli et al., *Nat. Comm.* (2022). [3] Z. Wang et al., *Sc. Adv.* (2022).

O 66.2 Thu 11:00 S053

Surface phonons and their coupling to the 2D electron liquid at the CTO/STO surface — ●M. DÖTTLING¹, E. B. GUEDES^{2,3}, T. P. VAN WAAS^{4,2}, S. PONCE^{4,5}, M. CAPUTO^{3,6}, N. C. PLUMB², N. MARZARI⁵, C. BERTHOD⁷, M. RADOVIĆ², J. H. DIL^{3,2}, and K. ZAKERI¹ — ¹PHI, Karlsruhe Institute of Technology — ²PSD, PSI — ³IPHYS, EPF Lausanne — ⁴IMCN, UC Louvain — ⁵THEOS, EPF Lausanne — ⁶Eletra, Trieste — ⁷DQMP, University of Geneva

Motivated by the recent discovery of a 2D electron liquid (2DEL) formed at the surface of $\text{CaTiO}_3/\text{SrTiO}_3(001)$ heterostructure, we probed the phonon spectrum of the system by means of high-resolution electron energy-loss spectroscopy (HREELS). Our main aim was to address any possible interaction of 2DEL with phonons.

The HREELS measurements revealed the existence of the Fuchs-Kliwer (FK) phonon modes at the energies of 20, 60 and 93 meV. Interestingly, the Eliashberg-function $\alpha^2F(\omega)$ constructed based on the quasiparticle band dispersion, probed by angle-resolved photoemission experiments, exhibits peaks at energies of 20, 60 and 80 meV.

The apparent redshift of the highest energy peak in $\alpha^2F(\omega)$, compared to the 93 meV FK mode, can be attributed to the formation of band-gap states (BGS). Such states form upon photon irradiation at the same time as 2DEL is formed. This is shown by the simulated HREEL spectra including BGS. Our results demonstrate the importance of BGS and the necessity of their consideration in describing the properties of oxide heterostructures. Supported by DFG via Heisenberg Programme ZA 902/3-1, ZA 902/6-1 and ZA 902/5-1.

O 66.3 Thu 11:15 S053

Reversible switching of the 2D electron gas of $\text{SrTiO}_3(001)$ studied by HREELS — ●HANNES HERRMANN, FLORIAN SCHUMANN, and WOLF WIDDRA — Martin-Luther-Universität Halle-Wittenberg, Institute of Physics, 06120 Halle, Germany

The formation of a 2D electron gas (2DEG) gained high interest in surface science as it became accessible under oxygen-poor conditions at the TiO_2 -terminated $\text{SrTiO}_3(001)$ surface [1]. In this work, we follow the 2DEG formation by studying the SrTiO_3 surface plasmon polaritons (SPP) by high-resolution electron energy loss spectroscopy (HREELS). The coupling of the SPP to the 2DEG leads to an asymmetric SPP line shape with extreme broadening. This strong electron-phonon coupling allows to quantify the 2DEG charge carrier density and is used to follow the reversible formation of the 2DEG by heating in UHV/ O_2 atmosphere or by adsorbing molecular oxygen at 100 K. The dielectric response will be discussed in terms of a two-layer model with a surface 2DEG which is modelled using a Drude-like response with a strongly frequency-dependent electronic mobility.

[1] A. F. Santander-Syro, O. Copie, A. Barthelemy, and M. J. Rozenberg, *Nature* **469**, 189 (2011).

O 66.4 Thu 11:30 S053

Structure determination of a dodecagonal oxide quasicrystal — ●SEBASTIAN SCHENK¹, OLIVER KRAHN¹, HOLGER L. MEYERHEIM², MARC DE BOISSIEU³, STEFAN FÖRSTER¹, and WOLF WIDDRA¹ — ¹Institute of Physics, Martin-Luther-Universität Halle-Wittenberg, 06120 Halle, Germany — ²Max-Planck-Institut für Mikrostrukturphysik, 06120 Halle, Germany — ³Universite Grenoble Alpes, CNRS, SIMaP, St Martin d Heres, France

The dodecagonal symmetry and the general tiling motive of oxide quasicrystals (OQC) have been proven by electron diffraction (LEED) and scanning tunneling microscopy (STM) from their first observations [1,2]. However, the detailed atomic structure, which includes the decoration of individual tiling elements with metal and oxygen atoms, has been under debate for more than eight years.

In this talk we solve the atomic structure by combination of STM and surface x-ray diffraction (SXR) of a quasicrystal approximant, which is derived from an ultrathin layer of SrTiO_3 on $\text{Pt}(111)$. The derived structure model can be generalized for all related ternary oxide quasicrystals and their approximants. The measured diffraction intensities will be compared with calculated ones by lifting the atomic structure of the OQC into its four-dimensional periodic superlattice. These intensities will be compared to SXR data obtained in synchrotron measurements.

[1] S. Förster et. al., *Nature* **502**, 215 (2013).

[2] S. Schenk et. al., *J. Phys.: Condens. Matter* **29**, 134002 (2017).

O 66.5 Thu 11:45 S053

Structural analysis of complex 2D Sr-Ti-O/Pd(111) films. — ●MARTIN HALLER, SEBASTIAN SCHENK, STEFAN FÖRSTER, and WOLF WIDDRA — Martin-Luther-Universität Halle-Wittenberg, Institute of Physics, Von-Danckelmann-Platz 3, 06120 Halle, Germany

In 2013 the first 2D oxide quasicrystal (OQC) in thin $\text{Ba-Ti-O/Pt}(111)$ films with astonishing structural properties has been discovered [1]. It features a twelvefold rotational symmetry that is incompatible with lattice periodicity. Instead, it is described with a self-similar quasicrystalline structure that involves squares, triangles and rhombuses. In the wake of this discovery combinations of ternary oxide layers and different hexagonal substrates have been investigated to study the epitaxial preconditions for the formation of the OQC. In this contribution, we present a structural analysis for Sr-Ti-O on $\text{Pd}(111)$. Globally, as seen from LEED, it forms a periodic structure with unit cell parameters $a = 1.32$ nm, $b = 2.96$ nm and $\alpha = 93.43^\circ$. However, locally a second phase has been identified in atomically-resolved STM data with twelvefold symmetric FFT and long range coherence in the 2D auto-correlation image. The analysis of the tiling statistics reveals a triangle:square:rhomb ratio of 2.84:1:0.39 which deviates slightly from the ideal OQC's ratio of 2.73:1:0.37 [2]. The given structure is discussed in terms of a disordered OQC which is further supported by a 4D hyperspace analysis.

[1] S. Förster et al., *Nature* **502**, 215 (2013)

[2] S. Schenk et al., *J. Phys. Condens. Matter*, **29** (2017)

O 66.6 Thu 12:00 S053

Transformation from honeycomb binary oxide to quasicrystalline ternary oxide — ●LOI V. TRAN, STEFAN FÖRSTER, and WOLF WIDDRA — Institute of Physics, Martin-Luther-Universität Halle-Wittenberg, Halle, Germany

Oxide quasicrystals (OQCs) are examples of aperiodically-ordered 2D materials. They have been found for 2D layers derived from BaTiO_3 on $\text{Pt}(111)$ [1]. Their dodecagonal structure results from Ba decoration of a Ti_nO_n network where $n = 4$ (decorated with no Ba atom), 7 (decorated with one Ba atom) and 10 (decorated with two Ba and two additional O atoms). In contrast, periodic Ti_2O_3 honeycomb structures with Ti_6O_6 rings are well known in literature [2,3]. Here, we report on the transition of such honeycomb Ti_2O_3 structures to dodecagonal OQCs by adsorption of Ba and subsequent annealing. The structural transition is monitored with LEED and workfunction measurements. Upon room temperature Ba deposition, Ti_2O_3 honeycomb structure remains and Ti_6O_6 rings are decorated with Ba, reducing the workfunction from 5.12 to 2.97 eV. Annealing to 873 K in oxygen converts the honeycomb structure into a dodecagonal OQC, for which the workfunction increases to 3.85 eV. The workfunction changes as

sociated with the transformation will be discussed in context of the height differences of Ba ions above the surface and the resulting dipole strength.

O 66.7 Thu 12:15 S053

Barium decorated Ti_2O_3 monolayers: a case study for Pd(111) substrates — •FRIEDERIKE WÜHRL, SEBASTIAN SCHENK, OLIVER KRAHN, STEFAN FÖRSTER, and WOLF WIDDRA — Institute of Physics, Martin-Luther-Universität Halle-Wittenberg, 06120 Halle, Germany

Oxides at the two-dimensional limit show a high flexibility in their structural properties ranging from hexagonal honeycomb structures to dodecagonal oxide quasicrystals (OQC) [1]. Recent work based on STM, surface x-ray diffraction (SXRD) and DFT calculations confirmed a structure model for oxide quasicrystals that explains this extraordinary structure as an aperiodically ordered Ti_2O_3 network with rings of different sizes on the metal support Pt(111), in which the largest rings are decorated with Ba ions [2]. The Ba ions form a self-similar tiling, which can be described through triangles, squares and rhombuses. In this contribution we report on a sequence of long-range ordered structures observed in $\text{Ba}_x\text{Ti}_2\text{O}_{3+y}$ on Pd(111) that are closely related to the OQC. We present a series of structures ranging from a $\text{Ba}_{0.66}\text{Ti}_2\text{O}_3$ to a $\text{BaTi}_2\text{O}_{3.5}$ stoichiometry. By varying the Ba content, we observe a transition from a triangle-square tiling via triangle-square-rhombus tilings to one consisting of triangles and rhombuses only [3]. It will be discussed how the Ba density sets the ratio of four to seven to ten membered rings in the Ti_2O_3 backbone.

[1] S. Förster *et al.*, *Nature* **502**, 215 (2013).

[2] E. Cockayne *et al.*, *Phys. Rev. B* **93**, 020101(R) (2016).

[2] F. E. Wühl *et al.*, *Phys. Status Solidi B*, 2100389 (2021).

O 66.8 Thu 12:30 S053

The (2x1) reconstruction of calcite(104) — JONAS HEGGEMANN¹, YASHASVI RANAWAT², ONDŘEJ KREJČÍ², ADAM S. FOSTER², and •PHILIPP RAHE¹ — ¹Fachbereich Physik, Universität Osnabrück, BarbarasträÙe 7, 49076 Osnabrück, Germany — ²Department of Applied Physics, Aalto University, Helsinki FI-00076, Finland

Calcite is an abundant material in the Earth's crust, a central constituent of biominerals in living organisms [1], and currently investigated as a capture material for CO₂ [2]. Despite intensive studies,

however, there is still serious ambiguity regarding the properties of this surface due to conflictive conclusions for the so-called row-pairing [3] and (2x1) reconstruction [4].

Here, we use a combination of non-contact atomic force microscopy (NC-AFM) with CO-functionalized tips at 5K, density functional theory with state-of-the-art dispersion corrections, and NC-AFM image simulations to clarify the microscopic geometry of calcite(104). A (2x1) reconstruction and a glide plane symmetry is consistently found in the NC-AFM data and DFT results. Most importantly, we identify two different adsorption positions for CO molecules within the (2x1) unit cell. These findings are most critical for future studies where processes on calcite(104)-(2x1) are influenced by the surface geometry.

[1] L. Addadi, S. Weiner, *Angew. Chem. Int. Ed. Engl.* **31**, 153 (1992). [2] P. A. E. Pogge von Strandmann, *et al.*, *Nat. Commun.* **10**, 1983 (2019). [3] A. L. Rachlin, *et al.*, *Am. Mineral.* **77**, 904 (1992). [4] S. L. S. Stipp, *et al.*, *Geochim. Cosmochim. Acta* **58**, 3023 (1994).

O 66.9 Thu 12:45 S053

Growth of ultra thin Eu_xO_y films on Pt(001): A HREELS, XPS and LEED study — •ANNE OELSCHLÄGER, HANNES HERMANN, STEFAN FÖRSTER, and WOLF WIDDRA — Martin-Luther-Universität Halle-Wittenberg, Institut of Physics, 06120 Halle, Germany

The gradually decreasing ionic radii along the series of lanthanides allow an exceptional fine tuning of lattice parameters, which makes this material class interesting for applications in epitaxial growth. In this contribution we report on the growth of thin Eu_xO_y films on Pt(001) and characterize the thin film oxidation upon annealing in various environments.

A 0.8 nm thin Eu layer has been deposited onto Pt(001) at room temperature in UHV conditions at a background pressure below $3 \cdot 10^{-10}$ mbar. By monitoring the surface phonons with HREELS and the valence state of Eu with XPS a continuous oxidation of Eu at room temperature by water from the residual gas as well as by molecular oxygen is observed as a transition from metallic Eu to Eu_2O_3 . The transition to Eu^{3+} can be followed by increasing (decreasing) intensities for the surface phonon polariton at 364 cm^{-1} (525 cm^{-1}) in HREELS and the high binding energy component of the Eu3d core level at 1135 eV (1125 eV) in XPS. The long-range order starts to develop in the 0.8 nm thin layer upon annealing to 1000 K. LEED exhibits a complex twelve-fold diffraction pattern.