KFM 17: Focus Session: Surfaces and Interfaces of (Incipient) Ferroelectrics (joint session O/KFM)

Ferroelectricity is a property of materials that allows spontaneous, switchable electric polarization. Recently, many surface-related applications have been proposed where ferroelectric or incipient-ferroelectric materials exhibit superior properties. These include catalysis, electron-hole separation in light harvesting, unique electronic properties such as a negative capacitance in heterostructures of ferroelectric materials, to name just a few. While (incipient) ferroelectrics clearly perform well in the aforementioned applications, there is very limited fundamental understanding of the processes involved on the surfaces of these materials.

Organizers: Martin Setvin (Charles University, Prague), Chiara Gattinoni (London South Bank University), and Michele Reticcioli (University of Vienna)

Time: Wednesday 15:00–18:30 Location: H3

Topical Talk KFM 17.1 Wed 15:00 H3

In search of electrostatic happiness at surfaces — •Nicola Spaldin — Materials Theory, ETH Zurich

We review the concept of surface charge in ionic insulators, first, in the context of the polarization in ferroelectric materials (traditionally discussed in the ferroelectrics community) and, second, in the context of layers of charged ions (traditionally discussed in the surface science community). In both cases, the surface charge leads to an electrostatic instability if it is not compensated, which is usually detrimental for the development of electronic devices based on ferroelectrics, but favorable for applications such as catalysis where surface reactivity is desirable.

Using the prototypical multiferroic bismuth ferrite, BiFeO3, as an example, we show how the spontaneous ferroelectric polarization and the charged ionic layers can in fact combine to yield stable, uncharged "happy" (100) surface geometries. Switching the polarization causes these (100) surfaces considerable electrostatic distress, which must be compensated by the introduction of charged point defects or adsorbates. We demonstrate that the relative happiness or unhappiness of the surfaces enables a cycle of alternating charged then neutral adsorbates on polarization switching, which can be exploited for water remediation and water splitting.

We close with a proposal that these physics can induce polarization in thin films of certain usually non-polar materials, and give a recipe for determining likely candidates.

In collaboration with Chiara Gattinoni, Ipek Efe and Marta Rossell

Topical Talk KFM 17.2 Wed 15:30 H3

Synthesis and Characterisation of Ultra-thin Aurivillius Phase Multiferroics — •Lynette Keeney — Tyndall National Institute, University College Cork, Lee Maltings Complex, Dyke Parade, Cork, Ireland, T12 R5CP

Multiferroic materials, possessing simultaneous ferroelectric and ferromagnetic memory states, have been road-mapped as promising multistate architectures for memory scaling beyond current technologies. In recent years, my team reported the design of such a novel room temperature multiferroic material with an Aurivillius phase structure that could ideally be suited to future fabrication of revolutionary memory devices. Electrostatic strain and elastic energy variations close to defect regions increase the extent of magnetic partitioning and also influence the formation of exotic charged domain walls and polar vortices. This further initiates technology prospects in ultra-compact data storage, energy-efficient neuromorphic computing and ultrahigh speed data processing. As miniaturisation of electronic devices continues, a crucial requirement is the enhancement of their functional properties at very small dimensions. In this presentation, I will discuss how direct liquid injection chemical vapour deposition allows for frontier-development of ultra-thin films at fundamental thickness. Via a two-dimensional layer-by-layer growth mode, films equating to half of one unit-cell (2.5 nm) of the Aurivillius structure are grown. The persistence of stable ferroelectricity, even when pushed to ultra-thin thicknesses, demonstrates the recent progress in the optimisation of Aurivillius phase materials for utilisation in future miniaturised multiferroic-based devices.

KFM 17.3 Wed 16:00 H3

Influence of Nb dopants on the polarization and screening on cleaved $SrTiO_3$(001) surfaces — •Igor Sokolović[1], Alexander Hoheneder[1], Jesus Redondo[2], Dominik Wrana[2], Michael Schmid[1], Ulrike Diebold[1], and Martin Setvín[2] — [1]Institute of Applied Physics, TU Wien, Vienna, Austria — [2]Faculty of Physics and Mathematics, Charles University, Prague, Czech Republic

The incipient ferroelectric $SrTiO_3$ can turn ferroelectric even at room temperature under the application of strain, and this quantum phase transition can be utilized to cleave $SrTiO_3$ single crystals that otherwise posses no preferable cleavage planes [1]. This cleaving procedure creates truly bulk-terminated $SrTiO_3$(001) surfaces that come the closest to being pristine [2]. In this talk, I will present how the SrO- and TiO_2-terminated surface domains of opposite polarity can be influenced by the small changes in the amounts of Nb doping. The cleaved $SrTiO_3$(001) surfaces with varying Nb doping levels were systematically studied with atomic resolution using noncontact atomic force microscopy (ncAFM) and scanning tunneling microscopy (STM). It was observed that Nb doping does not affect the magnitude of the strain-induced polarization, yet still significantly affects the morphology, the electronic structure, and the domain-wall structure on cleaved $SrTiO_3$(001) surfaces. Beside demonstrating the interplay between the domain distribution and electrostatic screening, these results show how the properties of these heterogeneous surfaces can be tuned.

[1] Sokolović *et al.*, Phys. Rev. Mater. 3, 034407 (2019)
[2] Sokolović *et al.*, Phys. Rev. B 103, L241406 (2021).

KFM 17.4 Wed 16:15 H3

Polaronic Properties of the weakly-polar $SrTiO_3$(001) Surface — •Florian Ellinger[1], Michele Reticcioli[1], Igor Sokolović[2], Ulrike Diebold[2], Martin Setvín[3], and Cesare Franchini[1,4] — [1]University of Vienna — [2]Technische Universität Wien — [3]Charles University Prague — [4]Università di Bologna

The $SrTiO_3$(001) surface shows ferroelectric-like distortions on the bulk-like termination, an out-of-plane dipole moment, and so-called "weak polarity". Recent experiments propose that these effects are compensated by Sr-adatoms and -vacancies, stabilizing the unreconstructed surface. [1]

We investigate the 1×1 $SrTiO_3$(001) surface with TiO_2- and SrO-terminations by means of density functional theory (DFT) simulations. Our calculations confirm the experimental interpretation and show that these polarity-compensating surface defects introduce additional charge. Adsorbing Sr-adatoms and doping with Nb leads to excess electrons in the crystal, facilitating the formation of electron-polarons. On the other hand, by creating Sr-vacancies on the surface we introduce excess holes to the system, which can localize as hole-polarons. For both kinds of polarons we analyze their general properties, e.g., the preferred localization site or stability. Further, we compare results of different structural phases of this crystal to achieve a comprehensive understanding of mentioned physical phenomena.

[1] Sokolović et al., *Incipient ferroelectricity: A route towards bulk-terminated $SrTiO_3$*, Phys. Rev. Materials 3, 034407 (2019)

KFM 17.5 Wed 16:30 H3

Ferroelectric domain imaging in barium titanate using infrared-visible sum-frequency generation microscopy — •Dorothee Mader[1], Daniel Lourens[2], Maarten Kwaaitaal[2], Richarda Niemann[1], Sören Wasserroth[1], Sandy Gewinner[1], Marco De Pas[1], Wieland Schöllkopf[1], Martin Wolf[1], Andrei Kirilyuk[2], Sebastian F. Maehrlein[1], and Alexander Paarmann[1] — [1]Fritz Haber Institute of the Max Planck Society, Berlin, Germany — [2]Radboud Universiteit, Nijmegen, The Netherlands

Phonons exhibit a mostly unexplored leverage on the mechanisms and

dynamics of domain formation in ferroics. Here, a new method is employed combining resonant phonon excitation and ferroelectric domain imaging of barium titanate (BTO) using infrared-visible (IR-VIS) sum-frequency generation (SFG) microscopy [1]. BTO is a non-centrosymmetric perovskite oxide with a strong ferroelectric polarization in its tetragonal phase. Typically, BTO samples exhibit a multi-domain structure. In this contribution, SFG microscopy is shown to naturally provide domain contrast due to the polarization-induced local variation of the nonlinear susceptibility. Additionally, our spectral analysis of the SFG response reveals the domain-selective phonon resonances for all high-frequency phonons in the IR spectral range of 500-800 cm^{-1}. By locally mapping phonon resonances in domains and domain walls, this approach may enable in-depth understanding of the underlying physics of domain formation and its dynamics. [1] R. Niemann et al., Appl. Phys. Lett. 120, 131102 (2022).

Topical Talk KFM 17.6 Wed 16:45 H3

Water-oxidation catalysis on surfaces of ferroelectrics — •Ulrich Aschauer[1], Nathalie Vonrüti[1], Zhenyun Lan[2], Didrik R. Småbråten[1], Tejs Vegge[2], and Ivano E. Castelli[2] — [1]University of Bern, Bern, Switzerland — [2]Technical University of Denmark, Kgs. Lyngby, Denmark

Surfaces of ferroelectrics have unique properties for catalysis since the binding strength of reaction intermediates can be modulated by switching the ferroelectric polarization. This could allow to overcome the limitations of the Sabatier principle and enable dynamical catalysts operation. In this talk, we will focus on the interplay between screening charge transfer to surfaces, the adsorbate coverage and the (photo)electrochemical water-oxidation activity of ferroelectric surfaces. We will compare different ferroelectric materials such as $BaTiO_3$, strained $LaTiO_2N$ and the hexagonal improper ferroelectric oxynitride $InSnO_2N$. Our results indicate that ferroelectric switching can indeed provide an economically interesting route to enhance the catalytic activity but that material-specific intricacies of the surface adsorbate coverage need to be understood and controlled to exploit the full potential of ferroelectric switching in (photo)electrocatalysis.

KFM 17.7 Wed 17:15 H3

The polar $KTaO_3$ (001) surface: Electronic structure and CO adsorption — Zhichang Wang[1], Michele Reticcioli[2], Zdenek Jakub[1], Michael Schmid[1], Gareth Parkinson[1], Ulrike Diebold[1], Cesare Franchini[2], and •Martin Setvin[3] — [1]TU Wien, Vienna, Austria — [2]University of Vienna, Vienna, Austria — [3]Charles University, Prague, Czech Republic

Polar surfaces offer intriguing physical and chemical properties applicable in electronics or catalysis. Cleaving the $KTaO_3$ perovskite along its polar (001) plane provides a well-defined, bulk-terminated surface with KO and TaO_2 terminations [1]. As-cleaved surfaces exhibit a high concentration of in-gap states; these electrons predominantly reside at the TaO_2-terminated parts of the surface. These electrons can affect surface chemistry, as is demonstrated for CO molecules. CO has two adsorption configurations on the TaO_2 termination, and the CO differs in how it couples to the excess electrons. DFT calculations indicate that CO preferentially couples to electron bipolarons.

The work was supported by FWF project P32148-N36, by GACR 20-21727X and GAUK Primus/20/SCI/009.

[1] M. Setvin, M. Reticcioli, F. Poelzleitner et al., Science 359, 572 (2018)

KFM 17.8 Wed 17:30 H3

Polarons and ferroelectricity: tip-induced phenomena on oxide perovskite surfaces — •Dominik Wrana[1], Igor Sokolović[2], Jesus Redondo[1], Pavel Kocán[1], Aji Alexander[1], Llorenç Albons[1], and Martin Setvin[1] — [1]Department of Surface and Plasma Science, Charles University, Prague, Czech Republic — [2]Institute of Applied Physics, TU Wien, Vienna, Austria

In this talk, I will present the similarities and differences between two representative perovskite oxide surfaces: $KTaO_3$(001) and $BaTiO_3$(001), showcasing the manifestation of the (incipient-) ferroelectricity on the atomic and electronic structure. Both surfaces were prepared by cleaving single crystals in situ and characterized by means of qPlus nc-AFM at temperatures ranging from 4K to 100K.

Bulk-terminated $KTaO_3$(001) develops two alternating domains of KO and TaO_2 [1]. Excess electrons injected from the AFM tip form quasiparticles called polarons (charges coupled with lattice distortions) which can be further shaped into 1D or 2D structures by emerging electric fields.

Different mechanism applies in the case of $BaTiO_3$(001), where at low temperatures titanium atoms can easily break the symmetry causing a spontaneous polarization. Hence, a biased tip allows for reversible manipulation of individual atoms on the surface: writing and erasing polarized ferroelectric domains.

[1] Setvin, Martin, et al. Science 359.6375 (2018): 572-575

KFM 17.9 Wed 17:45 H3

Optimisation and miniaturisation of naturally-layered multiferroic thin films — •Lynette Keeney — Tyndall National Institute, University College Cork, Lee Maltings Complex, Dyke Parade, Cork, Ireland, T12 R5CP

Multiferroic materials, possessing simultaneous ferroelectric and ferromagnetic memory states, are road-mapped as promising multistate architectures for memory scaling beyond current technologies. In recent years, my team reported the design of such a novel room temperature multiferroic material with an Aurivillius phase structure that could ideally be suited to future fabrication of revolutionary memory devices. In this presentation, I will discuss how electrostatic strain and elastic energy variations close to bismuth oxide interfaces and defect regions are key to promoting magnetic cation partitioning and multiferroic behaviour. These also influence the formation of exotic charged domain walls and polar vortices, further initiating technology prospects in ultra-compact data storage. As miniaturisation of electronic devices continues, a crucial requirement is the enhancement of their functional properties at very small dimensions. Direct liquid injection chemical vapour deposition allows for frontier-development of ultra-thin films at fundamental thickness. Via a two-dimensional layer-by-layer growth mode, films equating to half of one unit-cell (2.5 nm) of the Aurivillius structure are grown. The persistence of stable ferroelectricity, even when pushed to ultra-thin thicknesses, demonstrates the recent progress in the optimisation of Aurivillius phase materials for utilisation in future miniaturised multiferroic-based devices.

Topical Talk KFM 17.10 Wed 18:00 H3

Spin-orbitronics and superconductivity in KTaO3 twodimensional electron gases — •Srijani Mallik[1], Gerbold Ménard[2], Guilhem Saiz[2], Hugo Witt[1,2], Sara Varotto[1], Luis M. Vicente-Arche[1], Julien Bréhin[1], Annika Johansson[3], Börge Göbel[4], Raphaël Salazar[5], Ingrid Mertig[4], Lara Benfatto[6], Nicolas Bergeal[2], and Manuel Bibes[1] — [1]Unité Mixte de Physique CNRS/Thales, Palaiseau, France — [2]LPEM ESCPI, Paris, France — [3]MPI, Halle, Germany — [4]Martin-Luther-Universitat Halle-Wittenberg, Germany — [5]Synchrotron SOLEIL, France — [6]Sapienza University of Rome, Italy

Similar to SrTiO3 (STO) recent research has shown that KTaO3 (KTO) may also harbor a 2DEG at interfaces with several oxide materials. Due to the presence of Ta (5d element), it is expected that the Rashba spin-orbit coupling in KTO 2DEGs should be larger than in STO 2DEGs. Further, (110) and (111)-oriented KTO 2DEG show superconductivity at temperature a factor of ca. 10 higher than in STO 2DEGs. In this talk we will show that 2DEGs can be generated by the simple deposition of Al metal on KTO single crystals. We will report their electronic band structure by angle-resolved photoemission spectroscopy, evidencing a peculiar Rashba splitting. We will show that this Rashba state can be harnessed to achieve very efficient spin-charge interconversion. Finally, we will present microwave impedance spectroscopy measurements of the superconducting condensate and discuss the nature of superconductivity in these systems.