KFM 2: Ferroelectric Domain Walls I (joint session KFM/TT)

Organizer: Sergey Artyukhin - Istituto Italiano di Tecnologia - Genova (Italy)

Time: Monday 9:30–12:45 Location: EMH 225

Invited Talk KFM 2.1 Mon 9:30 EMH 225

Atomic-resolution imaging of electronic inversion layers at ferroelectric domain walls — •Julia Mundy[1], J. Schaab[2], Y. Kumagai[2], A. Cano[3], M. Stengel[4,5], I. Kung[6], D. Gottlob[7], H. Doganay[7], M. Holtz[8], R. Held[8], Z. Yan[2,9], E. Bourret[9], C. Schneider[7], D. Schlom[8], D. Muller[8], R. Ramesh[9,10], N. Spaldin[2], and D. Meier[2,11] — [1]Harvard University — [2]ETH Zurich — [3]Université de Bordeaux, ICMCB — [4]ICREA Institució Catalana de Recerca i Estudis Avançat — [5]Institut de Ciència de Materials de Barcelona (ICMAB-CSIC), Campus UAB — [6]TU Berlin — [7]Forschungszentrum Julich — [8]Cornell University — [9]Lawrence Berkeley National Laboratory — [10]UC Berkeley — [11]Norwegian University of Science and Technology

Ferroelectric domain walls hold great promise as functional two-dimensional materials because of their unusual electronic properties. Particularly intriguing are the so-called charged walls where a polarity mismatch causes local, diverging electrostatic potentials requiring charge compensation and hence a change in the electronic structure. These walls can exhibit significantly enhanced conductivity and serve as a circuit path. Here we use atomic-resolution STEM-EELS to directly probe the charge transfer at these charged ferroelectric domain walls in $ErMnO_3$. Our direct quantification of the charge transfer to the domain boundary gives insight into the the formation and eventual activation of an inversion layer that acts as the channel for the charge transport. The findings provide new insight into the domain-wall physics in ferroelectrics.

KFM 2.2 Mon 10:00 EMH 225

Charged domain walls and point defect-DW interactions in hexagonal manganites — Didrik Rene Småbråten[1], Quitin Meier[2], Sandra Helen Skjaervoe[1], Thomas Tybell[1], Dennis Meier[1], and •Sverre Magnus Selbach[1] — [1]NTNU Norwegian University of Science and Technology, Trondheim, Norway — [2]Materials Theory, ETH Zurich, Zürich, Switzerland

Charged head-to-head and tail-to-tail ferroelectric domain walls (DW) in hexagonal manganites are stable because of the improper nature of the ferroelectricity in these materials, and it has been experimentally shown that their electronic properties can differ strongly from bulk. First principles studies of charged DWs are scarce and the inherent electrostatic fields make DFT calculations challenging. Here we combine density functional theory (DFT) calculations with a continuum model based on Landau theory to study the properties of charged DWs in $YMnO_3$, $InMnO_3$ and isostructural $YGaO_3$. We find excellent agreement between the micro- and macroscopic models, and show that the Mexican hat energy landscape of hexagonal maganites derived from Landau theory also emerges naturally from DFT calculations of their DWs. Head-to-head and tail-to-tail DW are structurally inequivalent due to the different local chemical bonding. We formulate a general criterion based on polarization and band gap for when charged DWs become conducting. Finally, we study interactions between DWs and oxygen interstitials and vacancies by DFT.

KFM 2.3 Mon 10:15 EMH 225

Local control of chemical structure in a functional oxide — •Donald M. Evans[1], Theodor S. Holstad[1], Aleksander B. Mosberg[2], Per-Erik Vullum[2], Didrik Småbråten[1], Sverre Selbach[1], Antonius T. J. Van Helvoort[2], and Dennis Meier[1] — [1]Department of Materials Science and Engineering, NTNU, Norway — [2]Department of Physics, NTNU, Norway

Since the suggestion to use ferroelectric domain walls (DWs) in nanoelectronics, there has been a great deal of research into their properties. The most obvious use of DWs with enhanced conductivity was as nano-wires. But more recently, research is moving towards using the DW as the functional element within a circuit, e.g. as a switch or diode. This approach could allow whole circuit elements to be replaced by a single sub nanometre wide object - an option with clear technological potential. Attractive as this concept is, the research is still in its embryonic stage with many unanswered questions, not least, how to connect these DW circuit elements. In this work, we demonstrate how an atomic force microscope (AFM) can be used to change the functional properties locally: that is, we can use an AFM to write conducting strips on demand with all the position and control associated with AFM techniques. This is demonstrated on a hexagonal manganite ($ErMnO_3$) and foreshadows the possibility to interconnect functional DWs into nanoscale circuits. To better understand this ability to locally control functional properties, these modified regions were analysed with both TEM, and EELS.

KFM 2.4 Mon 10:30 EMH 225

Anomalous domain wall motion in Cu-Cl boracite: negative permittivity in an improper ferroelectric? — •Charlotte Cochard[1], Joseph G.M. Guy[1], Michael P. Campbell[1], Roger W. Whatmore[2], Amit Kumar[1], Raymond G.P. McQuaid[1], and Marty Gregg[1] — [1]Queen's University Belfast, Belfast UK — [2]Imperial College London, London, UK

Negative capacitance has attracted a lot of attention recently thanks to its potential to enable shorter switching time of transistors. It has been observed in systems as diverse as p-n junction, electrochemical systems, and ferroelectrics. To date, no single-phase material has been reported to exhibit negative capacitance.

In this work, we show that regions in a boracite crystal ($Cu_3B_7O_{13}Cl$) exhibit anomalous electric-field-induced movement of charged domain walls, consistent with negative permittivity. Boracites naturally display domain wall configurations, seen to be electrically active by current mapping [1]. While applying an electric field across some of these charged walls, we observed that domains with polarisation components pointing opposite to the electric field grow at the expense of domains with polarisation components aligned with the field. Thus dP/dE is negative and hence permittivity is negative. This behaviour is proposed to originate from the improper ferroelectric nature of the boracite: the elastic energy payoff, due to polarisation-strain coupling, is greater than the work done in generating increased polarisation against the applied electric field.

[1] R.G.P. McQuaid, et al. Nat. Commun. 8, 15105 (2017).

15 min break

KFM 2.5 Mon 11:00 EMH 225

Interplay between point defects and domain wall mobility in improper ferroelectric $YMnO_3$ — •Didrik René Småbråten, Dennis Meier, and Sverre Magnus Selbach — Norwegian University of Science and Technology (NTNU), Trondheim, Norway

Understanding the domain wall (DW) dynamics in ferroelectrics is key to controlling and fine-tune the domain structure and hence the ferroelectric properties. The DW dynamics strongly couple to the defect chemistry in the material, where stationary dopants may act as pinning centers or mobile defects may move with the DWs. The overall aim of this study is to give chemical guidelines for how to control the domain wall mobility via defect chemistry. Improper ferroelectric $YMnO_3$ has a complex and exotic DW structure, including neutral, as well as positively and negatively charged DWs. Furthermore, the material has a large chemical flexibility being robust against donor and acceptor doping of its cation sublattices, and it is stable under both oxygen deficiency and excess. This unique flexibility makes $YMnO_3$ an ideal model system for studying the interplay between DW mobility and defect chemistry. From density functional theory (DFT) calculations we show how changes in the two cation sublattices affect the DW mobility. In addition, we study how mobile anion defects couple to the DW movement and determine if they move with or pin the DWs.

KFM 2.6 Mon 11:15 EMH 225

Conducting domain wall networks in $TbMnO_3$ and $BiFeO_3$ — •Mart Salverda[1], Wilson Acevedo[2], Diego Rubi[2], Saeedeh Farokhipoor[1], and Beatriz Noheda[1] — [1]Zernike Institute for Advanced Materials, Groningen, The Netherlands — [2]CNEA and INN, Buenos Aires, Argentina

Ferroelastic domain walls in thin films of some complex oxides show a higher conductivity than the domains [1][2]. This effect is proposed to originate from the accumulation of ionic species at the domain walls due to the presence of strain gradients [2][3][4]. In a recent study [5]

we propose a model that accounts for the electrical behavior measured in $TbMnO_3$ thin films using macroscopic techniques, by assuming that the structural domain walls that are present in these films [6] are conducting. From the model, the value of the sheet resistance of the domain walls has been extracted. To further investigate the validity of this approach for other materials, we perform a similar analysis on systems incorporating thin films of $BiFeO_3$ where the domain walls are already proven to be conducting. Our aim is to elucidate the intrinsic transport properties of the domain walls.

[1] J. Seidel et al., *Nature Materials* **8**, 229 (2009) [2] S. Farokhipoor and B. Noheda, *Physical Review Letters* **107**, 127604 (2011) [3] E. Salje and H. Zhang, *Phase Transitions* **82**, 452 (2009) [4] T. Rojac et al., *Nature Materials* **16**, 322 (2017) [5] W. Román et al. (in preparation) [6] S. Farokhipoor et al., *Nature* **515**, 379 (2014)

Invited Talk KFM 2.7 Mon 11:30 EMH 225

Understanding the dielectric enhancement from domain walls in conventional and relaxor ferroelectrics — •Andrew Rappe — University of Pennsylvania, Philadelphia, PA, USA

The dielectric properties of ferroelectric materials are a key driver of smart materials applications. In this talk, two key aspects of anomalous dielectric enhancement will be analyzed: domain walls and relaxor ferroelectrics. A comprehensive theoretical viewpoint will be sketched that unifies these aspects, based on multi-scale materials modeling.

Incorporating quenched Coulombic disorder in ferroelectrics disrupts and changes the character of this transition; instead of a sharp transition in a small temperature range, these oxide alloys exhibit "relaxed" transitions over 100-200 K and are called "relaxor ferroelectrics." I will describe how a first-principles based multi-scale model can reveal the dynamic and statically correlated motions of ions that lead to relaxor behavior, and I will discuss their promise for next-generation piezoelectric and dielectric material systems, with emphasis on the emergent stabilization of a high density of low-angle domain walls.

I will also present molecular dynamics simulations of 90 degree domain walls (separating domains with orthogonal polarization directions) in the ferroelectric material $PbTiO_3$ to provide microscopic insights that enable the construction of a simple, universal, nucleation-and-growth-based analytical model that quantifies the dynamics of many types of domain walls in various ferroelectrics. This new model illuminates domain wall influence on the dielectric responses of conventional and relaxor ferroelectrics.

KFM 2.8 Mon 12:00 EMH 225

In-situ 4D observation of ferroelectric domain wall dynamics using second-harmonic generation microscopy — •Lukas Wehmeier, Alexander Haussmann, and Lukas M. Eng — Institute of Applied Physics, Technische Universität Dresden, 01062 Dresden, Germany

Second-harmonic generation microscopy (SHGM) allows for the three-dimensional (3D) observation of ferroelectric domain walls (DWs) across millimeter-thick bulk materials [1,2]. For example, this is of supreme value for exploring inclined and charged domain walls [1,3]. Here, we apply SHGM in order to quantify the DW dynamics in triglycine sulfate (TGS) single crystals upon the ferroelectric-to-paraelectric phase transition at the Curie temperature of $\approx 49\,^{\circ}C$ [4]. In addition, we study DW dynamics that are induced by external electric fields.

We show for TGS that SHGM allows exploring such electric-field-induced and temperature-driven DW dynamics in 4D, i.e. in real-time and full 3D imaging.

[1] T. Kämpfe et al., Phys. Rev. B 89, 035314 (2014).
[2] T. Kämpfe et al., Appl. Phys. Lett. 107, 152905 (2015).
[3] C. Godau et al., ACS Nano 11, 4816 (2017).
[4] L. Wehmeier et al., Phys. Stat. Solidi RRL 11, 1700267 (2017).

KFM 2.9 Mon 12:15 EMH 225

Electrical half-wave rectification at improper ferroelectric domain walls — •J. Schaab[1], S. H. Skjaervo[2], S. Krohns[3], X. Dai[1], M. Holtz[4], M. Lilienblum[1], D. A. Muller[4,5], M. Fiebig[1], S. M. Selbach[2], and D. Meier[1,2] — [1]ETH Zürich — [2]NTNU Trondheim — [3]University of Augsburg — [4]Cornell University — [5]Kavli Institute at Cornell for Nanoscale Science

Ferroelectric domain walls represent multifunctional 2D-elements that offer great potential for novel device paradigms. Improper ferroelectrics display particularly promising domain walls, which due to their unique robustness, are the ideal template for imposing the desired electronic behavior. Chemical doping, for instance, induces p- or n-type characteristics and electric fields reversibly switch between resistive and conductive domain-wall states.

Here, we demonstrate conversion of alternating current (AC) into direct current (DC) output based on neutral 180° domain walls in improper ferroelectric $ErMnO_3$. By combining scanning probe and dielectric spectroscopy, we show that the AC-to-DC conversion occurs for frequencies at which the domain walls are pegged to their equilibrium position. The practical frequency regime and magnitude of the output is controlled by the conductivity of the surrounding domains. Using density functional theory, we attribute the distinct transport behavior to oxygen defects that accumulate at the neutral walls. Our study reveals domain walls acting as 2D half-wave rectifiers, extending domain-wall-based nanoelectronics applications into the realm of AC-technology.

KFM 2.10 Mon 12:30 EMH 225

Unexpected $BiFeO_3$ 71 degree domain wall vibration — •Peng Chen and Sergey Artyukhin — Quantum Materials Theory, Istituto Italiano di Tecnologia, Genova (Italy)

Emergent phenomena excitations at domain walls are attracting enormous attention recently. Recent scanning impedance microscopy (SIM) measurements reveal AC conductance attributed to domain wall-localized phonons, that give important contributions to low-frequency dynamics in ferroic materials. In $BiFeO_3$ the polarization change across 71 degree domain walls is perpendicular to the electric field applied by the SIM tip, and therefore the DW-localized phonon should not be excited by the tip. However, the experimental observations show a violation of this intuitive picture. Here we use Landau-Ginzburg theory and first-principles calculations to address this puzzling behavior.