

## TT 59: Multiferroics I (jointly with DF, DS, KR, MA)

Time: Wednesday 9:30–13:00

Location: EB 107

TT 59.1 Wed 9:30 EB 107

**Magnetoelectric domain control in multiferroic TbMnO<sub>3</sub>** — ●SEBASTIAN MANZ<sup>1</sup>, MASAKAZU MATSUBARA<sup>1,2</sup>, MASAHIITO MOCHIZUKI<sup>3,4</sup>, TERESA KUBACKA<sup>1</sup>, AYATO IYAMA<sup>5</sup>, NADIR ALIOUANE<sup>6</sup>, TSUYOSHI KIMURA<sup>5</sup>, STEVEN JOHNSON<sup>1</sup>, DENNIS MEIER<sup>1</sup>, and MANFRED FIEBIG<sup>1</sup> — <sup>1</sup>ETH Zürich — <sup>2</sup>Tohoku University — <sup>3</sup>Aoyama Gakuin University — <sup>4</sup>Japan Science and Technology Agency — <sup>5</sup>Osaka University — <sup>6</sup>Paul Scherrer Institute

Spin-spiral multiferroics exhibit a strong coupling between the electric and magnetic subsystems which is of potential interest for technological applications. Although these systems have been investigated for more than a decade, the magnetoelectric domain evolution under external fields is still largely unknown. Using optical second harmonic generation we resolve how electric and magnetic fields affect the multiferroic domains in the archetypal spin-spiral multiferroic TbMnO<sub>3</sub>. In consecutive electric switching cycles, varying multi-domain patterns emerge before a single-domain state is obtained. This observation reflects that the domain walls can easily move without being pinned by, e.g., structural defects. In striking contrast to the electric-field response, multi-domain patterns persist when the polarization direction is flopped by applied magnetic fields. Here, a uniform polarization rotation is observed within all domains, which incorporates a transformation of neutral into nominally charged domain walls. Our results are explained based on numerical Landau-Lifshitz-Gilbert simulations and provide first evidence for the scalability of macroscopic magnetoelectric properties onto the level of domains.

TT 59.2 Wed 9:45 EB 107

**Critical behavior at the order-disorder transition in multiferroic DyMnO<sub>3</sub>** — ●MARKUS SCHIEBL, ALEXEY SHUVAEV, ANNA PIMENOV, GRAEME EGIN JOHNSTONE, ULADZISLAW DZIOM, and ANDREI PIMENOV — Institute for Solid State Physics, Vienna University of Technology, 1040 Vienna Austria

We present the results of detailed dielectric investigations of the relaxation dynamics in DyMnO<sub>3</sub> multiferroic manganite. In addition to known domain wall relaxation a second strong mode is observed at low frequencies. We provide an experimental evidence that the new relaxation mode is coupled to the chirality switching of the spin cycloid.

We demonstrate that the relaxation dynamics in DyMnO<sub>3</sub> is typical for an order-disorder phase transition. Therefore, DyMnO<sub>3</sub> follows an order-disorder transition scenario implicating that a short range cycloidal order of Mn-spins exists above  $T_C$ . The results suggest that the paramagnetic sinusoidal phase should be explained as a dynamic equilibrium between the clockwise and counterclockwise cycloidal magnetic orders. The short range order in the paraelectric phase is transformed to a long range cycloid at the ferroelectric transition temperature.

TT 59.3 Wed 10:00 EB 107

**Biquadratic and four-spin ring interactions in orthorhombic perovskite manganites** — ●NATALYA FEDOROVA, ANDREA SCARAMUCCI, CLAUDE EDERER, and NICOLA A. SPALDIN — ETH Zurich, Materials Theory, Wolfgang-Pauli-Strasse 27, CH-8093, Zurich, Switzerland

We use *ab initio* electronic structure calculations, based on DFT within the GGA+U approximation, to estimate the microscopic exchange interactions in the series of orthorhombic perovskite manganites (o-RMnO<sub>3</sub>), in order to find a model Hamiltonian which can provide an accurate description of the magnetism in these materials. At low temperatures o-RMnO<sub>3</sub> with small radii of  $R$  cations (therefore, large octahedral tiltings) demonstrate a spiral or E-type antiferromagnetic orderings (E-AFM), which drive their multiferroic properties. Usually the establishment of such magnetic orderings is explained within the framework of a Heisenberg model with competing nearest-neighbor (NN) and next-nearest-neighbor exchange interactions. However, we find that the mapping the results of *ab initio* calculations onto the Heisenberg Hamiltonian for o-RMnO<sub>3</sub> show a clear deviation from the Heisenberg-like behavior. We demonstrate that this deviation can be explained only by the presence of biquadratic and four-spin ring exchange couplings and show that they have the strongest effect in compounds where NN exchange interactions are weakened, for example, due to large octahedral tiltings.

TT 59.4 Wed 10:15 EB 107

**Time resolved polarized neutron scattering and dielectric spectroscopy reveal multiferroic domain dynamics in MnWO<sub>4</sub> and TbMnO<sub>3</sub>** — ●JONAS STEIN<sup>1</sup>, DANIEL NIERMANN<sup>1</sup>, CHRISTOPH GRAMS<sup>1</sup>, MAX BAUM<sup>1</sup>, TOBIAS CRONERT<sup>1</sup>, JEANNIS LEIST<sup>2</sup>, KARIN SCHMALZL<sup>3</sup>, A AGUNG NUGROHO<sup>4</sup>, ALEXANDER C KOMAREK<sup>5</sup>, GÖTZ ECKOLD<sup>2</sup>, PETRA BECKER<sup>6</sup>, LADISLAV BOHATÝ<sup>6</sup>, JOACHIM HEMBERGER<sup>1</sup>, and MARKUS BRADEN<sup>1</sup> — <sup>1</sup>II. Physikalisches Institut, Uni Köln — <sup>2</sup>Institut für Phys. Chemie, Uni Göttingen — <sup>3</sup>JCNS at ILL, France — <sup>4</sup>Institut Teknologi Bandung, Indonesia — <sup>5</sup>MPI Dresden — <sup>6</sup>Institut für Kristallographie, Uni Köln

Multiferroic materials are promising for future memory devices with low power consumption. The rise time between two states is a crucial parameter for a possible application and was investigated in the spin spiral multiferroics TbMnO<sub>3</sub> and MnWO<sub>4</sub>. Polarized neutron diffraction is able to determine the ratio of chiral domains, which can be controlled by an electric field. Using the stroboscopic technique we follow the reversion of chiral domains in the timescale of a few hundred microseconds to hours. In TbMnO<sub>3</sub> we find a simple logarithmic relation between the rise time and temperature that is fulfilled over 5 decades. Broadband linear and nonlinear dielectric spectroscopy revealed the domain dynamics in the MF phase of MnWO<sub>4</sub>. The rise time reaches values in the minute range in the middle of the multiferroic temperature regime at  $T \approx 10$  K but unexpectedly decays again on approaching the lower, first-order phase boundary at  $T_{N1} \approx 7.6$  K.

[1] Niermann et al. **PRB** **89**,134412 [2] Baum et al. **PRB** **89**,144406

TT 59.5 Wed 10:30 EB 107

**Polarization control at spin-driven ferroelectric domain walls** — ●NAËMI LEO<sup>1</sup>, ANDERS BERGMANN<sup>2</sup>, ANDRES CANO<sup>3</sup>, NARAYAN POUDEL<sup>4</sup>, BERND LORENZ<sup>4</sup>, MANFRED FIEBIG<sup>1</sup>, and DENNIS MEIER<sup>1</sup> — <sup>1</sup>ETH Zurich, Switzerland — <sup>2</sup>Uppsala University, Sweden — <sup>3</sup>University Bordeaux, France — <sup>4</sup>University of Houston, USA

As was recently demonstrated, domain walls in ferroelectric materials show emergent electronic properties, like enhanced conductivity tunable by the relative orientation of the polarisation in the adjacent domains. Here, multiferroic materials with a coexistence of magnetic and electric order offer a new route for the control of such localised functionalities at domain boundaries.

Using spatially-resolved optical second harmonic generation we demonstrate the magneto-electric-field control of the multiferroic domains in Co-doped MnWO<sub>4</sub>. In particular, the obtained domain distribution remains unchanged upon the magnetic-field-induced continuous 90°-rotation of the ferroelectric polarization.

This stability implies that multiferroic domain walls can accommodate for varying local polarisation configurations leading to local charging and discharging. We discuss the microscopic structure of the domain walls using micro-magnetic simulations.

TT 59.6 Wed 10:45 EB 107

**Tuning order-by-disorder multiferroicity in CuO by doping** — ●JOHAN HELLSVIK<sup>1,2</sup>, MARCELLO BALESTIERI<sup>1</sup>, TOMOYASU USUI<sup>3</sup>, ALESSANDRO STROPPA<sup>2</sup>, ANDERS BERGMAN<sup>4</sup>, LARS BERGQVIST<sup>5</sup>, DHARMALINGAM PRABHAKARAN<sup>6</sup>, OLLE ERIKSSON<sup>4</sup>, SILVIA PICOZZI<sup>2</sup>, TSUYOSHI KIMURA<sup>3</sup>, and JOSÉ LORENZANA<sup>1,2</sup> — <sup>1</sup>ISC-CNR, Rome, Italy — <sup>2</sup>CNR-SPIN, L'Aquila, Italy — <sup>3</sup>Osaka University, Osaka, Japan — <sup>4</sup>Uppsala University, Uppsala, Sweden — <sup>5</sup>KTH, Stockholm, Sweden — <sup>6</sup>University of Oxford, Oxford, United Kingdom

The high Curie temperature multiferroic compound CuO has a quasidegenerate magnetic ground state that makes it prone to manipulation by the so-called "order-by-disorder" mechanism. First principle computations supplemented with Monte Carlo simulations and experiments show that isovalent doping allows us to stabilize the multiferroic phase in nonferroelectric regions of the pristine material phase diagram with experiments reaching a 250% widening of the ferroelectric temperature window with 5% of Zn doping. Our results allow us to validate the importance of a quasidegenerate ground state on promoting multiferroicity on CuO at high temperatures and open a path to the material engineering of multiferroic materials. In addition we present a complete explanation of the CuO phase diagram and a computation on the incommensurability in excellent agreement with experiment without free parameters.

[1] J. Hellsvik et al., Phys. Rev. B 90, 014437 (2014) [2] T. Kimura et al., Nature Mat. 7, 291 (2008) [3] G. Giovannetti et al., Phys. Rev. Lett. 106, 026401 (2011)

TT 59.7 Wed 11:00 EB 107

**Dielectric properties and electrical switching behavior of the spin-driven multiferroic  $\text{LiCuVO}_4$**  — ●ALEXANDER RUFF<sup>1</sup>, STEPHAN KROHNS<sup>1</sup>, PETER LUNKENHEIMER<sup>1</sup>, ANDREY PROKOFIEV<sup>2</sup>, and ALOIS LOIDL<sup>1</sup> — <sup>1</sup>Experimental Physics V, Center for Electronic Correlations and Magnetism, University of Augsburg, Germany — <sup>2</sup>Solid State Physics, Vienna University of Technology, Austria

The spin-1/2 chain cuprate  $\text{LiCuVO}_4$  exhibits both ferroelectric and magnetic order at low temperatures. This so-called multiferroic behavior is of great scientific interest due to the underlying complex physical mechanisms, especially in the case of strong magnetoelectric coupling. Here we thoroughly discuss the multiferroic properties of the prototypical spin-driven ferroelectric material  $\text{LiCuVO}_4$ . At temperatures below about 2.5 K, it exhibits a three dimensional helical spiral spin order, with propagation in the  $b$  direction and a spin helix in the  $ab$  plane, which induces via an inverse Dzyaloshinskii-Moriya interaction a ferroelectric polarization in the  $a$  direction. In an external magnetic field, the direction of the spin spiral and thus the direction of the electrical polarization can be switched. This switching behavior of the polarization was demonstrated via dielectric spectroscopy on a single crystalline sample oriented in two different directions in magnetic fields up to 9 T. Detailed magnetic-field and temperature-dependent ferroelectric hysteresis-loop measurements imply the electric control of the spin helicity [1]. This rarely documented feature indicates the close coupling of electric and magnetic order of  $\text{LiCuVO}_4$ .

[1] A. Ruff et al., *J. Phys.: Condens. Matter*, **26**:485901 (2014).

## 15 min coffee break

TT 59.8 Wed 11:30 EB 107

**Emergence of ferroelectricity in multiferroic  $\text{h-YMnO}_3$**  — ●MARTIN LILIENBLUM<sup>1</sup>, THOMAS LOTTERMOSER<sup>1</sup>, SEBASTIAN MANZ<sup>1</sup>, SVERRE M. SELBACH<sup>2</sup>, ANDRES CANO<sup>3</sup> und MANFRED FIEBIG<sup>1</sup> — <sup>1</sup>Department of Materials, ETH Zurich, Vladimir-Prelog-Weg 4, 8093 Zurich, Switzerland — <sup>2</sup>Department of Material Science and Engineering, NTNU, N-7491 Trondheim, Norway — <sup>3</sup>CNRS, Université de Bordeaux, ICMCB, UPR 9048, F-33600 Pessac, France

Universal scaling laws, interfacial nano-electronics, and topological defects are currently studied using hexagonal manganites  $\text{RMnO}_3$  ( $R = \text{Sc}, \text{Y}, \text{Dy-Lu}$ ) as model system. In spite of the remarkably broad interest in the system, surprisingly little is known about the origin of the ferroelectric state. Here we solve the controversy about the emergence of the spontaneous polarization and its coupling to the underlying structural distortion by applying scanning probe microscopy (SPM) and optical second harmonic generation (SHG). We trace the spontaneous polarization by SHG from 100 K to 1450 K directly and contact-free. We find that only a single transition exists in which the polarization arises slower than expected as by-product of the structural distortion. By thermal treatments close to the structural transition and subsequent SPM scans, we show that the exceptionally robust ferroelectric domain pattern is determined only by the structural distortion. In summary we reveal that the ferroelectric order results from an interplay of electric polarization, topological effects, and temperature.

TT 59.9 Wed 11:45 EB 107

**Monte Carlo approach to the ferroelectric phase transition in hexagonal manganites** — ●THOMAS LOTTERMOSER<sup>1</sup>, MARTIN LILIENBLUM<sup>1</sup>, ANDRES CANO<sup>2</sup>, and MANFRED FIEBIG<sup>1</sup> — <sup>1</sup>ETH Zurich, Zurich, Switzerland — <sup>2</sup>Université de Bordeaux, Pessac, France

Despite several experimental and theoretical efforts in recent years the nature of the structural high temperature phase transition in the hexagonal manganites and its relation to the occurrence of a ferroelectric polarization in this materials is still not fully understood. Experimental data give two contradicting answers to this problem. Some experiments indicate a simultaneous appearance of the polarization in a single structural phase transition while others hint to a second phase transition several hundred Kelvin below the structural transition. In order to clarify these contradictions we performed Monte Carlo simulations based on the so-called clock model. In this model the six trimerization states of the manganite crystal structure are represented by six clock vectors in the complex plane. From the simulation data

we calculated the temperature dependence of the complex structural order parameter and the induced ferroelectric polarization. The results point to a single phase transition with a strongly suppressed polarization contribution at high temperatures. This is experimentally confirmed by direct measurements of the ferroelectric polarization using optical second harmonic generation. Contradictions with other experimental data can be explained as finite size effects depending on the length scale of the experimental probe.

TT 59.10 Wed 12:00 EB 107

**Magnon-phonon interactions in hexagonal multiferroic  $\text{YMnO}_3$**  — ●ANDREAS KREISEL<sup>1</sup>, SHANTANU MUKHERJEE<sup>1</sup>, BRIAN M. ANDERSEN<sup>1</sup>, TURI SCHÄFFER<sup>1</sup>, SONJA HOLM<sup>1</sup>, KIM LEFMANN<sup>1</sup>, NIELS C.R. MOMSEN<sup>1</sup>, JACOB LARSEN<sup>2</sup>, AMY FENNEL<sup>3</sup>, UWE STUHR<sup>3</sup>, and ZAHRA YAMANI<sup>4</sup> — <sup>1</sup>Niels Bohr Institute, University of Copenhagen, Denmark — <sup>2</sup>Institute of Physics, Technical University of Denmark — <sup>3</sup>Laboratory of Neutron Scattering, Paul Scherrer Institute, Switzerland — <sup>4</sup>Chalk River National Laboratory, Canada

The multiferroic material  $\text{YMnO}_3$  is known to show a large spin lattice coupling such that the spin and lattice degrees of freedom influence various properties, as for example the thermal conductivity that is found to have an anomalous contribution. The magnetoelastic modes have been measured recently in neutron diffraction experiments and linked to certain spectral features in Raman signals. Starting from a Heisenberg model on a triangular lattice with single ion anisotropies, we investigate the spin-phonon coupling via the magnetostriction mechanism and derive a coupled magnon-phonon model valid in the entire Brillouin zone. Within a spin-wave approach, where the coupling yields a hybrid magnon-phonon mode, we calculate the dynamic structure factor and compare to recent experimental neutron results.

TT 59.11 Wed 12:15 EB 107

**Stability of magnetic and electric domains against chemical doping in hexagonal manganites** — ●EHSAN HASSANPOUR YESAGHI, VIKTOR WEGMAYR, JAKOB SCHAAB, DENNIS MEIER, and MANFRED FIEBIG — Department of Materials, ETH Zürich, Zürich, Switzerland

The unique properties of magnetoelectric multiferroics are, to a large extent, determined by the coexistence and interaction of magnetic and electric domains. A major challenge towards future applications is to optimize the properties of these domains, such as their transport, without weakening or even losing the existing multiferroic order. Here, we present our study of ferroelectric and antiferromagnetic domains in chemically doped hexagonal manganites. We show that the electronic conductance of  $\text{ErMnO}_3$  can be enhanced or suppressed by introducing either divalent ( $\text{Ca}^{2+}$ ) or tetravalent ( $\text{Zr}^{4+}$ ,  $\text{Ti}^{4+}$ ) ions into the system. Using piezoresponse force microscopy (PFM) and optical second harmonic generation (SHG) we monitor the corresponding changes on the level of domains. We find that the  $\text{RMnO}_3$ -characteristic domain topography, as well as the multiferroic transition temperature, are robust against the applied ionic alteration, which demonstrates the usability of chemical doping for non-perturbative property-engineering of multiferroic domains.

TT 59.12 Wed 12:30 EB 107

**Anisotropy study of multiferroicity in the pyroxene  $\text{NaFeGe}_2\text{O}_6$**  — ●LIONEL ANDERSEN<sup>1</sup>, THOMAS LORENZ<sup>1</sup>, MATTHIAS ACKERMANN<sup>2</sup>, LADISLAV BOHATÝ<sup>2</sup>, and PETRA BECKER<sup>2</sup> — <sup>1</sup>II. Physikalisches Institut - Universität zu Köln, Germany — <sup>2</sup>Institut für Kristallographie - Universität zu Köln, Germany

Since the mineral aegirine was found to be the first multiferroic member of the pyroxenes an intensive search for further related multiferroics was initiated [1]. In this contribution, we present a detailed study of the dielectric, magnetic and magnetoelastic properties of the pyroxene  $\text{NaFeGe}_2\text{O}_6$  with special respect to the anisotropy. Unlike other investigations on  $\text{NaFeGe}_2\text{O}_6$  [2] large single crystals were synthesized to examine pyroelectric currents, dielectric constants and magnetic susceptibilities as well as the thermal expansion and the magnetostriction. The spontaneous electric polarization detected below  $T_C \approx 11.6$  K in an antiferromagnetically ordered state ( $T_N \approx 13$  K) is mainly lying within the  $ac$  plane with a small component along  $b$ , indicating a triclinic symmetry of the multiferroic phase of  $\text{NaFeGe}_2\text{O}_6$ . The electric polarization can be strongly modified by applying magnetic fields along different directions. We derive detailed magnetic-field versus temperature phase diagrams and identify three multiferroic low-temperature phases, which are separated by a non-ferroelectric, antiferromagnetically ordered state from the paramagnetic high-temperature phase [3].

- [1] S. Jodlauk *et al.* J. Phys.: Condens. Matter **19** (2007)
- [2] I. Kim *et al.* J. Phys.: Condens. Matter **24** (2012)
- [3] M. Ackermann *et al.* New J. Phys. (submitted, arXiv:1408.6772)

TT 59.13 Wed 12:45 EB 107

**Ab Initio analysis of ferroelectric and magnetic properties of potentially multiferroic aurivillius phases** — ●AXIEL YAEL BIRENBAUM, JAN VAN DEN BROEK, and CLAUDE EDERER — Materials Theory, ETH Zürich

A promising class of high temperature polar magnetic multiferroic materials are the Aurivillius family of layered-perovskites related compounds. They combine high temperature ferroelectric properties with a layered structure that allows for systematic introduction of magnetic ions. The simplest of such cases to have been studied is  $\text{Bi}_5\text{FeTi}_3\text{O}_{15}$ .

However, no well-established value exists for its spontaneous electric polarization, and contradictory reports as to its magnetic states.

We perform Density Functional Theory calculations on  $\text{Bi}_5\text{FeTi}_3\text{O}_{15}$ , and conclude on a high spontaneous electric polarization. To better understand the mechanism for ferroelectricity, we examine 9 systems, based on  $\text{SrBi}_2\text{Ta}_2\text{O}_9$  as reference. We find a high spontaneous polarization even in the case of with no nominally ferroelectrically-active cations. We discuss these results in light of the tri-linear coupling between soft and hard modes demonstrated for  $\text{SrBi}_2\text{Ta}_2\text{O}_9$  and the general concept of “hybrid improper ferroelectricity”. To clarify the range of temperatures expected for magnetic long range order despite a low concentration of magnetic ions and the short range of superexchange interactions, we perform Monte Carlo simulations. We discuss possible strategies to increase magnetic ordering temperatures.