

Energy Efficient Magnetoelectric Materials by Ionic Approaches: Fundamentals, Challenges and Perspectives

712. WE-Heraeus-Seminar

**26 – 29 January 2020
at the Physikzentrum Bad Honnef/Germany**

**WILHELM UND ELSE
HERAEUS-STIFTUNG**



Introduction

The Wilhelm und Else Heraeus-Stiftung is a private foundation that supports research and education in science with an emphasis on physics. It is recognized as Germany's most important private institution funding physics. Some of the activities of the foundation are carried out in close cooperation with the German Physical Society (Deutsche Physikalische Gesellschaft). For detailed information see <https://www.we-heraeus-stiftung.de>

Aims and scope of the 712. WE-Heraeus-Seminar:

Control of interfacial properties plays a crucial role in many modern nanoscale devices. Ionic mechanisms for the manipulation of interface magnetism is an emerging topic in the field of voltage control of magnetism for low-power nanoscale devices. In comparison to other magnetoelectric approaches, magneto-ionic manipulation offers the possibility of (i) triggering non-volatile magnetic response at room -temperature and (ii) accessing materials beyond ultra-thin films (2-3 nm), as shown in seminal magnetoelectric studies in metals. A manifold of solid and solid/liquid magneto-ionic architectures have been reported within the last few years. Electrochemical mechanisms like oxygen ion migration and reduction/oxidation of transition metals or Li intercalation are proposed to tune magnetic properties (e.g., magnetization, anisotropy, coercivity, domain wall pinning, exchange bias, or spin reorientation) in materials ranging from thin film ferromagnets to bulk ferrimagnets. Clear identification of the microscopic mechanisms governing magneto-ionics still remains rather challenging and will be tackled in the seminar. One example is the coexistence of electrochemical charge transfer and capacitive charging often discussed in voltage-control of magnetism. A deeper understanding of the origin of these effects is required, especially to overcome problems related to the limited kinetics determined by ionic migration. High charging speeds, similar to those attainable in resistive switching, should be considered and made possible in the near future in magneto-ionics. The most intense research activities currently deal with the nature of the ion involved, the impact of material defects and morphology, and the transfer to high surface area materials and magnetic nanostructures at critical points. The seminar aims at providing a forum for an overview of the current understanding of ionic effects in magnetoelectric materials. Fundamental ionic mechanisms and their correlation with magnetic phenomena, utilization of the spatial resolution achieved by advanced interface-sensitive measurement techniques, and routes toward the implementation of nanodevices will be covered.

Scientific Organizers:

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Program

Program

Sunday, 26 January 2020

16:00 – 21:00	Registration	
17:00 – 18:00	<i>COFFEE AND CAKE in the front of the lecture hall</i>	
18:00 – 18:15	Scientific organizers	Welcome
18:15 – 19:00	Kai Liu	Magneto-ionic control of heterostructures and interfaces
19:00 – 19:45	Horst Hahn	Controlling magnetism by electrochemical approaches
20:00	<i>BUFFET SUPPER and get-together</i>	

Monday, 27 January 2020

08:00	BREAKFAST	
09:00 – 09:45	Liza Herrera Diez	Ionic control of the Dzyaloshinskii Moriya Interaction through electric fields and ion irradiation
09:45 – 10:30	Geoffrey Beach	Magneto-ionic control of magnetism
10:30 – 10:50	COFFEE BREAK	

Program

Monday, 27 January 2020

10:50 – 11:35	Philippe Allongue	Electrochemical voltage control of the magnetism of ultrathin films
11:35 – 12:20	Motohiro Suzuki	Probing the microscopic mechanism of voltage-controlled magnetic anisotropy with X-ray absorption spectroscopy
12:20 – 12:40	Jonas Zehner	Magneto-ionic control of magnetic hysteresis, domains and exchange bias in FeO_x/Fe layers
12:45	<i>LUNCH</i>	
14:30 – 15:15	Roland Würschum	In-situ SQUID studies of electrochemically induced phenomena: Operando diagnosis of battery cathode charging and switching the magnetism of nanoporous alloys
15:15 – 16:00	Aliona Nicolenco	Magnetoelectric effects in nanoporous alloys and semiconductors
16:00 – 16:20	Xinglong Ye	Voltage-driven giant modulation of magnetism in bulk metallic ferromagnets by hydrogen atoms
16:20 – 19:00	Poster Session with poster minutes and <i>COFFEE</i>	
19:00	<i>DINNER</i>	

Program

Tuesday, 28 January 2020

08:00	<i>BREAKFAST</i>	
09:00 – 09:45	Dustin Gilbert	Controlling magnetic perovskites by ex-situ design of oxygen distributions
09:45 – 10:30	Chris Leighton	Electrolyte-gate-controlled ferromagnetism in perovskite oxides
10:30 – 10:50	Jeff Walter	Electrically-induced ferromagnetism in diamagnetic FeS ₂
10:50 – 11:15	<i>COFFEE BREAK</i>	
11:15 – 12:00	Regina Dittmann	Monitoring ionic movement in memristive oxide thin film devices by <i>operando</i> spectroscopy
12:00 – 12:45	Marjana Ležaić	Oxygen-deficient hafnia as a physicist's playground: efficient ReRAM material & binary ferroelectric
12:45 – 12:55	Conference photo (in the front of the lecture hall)	
13:00	<i>LUNCH</i>	

Program

Tuesday, 28 January 2020

14:00 – 16:00	Excursion	
16:30 – 17:15	Jörg Weißmüller	Electro-chemo-mechanical coupling in high surface area materials
17:15 – 17:35	Markus Gößler	Magneto-ionic switching of superparamagnetism
17:35 – 18:00	<i>COFFEE BREAK</i>	
18:00 – 18:45	Sarah H. Tolbert	Solution processed nanoporous and nanocrystal based magnetoelectric materials
18:45 – 19:05	Martin Nichterwitz	Voltage-controlled ON switching and manipulation of magnetization via the redox transformation of beta-FeOOH nanoplatelets
19:30	<i>HERAEUS DINNER</i> (social event with cold & warm buffet with complimentary drinks) and Poster Prize	

Program

Wednesday, 29 January 2020

08:00	<i>BREAKFAST</i>	
09:00 – 09:45	Judith Driscoll	Electric field control of magnetism at room temperature in multiferroic nanocomposite films without external magnetic field application
09:45 – 10:30	Kornelius Nielsch	Ferromagnetic 3D nano- and microstructures by atomic layer deposition
10:30 – 10:50	Julius De Rojas	Role of the electrical properties of substrates in the magneto-ionic behavior of Co_3O_4 thin films
10:50 – 11:15	<i>COFFEE BREAK</i>	
11:15 – 12:30	Round table discussion and closing remarks	
12:30	<i>LUNCH</i>	

End of the seminar and departure

NO DINNER for participants leaving on Thursday morning

Posters

Posters

Maria Ameziane	Solid-state ionic control of magnetism in systems with perpendicular magnetic anisotropy
Tanvi Bhatnagar	Voltage control of magnetism in $\text{La}_{0.67}\text{Sr}_{0.33}\text{MnO}_3/\text{PMN-PT}$ heterostructures
Matteo Cialone	Magnetoelectric effects in nanoporous CoPt microstructures
Sofya Danilova	Selective metallization of non-conductive material enabled by a gradient magnetic field application
Daniele Gastaldo	Growth and characterization of diluted amorphous GeMn thin films
Shanshan Guo	Two-dimensional magnetic mesocrystals for bit patterned media
Rico Huhnstock	Tailoring of exchange bias in thin film systems via electrochemical transformation of the ferromagnetic layer
Aatif Ijaz	Poly-(2-ethyl-2-oxazoline) as a novel additive for room temperature electrodeposition of Nickel
Maksim Kutuzau	Degradation mechanism and way of surface protection of nickel nanostructures
Davide Lamberti	Growth and magnetic characterization of Germanium manganese quantum dots
Tuhin Maity	Atomic-Scale Control of Exchange Bias at BaTiO_3 - $\text{La}_{0.67}\text{Sr}_{0.33}\text{MnO}_3$ interface
Nathan Missault	Electrodeposition of magnetic nanostructures

Posters

Vadim Morari	Porous GaAs layers and nanostructures decorated with magnetic materials
Prasanta Kumar Muduli	Detection of the interfacial exchange field at a ferromagnetic insulator-nonmagnetic metal interface with pure spin currents.
Stefania Pizzini	Tuning magnetic anisotropy and skyrmion stability with electric field
Heiko Reith	Voltage controlled magnetism in iron oxide/iron nanostructures
Stefan Röher	Voltage-induced hydrogen loading and magnetic changes in electrodeposited Fe/Pd-bilayers
Konstantin Rushchanskii	Ferroelectric switching in ϵ -Fe ₂ O ₃
Mamour Sall	Enhancing magnetic materials at the atomic scale using light ion irradiation
Sara Sheffels	Proton dynamics in a solid oxide hydrogen nanobattery
Ruby Singh	Reversible control of magnetism: on the conversion of hydrated FeF ₃ with Li to Fe and LiF
Veronica Sireus	Disentangling Highly Asymmetric Magnetoelectric Effects in Engineered Multiferroic Heterostructures
Katarzyna Skibinska	Electrodeposition of Co-Fe alloy 1D nanocone array inside AAO template with superimposed magnetic field
Marek Wilhelm	Transition of the magnetic exchange coupling induced by oxygen vacancies in La _{0.7} Sr _{0.3} MnO ₃ thin films

Abstracts of Talks

(in chronological order)

Magneto-Ionic Control of Heterostructures and Interfaces

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Magneto-ionic approaches for modifying ion distributions in metal/oxide heterostructures offer exciting potentials to control material properties. Our recent studies show that such magneto-ionic effect, even though initiated at metal/oxide interfaces, can extend deep into the rest of the oxide films and drastically tailor their physical properties [1-4].

In antiferromagnetic systems, we have previously demonstrated a controllable positive exchange bias in GdFe/NiCoO [1], and that the oxygen migration can be reversibly driven by an electric field [2]. Recently, we have observed a strong exchange bias in Gd/NiCoO due to the magneto-ionic effect, above the Gd T_c. After electric biasing, up to 35% enhancement of the exchange bias is observed, which can be reset by field-cooling.

In studies of cuprates, we show a simple, scalable approach to tune superconductivity [4]. A thin Gd layer (up to 20 nm) deposited onto epitaxial YBCO films (100nm), is found to leach oxygen from deep within the YBCO and suppress the superconductivity. These effects arise from the combined impact of redox-driven electron doping and modification of the YBCO microstructure.

In ferromagnets chemisorbed with submonolayer oxygen, we have observed strong DMI induced by chemisorption at room temperature. The sign of this DMI and its surprisingly large magnitude are derived by examining the oxygen coverage dependent evolution of domain wall chirality. The large induced DMI has enabled direct writing of magnetic skyrmions.

Our findings demonstrate an effective solid-state ionic approach to control a wide variety of magnetic functionalities, opening up possibilities for electric gating.

This work has been supported by the NSF (DMR-1610060, ECCS-1611424, DMR-1905468, ECCS-1933527) and the nCORE SMART center through SRC/NIST.

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- [4]. Murray, et al, arXiv: 1911.07275.

Controlling magnetism by electrochemical approaches

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The control of magnetic properties in a reversible way is of interest for basic understanding of fundamental concepts as well as for applications. Typically, the concepts require nanostructured materials and morphologies, in many cases in the form of thin films. New opportunities arise by employing electrical charges at interfaces to the magnetic materials exposed to electrolytes. In this case, an applied electrical potential results in large polarization at the interfaces, leading to substantial reversible changes of the magnetic properties at the surfaces. In case of extremely thin films, it has been demonstrated that complete on-off switching can be achieved. An extension of these magnetoelectric effects, still employing electrolytes, but now including reversible ion-intercalation driven magnetic control, addresses also the bulk materials volumes. The concept is demonstrated for various ferromagnetic spinel oxides, where a large and fully reversible change in room temperature magnetization is observed.

References

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'Ionic control of the Dzyaloshinskii Moriya Interaction through electric fields and ion irradiation'

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The Dzyaloshinskii Moriya interaction (DMI) has revealed itself as a key element in the design of novel spintronics devices since it can induce the formation of chiral magnetic structures like skyrmions and Néel like domain walls [1]. Controlling DMI is therefore of outstanding practical interest since it could allow for the dynamic and local tuning of chiral spin structures. DMI is commonly seeded at the magnetic material interfaces therefore designing methods to tune the structure and composition of these interfaces is a key aspect for the reliable control of DMI. In this presentation I will show our recent results on the manipulation DMI using electric fields [2] and He⁺ ion irradiation [4] in Pt/Co/HfO₂ and Ta/CoFeB/MgO layers with perpendicular anisotropy.

Electric fields applied through ionic liquid gating are shown to induce the migration of mobile oxygen-rich ionic species present in HfO₂ across a Pt/Co/HfO₂ magnetic stack inducing a gentle oxidation of Co. This produces a spin reorientation transition from in-plane to perpendicular anisotropy accompanied by a decrease in DMI which has been linked to a decoupling with the Pt substrate. On the other hand, He⁺ ion irradiation is a well-known method for interface design that has been shown to produce a large impact on anisotropy and disorder in perpendicularly magnetised materials such as Ta/CoFeB/MgO stacks. The changes in anisotropy occur mostly through atomic intermixing at the CoFeB/MgO interface. In our latest study we show that the intermixing also occurring at the Ta/CoFeB interface has a large impact on the value of DMI.

References:

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- [3] L. Herrera Diez *et al.* 'Enhancement of the Dzyaloshinskii-Moriya interaction and domain wall velocity through interface intermixing in Ta/CoFeB/MgO'. Phys. Rev. B 99, 054431 (2019).

Magneto-ionic control of magnetism

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Voltage control of magnetism has the potential to substantially reduce power consumption in spintronic devices, while offering new functionalities through field-effect operation. Magneto-electric coupling has usually been achieved using complex oxides such as ferroelectrics, piezoelectrics, or multiferroics. Here, I describe an alternative approach known as magneto-ionic switching [1,2], which relies on solid-state electrical gating of a mobile ionic species to modulate the properties of a thin ferromagnetic film.

First, I will review our initial discoveries of voltage control of magnetism through solid-state electrochemical switching of the interfacial oxidation state [1-3] in thin metallic ferromagnets. In ultrathin ferromagnet/oxide bilayers, perpendicular magnetic anisotropy (PMA) arises from interfacial hybridization between the ferromagnetic 3d and oxygen 2p orbitals. By using GdOx as a gate oxide with high oxygen ion mobility, I show that O^{2-} can be reversibly displaced at a Co/GdOx interface with a small gate voltage, leading to unprecedented large, non-volatile changes to interfacial PMA by $> 0.75 \text{ erg/cm}^2$ [3]. By optimizing the device structure and geometry these effects can be achieved with switching times down to < 100 microseconds [2], and can be integrated into devices [1,3] that can be gated locally to realize memory and logic functionalities.

In the second part of the talk, I focus on our recent discovery [4] that magnetic anisotropy can be reversibly and nondestructively toggled at room temperature with a small gate voltage through H^+ pumping in all-solid-state heterostructures, eliminating the irreversibility and structural degradation that occurs in oxygen redox-based structures. I show that H_2O hydrolysis in ambient atmosphere catalyzed by a rare-earth oxide/noble metal interface can serve as a solid-state proton pump that enables nondestructive magnetic property gating with a modest voltage. We demonstrate reversible 90° magnetization switching in a thin Co film at room temperature by either inserting H^+ at its interface with an oxide or loading hydrogen into an adjacent heavy metal layer. The mechanism permits both unipolar toggle switching and nonvolatile state retention, with no discernible irreversibility in magnetic properties of the ferromagnet after > 2000 cycles. Moreover, since heavy metals like Pt and Pd that exhibit strong spin-orbit coupling are also well-known hydrogen storage materials that can be driven between a metal and metal-hydride phase, a host of spin-orbit induced phenomena at heavy-metal/ferromagnetic interfaces becomes accessible to voltage gating despite the fact that electric fields cannot be applied directly. Finally, I will discuss opportunities beyond magnetism, such as voltage-gated optics and plasmonics that can be switched by proton pumping in solid-state architectures [5].

References

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Electrochemical Voltage Control of the Magnetism of Ultrathin films

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Voltage control of magnetism (VCM) has emerged as a promising approach to address individual components in devices as well as an efficient method to reduce device power consumption. An electric field effect on magnetic anisotropy energy (MAE) of a thin ferromagnetic layer was first reported in 2007 [1] but other effects [2], including full material conversion, also called magneto ionics [3], have been reported.

In this work, we make use of the solid / electrolyte contact to apply a soft and defect free electrical contact on an *oxide free* surface. It will be shown that electrochemical VCM of ultrathin epitaxial magnetic films encompasses very different physical mechanisms to control the MAE with very different amplitudes and without any material conversion (e.g. see Ref. [4]). Using in situ MOKE microscopy we also showed that electrochemical VCM affects domain wall propagation velocity [5] and domain nucleation. The presentation will make a survey of above recent results and will highlight analogies and differences with respect to solid state devices.

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Probing the microscopic mechanism of voltage-controlled magnetic anisotropy with X-ray absorption spectroscopy

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Controlling the magnetic anisotropy in ferromagnetic thin films by voltage application is an intriguing phenomenon [1, 2]. Among these, voltage-induced magnetic effects involving a purely electronic process (no chemical reaction accompanied) in fully solid-state devices are of technologically high importance because such phenomena are desirable for real applications for memories with a high-speed operation and long-term endurance.

In this study, we used synchrotron-based X-ray absorption spectroscopy and X-ray magnetic circular dichroism (XMCD) techniques to investigate the microscopic origin of the electric-field effects on the magnetic anisotropy in ferromagnetic metal/dielectric junctions [3–7]. We quantitatively determined the voltage-induced change in the magnetic moments as well as valence electronic states of the specified element. Based on our experimental and first-principle calculation results, we revealed that two different mechanisms are dominant in the electric-field modulation of the magneto-crystalline anisotropy energy of the system.

This work was partly supported by JSPS KAKENHI (18H03880, 26103002, 17H02823) and the ImPACT program of the Council for Science, Technology and Innovation (Cabinet Office, Government of Japan).

References

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Magneto-ionic control of magnetic hysteresis, domains and exchange bias in FeO_x/Fe layers

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Ionic motion and redox reactions applied to magnetic materials promise new energy-efficient device operation modes for neuromorphic computing, energy efficient spintronics or actuation. For instance, large and non-volatile magnetic property changes are achieved at a low voltage by electrolytic gating of metal nanostructures at room temperature [1-3]. The present study explores magneto-ionic effects in sputtered and natively oxidized FeO_x/Fe thin films. These films, due to oblique deposition, show a uniaxial in plane anisotropy. In situ Raman spectroscopy reveals that during the electrolytic gating, a transformation of the native oxide layer into magnetic metal and vice versa occurs. Simultaneously to the voltage-triggered reduction process, coercivity and remanence collapse to 5% and 9%, respectively, of the initial value. In situ Kerr microscopy reveals that this is accompanied by an increase in the magnetic equilibrium domain size. Further, 180° magnetization switching is demonstrated upon voltage appliance. The electrochemical and magnetic analysis suggest that the underlying mechanism is based on microstructure-related changes of anisotropy and pinning.

Going beyond magneto-ionic effects in single layers, the tunable FeO_x/Fe layer are then combined with an antiferromagnetic IrMn underlayer, yielding voltage-tunable exchange biased systems.[4] Non-volatile and reversible changes in the exchange bias system are observed upon reduction and applying open-circuit-potential or an oxidation potential, respectively. The Fe-layer thickness increase for a non-volatile treated sample is measured via x-ray photoelectron spectroscopy. An Fe layer thickness increase upon reduction is revealed, which, in consistency with an analytical exchange bias model, causes the alteration in exchange bias. These results are highly promising for designing exchange bias systems and future electrically controlled magnetic devices in general.

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In-situ SQUID studies of electrochemically induced phenomena: Operando diagnosis of battery cathode charging and switching the magnetism of nanoporous alloys

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Studying electrochemically induced phenomena by means of highly sensitive SQUID-magnetometry (superconducting quantum interference device) is very attractive, both for a deeper understanding of charging processes by a magnetic tool and for controlling magnetism by electrochemical stimuli. Both issues will be addressed in this talk.

The magnetic moment serves as highly sensitive fingerprint for the oxidation state of the transition metal ions in battery cathode materials thus enabling to identify the electrochemical "active" ions. An overview will be given on operando magnetometry studies of the important class of LiNiCoMn-oxide cathode materials (so-called NMC with Ni:Co:Mn ratios of 1:1:1 and 3:1:1 [1, 2]) as well as of sodium vanadium phosphate cathodes [3]. In addition, first operando positron annihilation studies on a battery cathode material (NMC 1:1:1) will be presented yielding insight into lattice defects induced by charging and discharging [4].

Regarding electrochemically induced variations of magnetism, nanoporous materials are particularly promising owing to their high surface-to-volume ratio. Measurements on nanoporous Pd(Co) obtained by dealloying will be presented which demonstrate reversible switching of magnetism by electrochemical hydrogen sorption [5].

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Magnetoelectric effects in nanoporous alloys and semiconductors

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Low-power voltage-programmable magnetic materials have an enormous potential to boost energy efficiency in nanoscale device applications. Among various types of magnetoelectric materials, porous alloys and oxides have gained considerable attention due to their very large surface-area-to-volume ratio which allows for (i) large electric surface charge accumulation and (ii) enhanced interfacial effects driven by ionic motion and electrochemical reactions. We have recently demonstrated the possibility to induce considerable reversible, non-volatile changes in the magnetic properties of nanoporous metal alloys, metal/metal oxide nanostructures and oxides, by applying an electric field through a liquid electrolyte gate at room temperature.

First, a drastic reduction of coercivity (H_c) is observed in electrodeposited nanoporous Cu-Ni (H_c decrease by 32%) and Fe-Cu (by 25%) films [1,2]. *Ab-initio* calculations indicate that the effect is mainly due to changes in the magnetic anisotropy energy at the surface of the pore walls caused by the accumulated electrostatic charges. Further enhancement of the magnetoelectric effects is accomplished in nanoporous Co-Pt/CoO_x lithographed micro-disks where a pronounced reduction of H_c (by 88%) and a remarkable increase of saturation magnetization (M_s) are observed upon voltage application [3]. The drastic changes in the magnetic properties in this case are assisted by partial reduction of CoO to metallic Co promoted by O²⁻ ions migration, *i.e.* magneto-ionic effect. Finally, magnetoelectric effects are also studied in nanoporous Co₂FeO₄ and FeO_x films prepared by the evaporation-induced self-assembly of sol-gel precursors with a sacrificial block-copolymer template [4,5]. In these cases, voltage-driven oxygen migration causes a partial reduction of the oxides into metallic species, thus leading to an increase in M_s and a pronounced reduction in H_c which depend on the voltage applied and degree of porosity.

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Voltage-Driven Giant Modulation of Magnetism in Bulk Metallic Ferromagnets by Hydrogen Atoms

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Controlling magnetic properties in metallic ferromagnets by small voltages is desirable for room-temperature applications. However, so far these effects are limited to a depth of a few nanometers and are usually very weak. We report that through electrochemically-controlled insertion and extraction of hydrogen atoms it is possible to modulate magnetic properties in bulk metallic ferromagnets to an unprecedented extent. Using micrometer-sized SmCo₅ powder as a model, we show that its coercivity can be tuned by ~ 1 T, two to three orders of magnitudes larger than by other methods, by applying voltages of only ~ 1 V. Moreover, voltage-assisted magnetization reversal at room temperature is demonstrated. The coercivity change can be attributed to the drastic reduction of nucleation field of magnetic domains, induced by hydrogen insertion into interstitial crystal sites. Our study offers an approach to control magnetic properties of metallic ferromagnets in macroscopic scale and with giant magnitudes.

Controlling magnetic perovskites by ex-situ design of oxygen distributions

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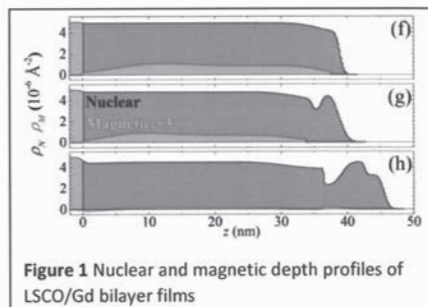


Figure 1 Nuclear and magnetic depth profiles of LSCO/Gd bilayer films

Magnetic perovskites offer a particularly promising opportunity for ionically controlled devices. In these materials, a delicate balance between double- and super-exchange interactions gives rise to highly flexible magnetic properties. Small changes to e.g. valence or strain can induce large changes in the magnetic ordering. Furthermore, these materials offer some of the most relevant magnetic properties to applications, including room-temperature ordering, large magnetic anisotropy, and multiferroic properties. One issue which exists with this approach is

designing perovskites with highly-mobile oxygen vacancies while preserving the high quality and structure of the material.

In this talk, I present our recent work on ionic control of (La, Sr)CoO₃, a high-anisotropy, conducting magnetic perovskite.[1, 2] This material is prepared as a pristine, compositionally balanced, epitaxial thin-film. By depositing a thin-film of reactive gadolinium on the surface, oxygen ions are extracted at room-temperature while preserving the epitaxy. As ions are extracted, the magnetism is fully suppressed throughout the film thickness and the electrical resistance increases by >3,400%. These results suggest that – despite oxygen being extracted from the top surface – ions re-distribute from throughout the film, illustrating a high ion mobility. These results are confirmed with transmission electron microscopy, which also shows that the oxygen vacancies agglomerate, causing localized transformations to a brownmillerite structure. Detailed investigations of the local structure show that there are ordered brownmillerite regions, as well as regions with disordered oxygen vacancies. These results are crucial to explaining the observed magnetic and electronic properties – simple electron doping cannot explain the observed results. Thus, these results offer a new challenge in using perovskites – that aggregation of vacancies can suppress control – and opportunities – that structural transformations might significantly increase the range of control of these materials.

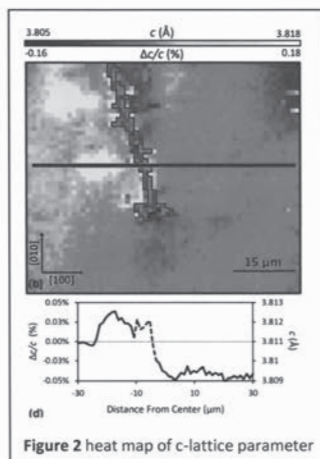


Figure 2 heat map of c-lattice parameter

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Electrolyte-Gate-Controlled Ferromagnetism in Perovskite Oxides

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Incorporation of electrolytes such as ionic liquids into field-effect devices to form electric double layer transistors (EDLTs) enables induction of surface carrier densities up to 10^{15} cm^{-2} . This corresponds to significant fractions of an electron/hole per unit cell in most materials, sufficient to *electrically control* electronic/magnetic phase transitions. This has generated interest from several fields, including magnetoionics, but many challenges remain. It is imperative that we understand the gating mechanisms in EDLTs, for example (*i.e.*, that we deconvolute electrostatic and electrochemical mechanisms [1]), that we develop *operando* characterization methods, and that we assess the full power and universality of electrolyte gating. In this talk I will review our work applying electrolyte gating using solid "ion gels" [1-7] to perovskite oxides, particularly $\text{La}_{1-x}\text{Sr}_x\text{CoO}_{3-\delta}$, focused on control of ferromagnetism. Our findings first clarify the complex issue of electrostatic vs. electrochemical gate response, culminating in a picture where electrostatic doping vs. oxygen vacancy creation/annihilation can be qualitatively understood based on bias polarity, and the enthalpy of formation and diffusivity of oxygen vacancies [1-5]. This understanding was achieved *via* a battery of *operando* probes, including synchrotron X-ray diffraction [3,4], polarized neutron reflectometry [3,6], X-ray absorption spectroscopy [5], and X-ray magnetic circular dichroism [5]. Electrical control of magnetism in $\text{La}_{1-x}\text{Sr}_x\text{CoO}_{3-\delta}$ is then demonstrated using predominantly electrochemical [2,3,5] and predominantly electrostatic [2,6] mechanisms. Electrochemical control of Curie temperature is demonstrated over an $\sim 200 \text{ K}$ window [3,5], including a gate-triggered transformation from perovskite to oxygen-vacancy-ordered brownmillerite. Predominantly electrostatic control of Curie temperature is also demonstrated, over a record $>150 \text{ K}$ window, based on a gate-induced cluster percolation mechanism [6,7].

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Electrically-induced ferromagnetism in diamagnetic FeS₂

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Recent years have seen increasingly impressive demonstrations of all-electrical control of magnetism, including electrolyte-gating-induced ferromagnetism in non-ferromagnetic materials. These demonstrations, however, involve induction of ferromagnetism from some other finite-spin magnetic state, *e.g.*, antiferromagnetic, paramagnetic, *etc.* In this work we use ionic liquid gating, which can induce surface electron/hole densities $>10^{14}$ cm⁻², to achieve voltage-induced ferromagnetism in *diamagnetic* (*i.e.*, zero-spin) FeS₂ single crystals. FeS₂ is a 0.95-eV-band-gap semiconducting pyrite material (of high interest for earth-abundant photovoltaics [1-3]), with electronic configuration $t_{2g}^6e_g^0$, resulting in diamagnetism. Electron doping with Co is known to result in rapid stabilization of itinerant ferromagnetism, however, with Curie temperature T_c up to ~ 150 K. Through temperature-dependent transport measurements on ionic-liquid-gated single crystals we first establish a positive-bias-induced insulator-metal transition, accompanied by inversion of the FeS₂ surface conduction channel [2] from *p*- to *n*-type. This transition is found to be remarkably reversible, which, when combined with the delicate nature of surface conduction in FeS₂ single crystals [2], strongly implicates an electrostatic mechanism. Most importantly, anomalous Hall effect measurements reveal an accompanying systematic onset of voltage-induced ferromagnetism, with T_c up to ~ 20 K [4]. One feature of this voltage-induced ferromagnetism from a diamagnetic starting state is that ferromagnetic correlations emerge at high temperatures, while ferromagnetic order occurs at much lower temperatures. This evidences 2D character to the induced ferromagnetism, consistent with the soft nature of the FM. These findings are supported by density-functional-theory-based tight-binding modelling that indicates that Stoner ferromagnetism can be induced by gate-controlled band filling alone [5].

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Monitoring ionic movement in memristive oxide thin film devices by *operando* spectroscopy

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Memristive devices have attracted considerable attention in industry and academia in the last two decades due to their high potential as energy-efficient non-volatile memory or as hardware synapse in neuromorphic circuits [1]. In the most common type of memristive device, the so-called valence change memory (VCM) [2], the field-driven motion of oxygen vacancies causes a valence change in the metal ions and induces thereby strong changes of the electronic conductivity. We have studied the changes of the electronic and atomic structure of different VCM systems such as titanates [3], ferrates [4] and manganites [5] by employing spectroscopic and spectromicroscopic techniques and correlated it to the observed changes in the electronic transport. *In operando* photoemission electron microscopy (PEEM) on SrTiO₃ devices enabled us to determine the oxygen vacancy concentration induced by electrical biasing and how it changes during repeated switching of the device [3]. The observed change of the oxygen vacancy concentration results in a modulation of the Schottky-barrier height at the interface, causing a strongly non-linear change of the resistance. *In operando* hard X-ray spectroscopy of Pr_{1-x}Ca_xMnO₃/Ti devices showed that electrical biasing induces a redox-reaction between the Pr_{1-x}Ca_xMnO₃ and a TiO_x layer formed at the interface [4]. Although the oxygen content of the Pr_{1-x}Ca_xMnO₃ is modulated during biasing, the resistance change during switching is mainly induced by a reversible formation and dissolution of an insulating TiO₂ tunnel barrier at the Pr_{1-x}Ca_xMnO₃ interface. For insulating Brownmillerite SrFeO_{2.5} thin films we could show that a topotactic phase transition to the conducting perovskite is induced during electrical biasing and that the size of the transformed device region depends on the crystal orientation [5]. For both, manganites as well as ferrates, the magnetic coupling is strongly changing with the oxygen content. Therefore electrical biasing provides the possibility to locally modify the magnetic coupling, demonstrating a pathway towards magneto-ionotronics.

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Oxygen-deficient hafnia as a physicist's playground: efficient ReRAM material & binary ferroelectric

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Resistive Random Access Memory (ReRAM) is based on defective oxides: within an initially insulating oxide material, conductive oxygen-deficient filaments are made during the so-called forming step. when local heating in a strong electric field enables ionic transport; this leads to a strong deviation of the stoichiometry in the active area of the device, and, possibly, to formation of multiple phases and/or extended defects. Due to the forming conditions which are far from equilibrium, theoretical investigations that have the purpose of optimizing the ReRAM are quite complicated and linked across multiple length scales. Here, I will present our Density Functional Theory-based study of oxygen-deficient hafnia, which, in combination with an evolutionary algorithm, shows that formation of phases with properties optimal for the resistive switching is possible under specific conditions [1]. I will discuss the structural and electronic properties of these phases as well as to what extent the conclusions are transferable to other oxide materials [2]. Our simulations of the ferroelectric switching in this material, which can explain the measured polarization values as well as the wake-up and fatigue effects observed in real samples [3-5], will also be shown.

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Electro-chemo-mechanical coupling in high surface area materials

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The manipulation of magnetism by ionic approaches requires firstly a scheme for manipulating space charge regions at interfaces and secondly a material in which interfaces abound, so that the local changes contribute significantly to the overall materials behavior. This talk will provide the speaker's perspective of several issues related to these requirements. Firstly, nanoporous metals with a bicontinuous microstructure – consisting of pore and metal as contiguous and interpenetrating phases – can be made by dealloying. The technique provides macroscopic monolithic porous bodies with exceptional homogeneity, reproducibility, and purity. Characteristic structure sizes can be tuned between few nanometers and few micron. These materials can be converted into hybrid nanomaterials by filling the pore space with an ionic conductor, in the simplest case aqueous electrolyte. The capacitive coupling between that ionic conduction path and the electronic one in the metal affords tuning of the local space charge at the internal interfaces, as well as controlled and reversible injection/removal of ions. Secondly, electronic space charge layers at metal surfaces are fascinating objects of study, since the electronic charge is extremely localized – with a characteristic width of less than one interatomic spacing – and, therefore, concentrated. The nature of these layers and of their dependency on the metal and on its surface crystallography have been studied, yet these issues remain poorly understood. Thirdly, electronic as well as ionic exchange schemes involve a strong electrical-mechanic or chemo-mechanical coupling. This is of relevance to magnetism, since the mechanical interactions are long-range. Thereby, they provide one (out of several) mechanism for coupling the magnetism in the bulk of the material to electric phenomena at its surface, and this mechanism is typically strong. There is a robust experimental database for the local electro-chemo-mechanical coupling at interfaces and for how the local effects propagate into the bulk.

Magneto-Ionic Switching of Superparamagnetism

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Nanoporous materials are promising candidates for the voltage-control of magnetism in electrochemical setups due to their large surface-to-volume ratios. Here, we introduce the class of dealloyed nanoporous metals in the field of magneto-ionics. Electrochemical dealloying is a selective corrosion process from an alloy, which allows preparing a great variety of metallic nanoporous structures. While the lesser noble element is gradually removed, the nobler component rearranges during the corrosion process forming nanometre-size ligaments. Inevitably a small fraction of the sacrificial element is buried in 'clusters' under the noble metal surface during dealloying [1], which we utilised for the magnetic functionalisation of our structures. A ferromagnetic sacrificial element in the dealloying process, gives the option to prepare nanoporous structures with embedded magnetic nanoparticles in a one-step process.

In this work nanoporous palladium containing clusters of cobalt -npPd(Co)- is prepared from a CoPd alloy. High-resolution TEM in combination with elemental mapping techniques revealed a residual cobalt concentration of about 8 at% agglomerated in clusters with an average size of 1.5-2 nm. Palladium is not only a high-susceptibility paramagnet attractive for magnetic tuning, but also known for its ability to store large amounts of hydrogen in the crystal lattice. Our magneto-ionic approach attempts to bias magnetic properties of Co-clusters in the Pd-matrix via electrochemical hydrogenation.

Hydrogenation was conducted in an *in situ* electrochemical cell in a SQUID-magnetometer, allowing a direct determination of the changes in magnetisation. Upon voltammetric cycling in the electrochemical hydrogen regime magnetisation was reversibly altered by more than 600%, corresponding to a complete On- and Off-switching of magnetism. A novel magneto-ionic mechanism, based on a RKKY-mediated cluster coupling upon hydrogenation, is proposed to account for the unexpectedly large changes upon hydrogenation [2].

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Solution Processed Nanoporous and Nanocrystal Based Magnetoelectric Materials

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In this talk, we examine multiple ways to control magnetism in solution processed nanostructured materials using an applied electrical bias. We begin with traditional multiferroic coupling, where electricity and magnetism are coupled through strain, and consider two systems. The first is a nanoporous magnetic or ferroelectric network produced using polymer templating of sol-gel oxides. The pores are then conformally filled with the opposite phase (either ferroelectric or magnetic) using atomic layer deposition to produce a three dimensional nanoscale composite. For these materials, we find the largest multiferroic response in materials with partly filled pores, emphasizing the role of residual porosity in controlling the elastic behavior and thus the multiferroic coupling of these composite materials. We next consider strain mediated switching in monolayer nanocrystal arrays. Here we show that nanocrystals can be controllably and reversibly switched from a superparamagnetic state, which has no time-averaged magnetic moment, to a ferromagnetic state using an applied bias. Finally, we explore a new type of multiferroic material, termed granular multiferroics, where exchange coupling between closely spaced magnetic nanocrystals can be modified by tuning the dielectric environment around the nanocrystals using either temperature or an applied electric field. In this work on nickel nanocrystals coupled to a soft ferroelectric, both temperature and field dependent changes in magnetism are observed in the vicinity of the ferroelectric Currie temperature, indicating that magnetism in nanocrystal arrays can indeed be tuned using dielectric changes.

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Voltage-controlled ON switching and manipulation of magnetization via the redox transformation of beta-FeOOH nanoplatelets

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Voltage control of magnetism by ionic approaches, such as the transformation between metal oxide and metal in gated architectures, presents a promising pathway to low-power magnetic devices or magnetic actuation. Up to now, magneto-ionic manipulation has been reported mainly for ultrathin films and nanoporous metal alloy structures.

We investigate paramagnetic beta-FeOOH nanoplatelets as porous starting material, which can be electrodeposited easily and cost-efficiently. Beta-FeOOH is known as porous and electrochemically active material from oxygen evolution reaction catalysis research.[1] These nanoplatelets are polarized in aqueous alkaline solution at room temperature. The voltage-induced structural and morphological changes are probed in detail and correlated to the magnetic changes measured in an in situ anomalous Hall effect setup. This approach, starting from paramagnetic FeOOH, enables complete and non-volatile ON switching of ferromagnetic layers at a low voltage of below -2 V and large reversible magneto-ionic effects.[2] During first reduction we transform beta-FeOOH nanoplatelets into a rough granular Fe layer. This high surface Fe layer is then switched reversibly several tens of times via a redox transformation. As a result, large voltage-induced changes in magnetization are achieved, which exceed those obtained for sputtered Fe films [3] and Fe nanoislands.[4]

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Electric Field Control of Magnetism at Room temperature in Multiferroic Nanocomposite Films without external magnetic field application

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3-1 type multiferroic nanocomposites have been widely studied for the promisingly large magnetoelectric (ME) effects but they usually show large leakage, which hinders the exhibition of large ME responses. In this paper, a three-phase thin film vertically aligned nanocomposites have been developed, which demonstrates significantly improved ME properties at room temperature. A prominent reduction of the leakage is achieved, compared to reference two-phase composites. A phase is added to the two phase system which enable a room temperature exchange bias effect, lower leakage and an additional magnetostrictive (MS) contribution, in addition to the main MS phase. The coupling between the MS phases and a ferroelectric phase which deforms under an applied electric field yields significant electric field control of the exchange bias effect. Furthermore, the effect is a *self-biased* ME effect owing to exchange bias in the system, with coefficient of up to $1.38 \times 10^{-9} \text{ s m}^{-1}$ achieved, large enough to switch the magnetic anisotropy from the easy-axis to the easy-plane. The result is a significant step towards simple magnetoelectric devices for memory.

Ferromagnetic 3D Nano- and Microstructures by Atomic Layer Deposition

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A broad range of potential applications of magnetic nanostructures have been developed in the recent years. Magnetic data storage, microelectronics, or biomedical uses such as cell separation or biosensing present a special interest among these applications. Atomic layer deposition (ALD) is a very suitable method for the conformal deposition of magnetic thin films in pore structures of high aspect ratio, while offering the precise tuning of the layer thickness and high uniformity [1].

By ALD coating of self-ordered Al_2O_3 membranes, arrays of magnetic nanotubes with diameters down to 20 nm and wall thicknesses of less than 5 nm have been achieved [2]. The magnetic properties of the nanotube arrays as a function of wall thickness and tube diameter have been studied by using SQUID magnetometry and compared with magnetic simulations. We will discuss the properties of magnetic multi-layered nanotubes (core-shell) and the application of conformal magnetic coatings of other template systems and 3D nanostructures.

The use of atomic layer deposition is very attractive for the development of magneto-ionic films [3] and 3D microstructures. I will give a general outlook about the potentials for atomic layer deposition in magneto-ionics.

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Role of the electrical properties of substrates in the magneto-ionic behavior of Co_3O_4 thin films

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Voltage-controlled magnetism is expected to allow for ultra-low power magneto-electronic devices via the partial substitution of electric currents by electric fields to manipulate such devices, resulting in a remarkable energy saving. To achieve this, a stable, strong, tunable, and non-volatile magnetoelectric effect to tailor magnetism is crucial for future applications. Electric field control of magnetism through voltage-induced ionic motion (magneto-ionics) is attracting increasing interest driven by its potential for an electrical modulation of magnetism to an extent not attained by other magnetoelectric coupling mechanisms. Recently, we have investigated the role of the electric properties of the substrate in the magneto-ionic behavior of Co_3O_4 thin films. Polycrystalline 110 nm-thick Co_3O_4 films have been grown by atomic layer deposition on either (i) conducting TiN or (ii) insulating SiO_2 . The use of a conducting rather than an insulating substrate boosts magneto-ionics in terms of both generated magnetization (one order of magnitude larger) and speed (35 times faster). Upon gating, transmission electron microscopy and electron energy loss spectroscopy show the emergence of Co-rich areas at a greater intensity for the Co_3O_4 grown on a conducting substrate. This dissimilar behavior between the use of either an insulating or a conducting substrate arises from the intensity and uniformity of the electric field, which are maximized when using a conducting substrate. These results demonstrate the powerful role the substrate plays in modifying the strength and uniformity of the magneto-ionic effect, which is highly desirable for voltage-controlled magnetism applications.

Abstracts of Posters

(in alphabetical order)

Solid-state ionic control of magnetism in systems with perpendicular magnetic anisotropy

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Deterministic and reversible control of magnetic properties using low-energy electric fields is a much-coveted goal due to its potential for achieving low-dissipation, ultra-low power consumption in information technologies. Alongside several mechanisms already available for the control of magnetic properties in spin-based devices, i.e. charge carrier modulation, strain and exchange coupling, solid-state ionic gating offers an additional degree of freedom for the manipulation of these properties through the modification of interfacial magnetic anisotropy, saturation magnetization, Curie temperature, coercivity, or exchange bias, for instance. Here, we present a few examples of materials investigated in the emerging field of magneto-ionics and review the often-concurrent mechanisms underlying the solid-state ionic control of magnetism with a special focus on structures that exhibit perpendicular magnetic anisotropy (PMA). In addition, we propose an experimental process flow for the systematic fabrication and characterization of PMA magneto-ionic devices along with preliminary results.

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Voltage control of magnetism in $\text{La}_{0.67}\text{Sr}_{0.33}\text{MnO}_3/\text{PMN-PT}$ heterostructures

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The demand for energy-efficient devices for future technological applications is driving research in the field of “voltage control of magnetism”. New developments in oxide heterostructures offer great promise for improvements in magnetic data storage, spintronics and high frequency magnetic devices. Most current information storage devices require high current densities to read or write information in the form of local variations in magnetization [1]. Since correlated complex oxides possess strong coupling between lattice, charge, spin and orbital degrees of freedom, they offer the prospect of device concepts based on magnetoelectric (ME) coupling [2]. Here, we report on the growth and characterization of epitaxial multiferroic ferromagnetic/ (ferroelectric, piezoelectric) heterostructures of $\text{La}_{0.67}\text{Sr}_{0.33}\text{MnO}_3/0.7(\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3)-0.3(\text{PbTiO}_3)(001)$: LSMO/PMN-PT(001). Measurements of magnetization, which are performed using SQUID-VSM, reveal ME coupling when a voltage is applied between the layers. Magnetic depth profiles of the heterostructures are obtained using polarized neutron reflectometry, while structural characterization of interfacial morphology is performed using transmission electron microscopy.

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Magnetoelectric effects in nanoporous CoPt microstructures

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The challenge of controlling the magnetic properties of materials by using an electric field, instead of an electric current, has attracted increased attention among the scientific community. Nowadays, most of the magnetic devices are operated via magnetic field, generated via electrical current. Yet, the major drawback is that a large fraction of incoming electric power is wasted in the form of heat dissipation. Hence, it is of great importance to find an alternative for a smarter use of energy in actuating magnetic devices, therefore, the need to investigate new materials and new operating strategies. Here, we present magnetoelectric properties of nanoporous CoPt disks for aspect ratios. The nanoporous disks were synthesized using micelle assisted electrodeposition into pre-patterned substrates. The composition of the electrolyte was formulated to ensure controlled incorporation of oxygen in the deposited material, and hence selective oxidation of part of the metallic alloy. Magnetoelectric experiments were performed using an electrochemical cell, using as a liquid gate an anhydrous propylene carbonate electrolyte. In this configuration, the electric field is generated by the formation of an electrical double layer at the interface between the liquid and the surface of the nanoporous material. We have previously demonstrated that, the presence of nanoporosity strongly enhances the magnetoelectric effect, ensuring that the whole disks are magnetoelectrically active. The magnetoelectric response of the CoPt disks was characterized *in-situ* while applying different electric fields, both by MOKE and by VSM. Interestingly, changes in the coercive field and saturation magnetization have been observed as a consequence of the application of an electric field. These variations are attributed to the effective electric charge accumulation at the surface of the ultrathin pore walls and the concomitant magneto-ionic effect, which results in partial reduction from CoO to Co.

Selective metallization of non-conductive material enabled by a gradient magnetic field application

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Selective metallization of non-conductive material is required for electronic device manufacturing. It is usually achieved by a combination of the photolithography and metal deposition processes. However, this approach is expensive and results in production of hazardous waste. The present research suggest a cost-effective alternative way of selective metallisation. The gradient magnetic field is applied during catalyst deposition, prior to electroless copper plating.

In order to enable interaction with the magnetic field, the standard Pd/Sn catalyst was replaced by a novel magnetic catalyst - Fe_3O_4 - Ag composite nanoparticles. The catalyst was synthesised by a one-pot wet-chemical method. The structure of the material was confirmed by scanning electron microscopy and energy dispersive x-ray spectroscopy. The magnetic properties were confirmed whilst the catalytic activity towards formaldehyde oxidation was proven by cyclic voltammetry.

The gradient magnetic field was achieved by combined application of a permanent magnet and steel template. The distribution of the magnetic field was simulated prior to template fabrication.

The catalyst was attracted by the magnetic field and deposited only at the areas with the maximum magnetic field influence. Subsequent copper electroless plating occurred exclusively at the areas where the magnetic field was applied. Selective electroless copper was deposited in a pattern with mm and sub-mm dimensions.

Growth and characterization of diluted amorphous GeMn thin films

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In diluted magnetic semiconductors (DMS), transition metal ions typically dope a diamagnetic semiconductor host. DMS have received and still arise widespread interest because their magnetic behaviour can be modified in several ways, including interactions with both light and electrostatic fields [1].

This presentation will focus on the results obtained on amorphous Ge-Mn thin films. The amorphous phase was chosen with the aim of avoid as much as possible the formation of transition metal precipitates or transition metal atoms clustering [2] due to the low manganese solubility in crystalline germanium [3,4].

Samples were grown at low temperature (50 °C) in a Molecular Beam Epitaxy (MBE) apparatus on silicon substrates covered with both native and thermal (500 nm thick) silicon dioxide, and were characterised on site using the Reflection High Energy Electron Diffraction (RHEED) technique.

Transmission Electron Microscopy (TEM) was exploited to check the homogeneity of as-grown thin films. The magnetic properties were investigated by means of a Superconductive Quantum Interference Device (SQUID); selected results will be reported about isothermal magnetization loops up to 70 kOe and FC/ZFC magnetization curves. The results are compatible with a granular behaviour of the as-prepared films, with a blocking temperature of the order of 20 K. The origin and nature of this granular behaviour will be discussed.

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Two-Dimensional Magnetic Mesocrystals for Bit Patterned Media

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The increasing demand for hard drives with higher storage density has motivated a technology shift from continuous magnetic media to bit patterned media (BPM), in which one single bit of information is stored in an individual nanostructure. At the present research and development stage, BPM is fabricated using a combination implementation of e-beam lithography, template fabrication, nanoimprint and magnetic film evaporation, and these isolated islands on BPM exhibit polycrystal structure. However, these polycrystal islands suffer from non-uniform microstructure, which inevitably results in variation of magnetic anisotropy among islands, which in turn leads to wide variation of switching field that affects the addressability of individual predefined bits and may cause overwriting of adjacent bits.

In this work, we have developed a new method to fabricate 2D magnetic mesocrystals consisting of monodisperse CoFe_2O_4 (CFO) nanomagnets. The monodisperse CFO nanomagnets are single crystal with uniform pyramid-like shape and specific crystallographic orientation, and fully relaxed. All of these features should play positive roles in eliminating the intrinsic SFD for BPM application. Furthermore, systematic characterizations confirm the switchable single domain state (Fig. 2), good thermal stability and large magnetic anisotropy, which should satisfy the demands of storage medium. The method shows great flexibility in controlling the island size. Last but not least, if combined with nano-patterned substrates, ordered nanomagnet arrays can be fabricated. The technique reported here is definitely of interest for both fundamental study and technology development.

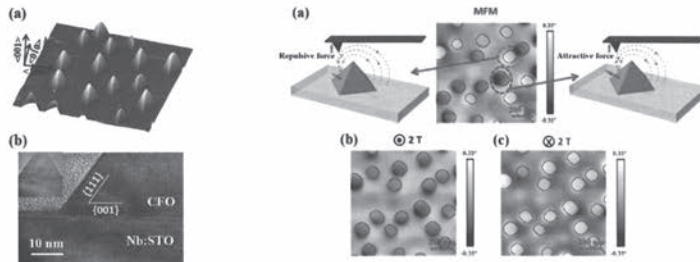


Fig.1 Structure of the CFO mesocrystals Fig.2 Magnetic property of the CFO mesocrystals

Tailoring of exchange bias in thin film systems via electrochemical transformation of the ferromagnetic layer

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In recent research targeted modification of the interface related Exchange Bias (EB) effect in magnetic thin film systems plays a crucial role in designing artificial magnetic stray field landscapes which can be employed in e.g. biomedical point-of-care diagnostics or switchable light diffraction gratings [1,2]. In this regard, the challenge of tuning the EB in a reversible and non-volatile manner opens up exciting prospects with the application of magnetoionic approaches potentially playing a key role in overcoming present obstacles. Hence in this work, we demonstrate an electrochemical routine for the electric control of EB by a Redox transformation of the ferromagnetic layer in a FeO_x/Fe/IrMn based thin film system [3].

Here, alteration of EB is achieved by increasing the Fe layer thickness through an initial reduction of the native oxide exploiting the correlation between EB strength and ferromagnetic layer thickness. This mechanism is confirmed by magnetic and structural characterization of a prototype system. It can be shown, that alternate applications of reduction and oxidation potentials lead to a reversible modification of EB, thus, emphasizing the potential use of this procedure in realizing dynamically on and off switchable magnetic stray field landscapes. Picking up on this, the influence of thin film architecture on the here investigated tailoring of EB and a proposed structuring of EB systems magnetically with the presented technique will be discussed.

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Poly-(2-ethyl-2-oxazoline) as a novel additive for Room Temperature Electrodeposition of Nickel

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Nickel coatings are widely used in various applications due to their decorative, superior electromagnetic, corrosion and wear properties. Structural properties of electrodeposited Ni coatings are strongly affected by chemical composition of deposition bath, pH and temperature of the deposition bath and deposition current densities. The presence of additives in deposition bath strongly affects the properties of electrodeposited Ni coatings. These additives impart levelling, improve the tensile strength, ductility, refine grain structure and act as brighteners. There is continuous need of novel additive [1, 2] to produce high quality thin films but without adversely affecting the magnetic properties of the layers.

Small grain sized, hard, smooth and bright electrodeposited Ni coatings with great interfacial adhesion were produced by Watt's type bath containing Poly-2-ethyl-2-oxazoline (PEOX) as a novel bath additive. The effect of PEOX in combination with current density on electrodeposition, surface morphology, hardness, brightness, and corrosion resistance of electrodeposited Ni coatings was investigated by surface analysis and electrochemical techniques. SEM and AFM images showed that the surface roughness is decreased by the addition of PEOX in deposition bath. XRD, microhardness and UV-Vis measurements showed that the progressive addition of PEOX in deposition bath resulted in preferred orientation of electrodeposited Ni coating from (111) and (200) to (220) planes. The nickel layers were built up from very fine grains (~7 nm) and the combination with highly oriented structure resulted in bright, high hardness (6.5 GPa) films.

The assembly of the magnetic domains in highly oriented nano-crystalline films were investigated with Magnetic Force Microscopy measurements and were compared with traditionally deposited nickel layers.

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Degradation mechanism and way of surface protection of nickel nanostructures

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Stability of nanomaterials during their life cycle is a crucial problem of modern nanoscience [1]. In order to understand the processes, which are going in the nanostructures, the comprehensive study of the influence of media with different acidity on the nickel nanotubes morphology and structure was carried out. On the base of the analysis of nanotubes characteristics, sequential evolution of degradation stages involving the surface passivation, formation of point defects, pitting and destruction of nanotubes walls was determined. The results are of importance for the wide range of potential nickel nanostructures applications, which are associated with their using in real-life conditions. To improve Ni nanostructures stability, the possible ways of surface protections from the aggressive environment effect and the routes of nanostructures covering with gold, organosilicon compounds and polymer coatings were considered. Demonstrated approaches for nanostructures covering provide an opportunity of surface functionalization for attaching of different molecules, that can be useful for targeted delivery of drugs and genes, biodetection, bioseparation and catalysis application [2,3].

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Growth and magnetic characterization of germanium manganese Quantum Dots

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Germanium-manganese alloys are an interesting playground for fundamental studies on the physics of magnetic interactions. It is also well known that the physical properties of a material are usually changed by nanostructuration. However, a proper combination of high density and low sizes of the nanostructures is required to effectively affect the physical properties of a material [1].

In this work, molecular beam epitaxy (MBE) has been employed to grow nanostructured crystalline GeMn alloys in the form of Q-Dots through a 3-step process. First, we oxidized a silicon substrate surface and then, with a dip in a diluted HF solution, this oxidized layer was etched, simultaneously creating a clean hydrogenated surface [2]. GeMn Q-Dots were then grown in a self-assembled mode by exploiting the Stranski-Krastanov epitaxial growth. We were able to synthesize denser Q-Dots arrays and control the substrate surface by hydrogen thermal desorption.

Samples were characterized both on site by means of Reflection High Energy Electron Diffraction (RHEED) and ex-situ by Scanning Electron Microscopy (SEM, figure 1a). Atomic Force Microscopy (AFM) was used to measure size and density of nanostructures (figure 1b). Magnetic hysteresis loops were obtained between 2.5 and 300 K under a maximum applied field $H = 70$ kOe; some selected results are shown in figure 1c. The unsaturating behaviour of $M(H)$ emerging at low temperature may be related to disordered magnetic states at the Q-dot surfaces.

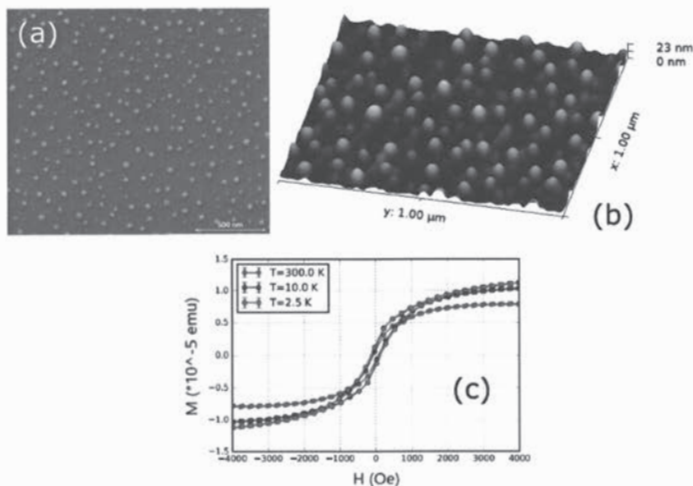


Figure 1: (a) SEM image, (b) corresponding AFM 3D image and (c) hysteresis loops of a Q-Dots

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Atomic-Scale Control of Exchange Bias at BaTiO_3 - $\text{La}_{0.67}\text{Sr}_{0.33}\text{MnO}_3$ interface

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The atomic-scale interfaces of 3D transition-metals oxides are the fascinating playground for atomic-scale interaction of spins. New physical phenomena originate at such interface has huge potential for next-generation nanoscale spintronics devices. Examples of such intriguing phenomena include magnetoelectric coupling, unconventional exchange coupling, etc. Among them, exchange bias is the most studied due to its importance for device applications such as high-density memory and sensor. Here, we demonstrate exchange bias coupling (exchange bias shift, $H_{\text{EB}} \sim 40$ Oe at 2 K) at the interface of epitaxially grown ferromagnetic $\text{La}_{0.67}\text{Sr}_{0.33}\text{MnO}_3$ (LSMO) – ferroelectric BaTiO_3 (BTO) bilayer thin films on SrTiO_3 (STO) single crystal substrates in absence of any conventional antiferromagnetic material. Such exchange bias is only observed when the thickness of LSMO is only a few unit cells ($<10\text{nm}$). Importantly, we find that the exchange bias coupling follows training effect, bias field dependency, and temperature dependency. By X-ray magnetic circular dichroism (XMCD) measurement, it is observed that in such epitaxial heterostructure Ti of BTO poses magnetisation at 2K and can reversibly switch between two distinct magnetization states by switching magnetic field. A remanent magnetization (M_{R}) in Ti is also observed. The magnetization of Ti as well the exchange bias vanishes at high temperature (300K) which confirms the exchange bias coupling between Ti of BTO and Mn of LSMO at low temperature. This is an important step towards creating exchange bias coupling between ferromagnetic and ferroelectric materials without conventional antiferromagnetic materials, which may enable a new class of multi-state memory devices by switching magnetization, ferroelectric polarisation and exchange bias coupling in the same device.

References:

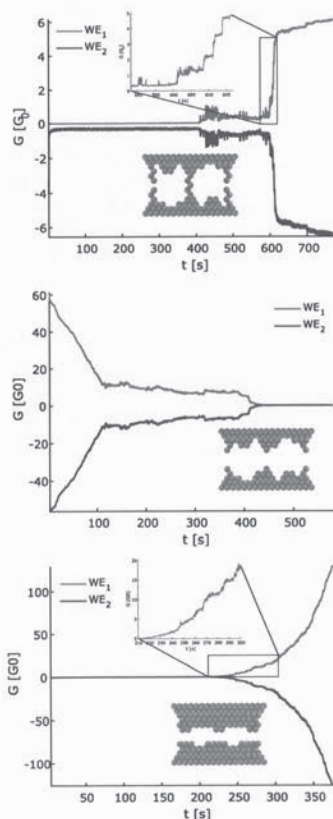
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Electrodeposition of Magnetic Nanostructures

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AuNaS₂O₃, commonly used for cyanide free gold plating, has been found to exhibit excellent deposition quality at the nanoscale. In this work, this complex is used in combination with Ni to grow magnetic superlattices and layered nanowires from a single electrolyte solution. Similar structures grown with Cu and Ni exhibit anisotropic magnetoresistance (AMR) and giant magnetoresistance (GMR) with the addition of Co. The gold compound gives high quality films but the magnetic properties of the Ni film with Au and S inclusion are investigated using a vibrating sample magnetometer (VSM), magnetoresistance measurements and energy dispersive X-ray spectroscopy (EDS).



Additionally, the compound is used to reduce the separation between the metal layers of a metal-insulator-metal structure (MIM), down to less than a nanometer. Such a structure can be used for molecular conductance measurements, and when the metal layers are ferromagnetic, the structure forms a robust molecular spin valve for molecular spin transport studies. The changes in conductance of the MIM during deposition on the two separate metal layers shows conductance quantum steps in the first deposition, and an exponential trend after repeated making and breaking of metallic contacts (see figure). This behavior can be explained by a near dendritic growth of the gold contact, which is annealed after cycling, resulting in an average separation where tunneling transport becomes dominant. Similar Ni contacts will also be investigated.

Porous GaAs layers and nanostructures decorated with magnetic materials

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Herein, we present the results of the elaborated technology of the triangular GaAs nanowires obtaining via one step anodic etching of bulk GaAs substrates. In comparison to other techniques, electrochemical etching is easy, cost-effective and very fast. The nanowires obtained by using different growth techniques have crystallographic defects due to impurities from electrolytes, precursors and different transport gases in the growth process. The idea of the elaborated technology is that the nanowires are not grown, but the space around of nanowires or ultrathin walls is etched. The following electrolytes have been used in the investigations: HCl, HNO₃, HBr, and environmentally friendly electrolyte based on NaCl. The shape of obtained GaAs nanowires is triangular in contrast to the circular shape of nanowires obtained by traditional techniques. The diameter of nanowires can be modified by concentration of the electrolyte and applied potential. The difference between the crystallographic orientations is that for (111)B GaAs the nanowires are oriented strictly perpendicular to the top surface and for (001) GaAs crystals the nanowires are tilted and are more parallel to the top surface. The length of the resulted nanowires on (111)B GaAs for 40 min of anodization is around 260 μm.

We used GaAs crystals with (001) [1] and (111) orientations and demonstrated that it is possible to obtain different shapes of deposited Fe. Also the experimental results for deposition of magnetic nanodots (Fe, Ni, Co) via electrochemical deposition on the 1D nanostructures are presented.

The crystallographic orientation of used crystals has pronounced influence not only on electrochemical deposition but also on electrochemical etching. It was established that during the electrochemical etching on (001) GaAs crystals the nucleation is in the form of the rectangle, while in the (111)B is triangular. These structures may be interesting as starting material for magneto-ionics to study geometry effects and go towards 3D magneto-ionics.

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Detection of the interfacial exchange field at a ferromagnetic insulator-nonmagnetic metal interface with pure spin currents.

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Interfacial spin-orbit and exchange fields at the surface of a ferromagnetic insulator can be studied with the help of a lateral spin valve (LSV) device [1]. We report spin transport measurements in LSV devices where the Cu spin transport channel is in proximity with ferromagnetic insulators, EuS (EuS-LSV) and yttrium iron garnet Y₃Fe₅O₁₂ (YIG-LSV). The spin signals in these LSV devices were compared with reference devices fabricated on nonmagnetic Si/SiO₂ substrate with MgO or AlO_x capping. The spin signal was found to be suppressed in the EuS-LSV and YIG-LSV compared to the reference LSV (Fig. 1(a)). We also found a widely observed low temperature peak in the spin signal at $T \sim 30$ K is shifted to higher temperature in the LSV devices in contact with EuS or YIG (Fig. 1(b)). These ancillary spin transport features can be explained by considering additional spin relaxation arising from fluctuating exchange field at the Cu-EuS (or Cu-YIG) interface.

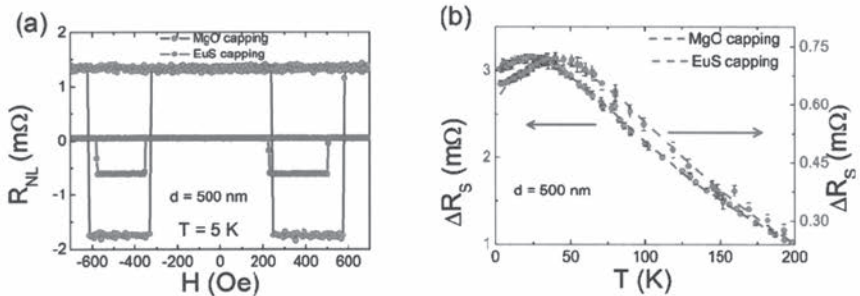


Fig. 1(a) Nonlocal resistance R_{NL} measured at 5 K for LSV devices fabricated on Si/SiO₂ substrate with 3 nm MgO (blue) and 5 nm EuS (red) capping. (b) Temperature-dependent spin signal ΔR_S for the same LSVs with injector-detector distance $d = 500$ nm.

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Tuning magnetic anisotropy and skyrmion stability with electric field

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In 2017, some of us showed that the nucleation and annihilation of skyrmion bubbles can be controlled by electric field (1). This is an easily integrable and energetically efficient solution that might ease the use of magnetic skyrmions as information carriers in future spintronic devices. In that work, skyrmion bubbles having 1-2 micron size were studied in Pt/Co/AlOx trilayers by magneto-optical Kerr microscopy. In this poster presentation, we will show our present efforts to extend this concept to smaller skyrmions, down to 50nm sizes. For this, we have chosen the Pt/Co(1nm)/MgO system, in which we showed that sub-100nm skyrmions can be stabilized at room temperature (2).

The thin films were patterned into stripes (50um to 0.5um width) by electron beam lithography and ion beam etching, and covered with a 10nm thick ZrO2 dielectric layer. Using MFM imaging, we could show that starting from a stable skyrmion network (at zero field), a positive electric field leads to the increase of the perpendicular magnetic anisotropy and to the annihilation of the skyrmions. This result is confirmed by the variation of the hysteresis loops taken with polar MOKE. Probably due to the stabilization of the stable, stoichiometric MgO phase induced by oxygen migration, the process has been found to be irreversible. On the contrary, for Pt/Co/AlOx trilayers patterned using the same process as Pt/Co/MgO and using the same dielectric layer, the electric field allows us to tune reversibly the nucleation and annihilation of magnetic skyrmions. This is probably due to the fact that oxygen migration does not occur within the AlOx layer. This work is in progress.

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Voltage Controlled Magnetism in Iron Oxide/Iron Nanostructures

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Voltage control of magnetism by ionic approaches, such as the transformation between metal oxide and metal in gated architectures, presents a promising pathway to low-power magnetic devices. Up to now, magneto-ionic manipulation has been reported mainly for ultrathin films and nanoporous structures.^[1-3] Since the mechanism is based on electrochemical charge transfer at the electrode/electrolyte interface, the morphology may be key to the magneto-ionic efficiency.

We investigate the influence of morphology during electrolytic gating by comparing sputtered continuous and electrodeposited granular FeO_x/Fe films. The variation of deposition conditions and substrate allows us to synthesize nanostructures with different morphologies, ranging from hemispherical nanoparticles to nanocuboids.^[4] In nanoislands, the voltage-induced magnetic changes are enhanced compared to continuous films and close to ON/OFF switching of magnetization is achieved.^[5]

In particular, patterning techniques, based on UV lithography and ion etching, will be discussed to obtain precisely aligned structures, like antidot areas, to further enhance the magneto-ionic efficiency.

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Voltage-induced hydrogen loading and magnetic changes in electrodeposited Fe/Pd-bilayers

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Oxygen-ions are currently the most-studied ions for magneto-ionic switching of magnetism. There are current efforts in replacing it with the smaller and therefore faster hydrogen. In our study, we utilize iron as magnetic material and palladium as hydrogen storage layer to achieve a simple magnetization-changing device. The electrodeposition of the Fe/Pd layers was carried out in a liquid electrolyte using a three-electrode-system. The Pd protected Fe layers are stable against oxidation in air and oxidative potentials. Subsequent studies on the hydrogenation of the Fe/Pd layers revealed the electrochemical conditions required to avoid both hydrogen embrittlement and Fe dissolution. First results of in-situ magnetization measurements show reversible magnetization changes by voltage-induced hydrogenation.

Ferroelectric switching in ε -Fe₂O₃

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Isostructural Ga_{0.6}Fe_{1.4}O₃ (GFO) [1] and \square -Fe₂O₃ (eFO) [2] are known as rare representatives of room-temperature multiferroics, simultaneously combining ferroelectric and ferromagnetic ordering. This makes them prospective materials for electronic devices with functionality based on multiple ferroic orders, such as the multistate non-volatile memory cells.

In contrast to GFO, where disorder in the occupancy of Ga and Fe sites is presented, the eFO is a fully ordered compound. In order to understand the microscopic mechanism of ferroelectric switching in these materials, we employ an evolutionary algorithm [3] to explore possible structures as a function of the relative ordering of Ga and Fe cations in GFO, as well as the evolutionary metadynamics [3] to model ferroelectric domain switching in eFO. This allows us to understand the role of disorder in possible ferroelectric properties and to develop the criteria to maximize the effect.

We will show the condition, at which the proper ferroelectricity arises in GFO and eFO multiferroics and characterize the parameters of the ferroelectric phase transition. We will compare our theoretical results with recent experimental observations [4].

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ENHANCING MAGNETIC MATERIALS AT THE ATOMIC SCALE USING LIGHT ION IRRADIATION

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Ultra-thin films with Perpendicular Magnetic Anisotropy (PMA) are considered as the most promising candidates for the next generation of ultra-high density Magnetic Random Access Memory (MRAM) devices. One crucial issue for MRAM technologies is to better understand and minimize the role played by structural inhomogeneities at interfaces that induce a distribution of magnetic properties and stochastic behavior.

Light ion (He) irradiation is an elegant tool to address this issue. Since only interatomic displacements are induced with no cascade collisions, light ion irradiation allows controlling at the atomic scale the magnetic properties of magnetic thin films and multilayers [1-6].

In this study, we have combined TEM structural characterization and magnetic characterization to investigate the effect of He ion irradiation on both the structural and magnetic properties of CoFeB-MgO ultra-thin films with PMA, which are considered as the best materials for MRAM applications. We demonstrate that using He ion irradiation, crystallization of CoFeB-MgO layer can be obtained at much lower temperatures than pure annealing with higher anisotropy value. This suggests a pathway to optimize MRAM devices by using He ion irradiation. Furthermore, irradiation through a mask creates local modulation of magnetic anisotropy that can bring new functionalities for memory and logic applications.

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Proton dynamics in a solid oxide hydrogen nanobattery

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The growth of computing power in mobile devices, together with miniaturization has imposed increasingly stringent requirement on power sources in terms of size and capacity. In this work, we demonstrate for the first time a solid state nanobattery based on hydrogen storage with a cell dimension down to 20nm, which is the thinnest battery reported in literature. The battery is based on a hydrogen loading mechanism that has previously been used to switch magnetic anisotropy in a ferromagnetic film [1]. It exhibits a peak volumetric power density of 2500 $\mu\text{W}/\text{cm}^2\cdot\mu\text{m}$, which is two orders of magnitude larger than most microbatteries. The battery has a very simple structure, consisting only of an oxide layer sandwiched by two metallic electrodes and can be easily fabricated using standard thin film processes. Because of this, the nanobattery can be fabricated on both rigid and flexible substrates or deposited as a coating, allowing for a wide range of applications. Previous work has shown that exposure of the metal oxide electrolyte to high humidity causes a phase change and affects the hydrogen conduction properties of the oxide [2]. We evaluate the performance of the battery and use electrochemical, magneto-optical, and x-ray and neutron reflectometry techniques to characterize the structure of the oxide and the movement of protons during charge and discharge. This work provides insight into the role of hydrogen in metal oxide thin film devices during voltage gating, and these insights can be applied to a range of magnetic switching devices that operate using this same hydrogen loading mechanism.

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Reversible control of magnetism: on the conversion of hydrated FeF₃ with Li to Fe and LiF

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Materials with tailorable and tunable properties are receiving great interest in materials science. The possibility to tailor or tune properties is a desired feature for the development of functional materials for various applications. While tailoring means generating a specific structure or architecture of the material to achieve a certain property, the tuning concept addresses reversible changes of properties by means of an external control parameter. One possibility to reversibly change the characteristics of a material is to vary the magnetic interactions between electrons, thus leading to different types of magnetic responses in a magnetic field. This concept of magnetization tuning has been shown e.g., magnetoelectric coupling at ferromagnetic/ferroelectric interfaces.¹⁻⁵

Conversion-type electrode materials are prominent examples of potential Li-ion battery cathodes and/or anodes with large specific capacities. Conversion reactions often rely on complete reduction or oxidation of a transition metal, leading to multi-electron redox processes per formula unit, accompanied by changes of crystal structure and electronic configuration and, consequently, of materials properties such as magnetization. Here, we report on the utilization of the FeF₃/Fe conversion reaction to reversibly control the magnetization. Hydrated FeF₃ was chosen as electrode material and the changes in magnetization upon reversible redox reaction against Li counter electrode monitored by means of Superconducting Quantum Interference Device magnetometry (SQUID). *In situ* measurements provide insights into the changes in magnetization occurring during the conversion reaction, specifically revealing the transition from paramagnetism to ferromagnetism.

In the present work, the concept of *in situ* monitoring the lithiation of an electrochemically active material is extended from the intercalation approach to the reversible conversion approach. These measurements were performed by coupling SQUID magnetometry with cyclic voltammetry (CV) measurements. The changes in magnetization during the reversible FeF₃/Fe conversion were tracked and the features assigned to the respective increase and decrease of current during cycling operation.

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Disentangling Highly Asymmetric Magnetoelectric Effects in Engineered Multiferroic Heterostructures

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One of the main strategies to control magnetism by voltage is the use of magnetostrictive-piezoelectric hybrid materials, such as ferromagnetic-ferroelectric heterostructures. When such heterostructures are subjected to an electric field, piezostain-mediated effects, electronic charging, and voltage-driven oxygen migration (magnetoionic) may simultaneously occur, making the interpretation of the magnetoelectric effects not straightforward and often leading to misconceptions. Typically, the strain-mediated magnetoelectric response is symmetric with respect to the sign of the applied voltage because the induced strain (and variations in the magnetization) depends on the square of the ferroelectric polarization. Conversely, asymmetric responses can be obtained from electronic charging and voltage-driven oxygen migration. We engineer a ferromagnetic-ferroelectric hybrid consisting of a magnetically soft 50-nm thick $\text{Fe}_{75}\text{Al}_{25}$ (at. %) thin film on top of a $\langle 110 \rangle$ -oriented $\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3\text{-}32\text{PbTiO}_3$ ferroelectric crystal, a highly asymmetric magnetoelectric response is obtained and the aforementioned magnetoelectric effects can be disentangled. Specifically, the large thickness of the $\text{Fe}_{75}\text{Al}_{25}$ layer allows dismissing any possible charge accumulation effect, whereas no evidence of magnetoionic is observed experimentally, as expected from the high resistance to oxidation of $\text{Fe}_{75}\text{Al}_{25}$, leaving strain as the only mechanism to modulate the asymmetric magnetoelectric response. Along the in-plane $[001]$ direction of the ferroelectric crystal, the remanence of the hysteresis loops follows a butterfly-like dependence with the applied electric field, while, along the $[1-10]$ direction, a non-volatile loop-like behaviour is observed. The origin of this asymmetric strain-induced magnetoelectric effect arises from the asymmetry of the polarization reversal in the particular crystallographic orientation of the ferroelectric substrate.

Electrodeposition of Co-Fe alloy 1D nanocone array inside AAO template with superimposed magnetic field

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Porous anodic alumina oxide (AAO) fabricated in two-step anodization is widely used to fabrication template for synthesis of ordered arrays of one-dimensional (1D) nanostructures such as nanotubes, nanopores, nanodots and nanocones. These materials are characterised by better catalytic properties than bulk material due to their large active surface area and small geometrical size [1]. By the controlling of anodization conditions or applying an appropriate post-anodization treatment the internal pore structure can be changed. Conical pores can be obtained basing on alternating repetition of the anodization in oxalic acid and pore widening process in phosphoric acid. To obtain free standing nanocones the Al_2O_3 template has to be chemically etched.

Co-Fe alloy nanocones electrodeposition were carried out using AAO templates. The magnetic field with different intensity has been superimposed during electrodeposition. The magnetic field lead to change hydrodynamic conditions during electrochemical process. This cause the modification of morphology and composition of nanocones. The electrocatalytic properties of synthesised nanostructures were measured in 1M NaOH and compared with bulk materials. The active surface area of samples were calculated from SEM photos.

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Transition of the magnetic exchange coupling induced by oxygen vacancies in $\text{La}_{0.7}\text{Sr}_{0.3}\text{MnO}_3$ thin films

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Voltage-driven migration of oxygen vacancies (V_O) in magnetoelectric (ME) complex oxides can have considerable effects on chemical and magnetic properties, which can find its potential use in ME spintronics. Here, we report on the strong correlation of the electronic structure and the magnetism of a resistively switched $\text{La}_{0.7}\text{Sr}_{0.3}\text{MnO}_3$ thin film, grown by pulsed laser deposition on a conductive niobium doped SrTiO_3 (1 0 0) substrate, using spatially resolved X-ray absorption (XAS-PEEM) and magnetic circular dichroism (XMCD-PEEM). The electric field induced migration of oxygen vacancies leads to significant spectromicroscopic changes, reflecting a significant valence change, a metal-to-insulator transition, and a change of the magnetic coupling mechanism. Depending on the applied voltage polarity an incorporation/removal of oxygen ions in the bulk is expected. Since the presence of V_O disturbs the double-exchange mechanism, which is responsible for the conductivity and the ferromagnetism inside the LSMO, this incorporation/removal goes along with a local decrease/increase in conductivity. The formation of V_O can be directly derived from the O K-Edge, and indirectly from valence changes apparent in the Mn L (2p to 3d) absorption spectrum in LSMO. Our findings reveal a clear emerging Mn^{2+} contribution for the HR state, which is proven by significant changes in the linear fingerprints of the Mn $L_{3,2}$ - and O K-edge. As a consequence thereof, the XMCD signal shows a reduced magnetic moment and also a change in the spectral shape, indicating a new ordering of the magnetic structure.