

# **3rd internal biennial science meeting of the MLZ**

Monday, 19 June 2017 - Thursday, 22 June 2017

Seminarhaus Grainau

## **Book of Abstracts**



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## Departure: Gate FRM II

Plenary Session / 43

### Welcome

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Plenary Session / 10

## Chemical analysis with neutrons: from activation analyses to neutron depth profiling

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When an atomic nucleus absorbs a neutron, the excitation energy is emitted in different forms of characteristic radiation. In most cases, prompt and delayed gamma rays are released, whose energy identifies the nuclides, and their intensity is proportional to their amounts, i.e. chemical analysis can be performed when using gamma spectrometry. More than 80 years after its discovery, neutron activation analysis is still one of the most sensitive analytical techniques for trace elements, while prompt gamma activation analysis is suitable for the bulk analysis of the matrix components. With the combination of the activation analyses, a broad range of samples have been analyzed in archaeometry, geology, material science, investigating the contents of closed container, or following in situ chemical processes.

Charged particles are sometimes also released after the neutron capture and their detection opens new horizons in nuclear analytical techniques. The detection of beta particles following the radioactive decay enable the determination of components not emitting (strong enough) gamma radiation. Neutron Depth Profiling has been successfully used in the investigation of the distribution of B, Li, and N in thin layers for decades, and recently, the interest has further increased because of its prosperous use in the investigation of Li-ion batteries.

Plenary Session / 44

## MLZ Sample Environment

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Parallel Session / 47

## **Input for plenary discussions the following days**

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## **Overview ESS**

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Plenary Session / 80

## **Iron-based superconductors**

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The discovery of iron-based superconductors in 2008 has attracted worldwide attention in the unconventional high-temperature superconductivity research. Among various classes of Fe-based superconductors, the ternary “EuFe<sub>2</sub>As<sub>2</sub>” system is a unique representative, due to the two magnetic sublattices and the strong coupling between spin-, lattice- and charge degrees of freedom. Superconductivity can be achieved in this system by chemical substitution or applying external pressure. In this talk, I will talk about how the superconductivity and magnetism can be tuned by means of chemical doping or physical compression and how they are correlated, by presenting some recent progresses on iron-based superconductors from Quantum Phenomena Group at MLZ.

Parallel Session / 25

## **Following the Formation of Metal Electrodes for Organic Photovoltaics**



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With their easy processability, high flexibility and tunable optical properties, organic photovoltaics offer a wide range of potential applications. Although based on organic materials, photovoltaic devices typically contain metal contacts due to their unrivaled electronic conductivity. These contacts have a major influence on the solar cell performance. Our work focuses on the nanostructure evolution of metal-polymer interfaces inherent in organic solar cells. We follow the morphological changes during the sputter deposition of metal electrodes onto photoactive layers using in-situ GISAXS and GIWAXS. This technique allows us to investigate the deposition process with a high spatial as well as temporal resolution. Comparing the deposition behavior of typical electrode materials (such as Au or Al) on thin films of photoactive organic materials (e.g. PTB7) helps to understand their influence on the respective photovoltaic performance.

**Parallel Session / 54**

**TBD**

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**Parallel Session / 86**

**Horizontal Magnet**

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**Parallel Session / 18**

**Morphology improvement of ZnO/P3HT-b-PEO bulk heterojunction films by using a low temperature route**

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Hybrid solar cells, a combination of conventional inorganic and organic photovoltaic systems, offer outstanding potential due to their minor investment compared to inorganic solar cells and higher stability compared to organic solar cells. However, so far device efficiencies are significantly lower as compared to the other photovoltaic systems. A possible way to improve the film structure and thereby the device efficiency is to introduce amphiphilic block copolymers into the sol-gel synthesis of the inorganic part such as ZnO. Unlike the traditional diblock copolymer, in the present approach we make use of a new functional block copolymer PEO-b-P3HT. In the PEO block the ZnO phase is synthesized and the P3HT block can be used directly as the hole transporting layer. The nanostructure inside thin films is probed with GISAXS. Moreover, SEM and AFM detect the surface morphology of the composite films. The crystallization of ZnO nanostructures are examined with XRD and the thickness is investigated by profilometry measurements.

**Parallel Session / 87**

## 15 T SANS magnet

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## Neutron Imaging at the ESS: The ODIN Project

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ODIN (Optical and Diffraction Imaging with Neutrons) is a beamline project at the European Spallation Source (ESS). It is a collaboration between the ESS, PSI and TUM, with TUM as lead institution. ODIN will provide a multi-purpose imaging capability with spatial resolutions down to the  $\mu\text{m}$ -range. The pulsed nature of the ESS source will give access to wavelength- resolved information. Different imaging techniques, from traditional attenuation-based imaging to advanced dark field, polarized neutron or Bragg edge imaging, will be available within the full scope of ODIN with unprecedented efficiency and resolution. As a multi-purpose imaging instrument ODIN is designed to satisfy a wide range of scientific needs. Given the wide range of applications in various scientific fields, only a few examples will be given alongside the conceptual design of the instrument.

**Parallel Session / 26**

## Monitoring the swelling behaviour of PEDOT:PSS thin films under high humidity conditions

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Towards flexible substrates for organic light emitting diodes and organic photovoltaics it is of significant interest to replace brittle and costly electrodes like ITO or FTO as well. PEDOT:PSS offers with its good conductivity, easy processibility, and inherent flexibility a suitable alternative to its rigid and transparent conducting oxide counterparts.

The hygroscopic behavior of the PSS content yields a high potential water uptake of the PEDOT:PSS electrode itself. This is known to have an influence on its electronic conductivity but also on its film thickness. Furthermore, an increasing film thickness due to water uptake may lead to stress onto the organic devices and their containing layers, which yields an additional failure potential due to mechanical stress.

Hence, in-situ time of flight neutron reflectometry measurements were performed on different PEDOT:PSS films, which were exposed to high moisture conditions. By monitoring the swelling behavior of the spin-coated thin films, we were able to follow the thickness evolution and the water

uptake of the film regarding to the ambient relative humidity conditions.  
The experiments were conducted at the REFSANS beamline at FRM II, Garching.

**Parallel Session / 29**

## Manipulating the morphology in printed organic solar cells

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The nanomorphology can strongly influence the physical properties of organic thin films. For example, polymer:fullerene blends used in organic photovoltaics vary significantly in performance depending on the inner film morphology. To allow large-scale production of these devices, control of the nanostructure during the processing of the active layer is important. This needs an understanding of the processes involved during the drying of the film. Using an industrial slot-die coater implemented into a synchrotron beamline we have successfully characterized the solidification process of an active layer using grazing incidence small and wide angle X-ray scattering (GISAXS/GIWAXS). We use the gained knowledge to further manipulate the structure of printed organic thin films by external intervention while printing. With this manipulation, we are able to positively influence the morphology and thus the performance of the produced devices.

**Parallel Session / 88**

## 25 T Magnet

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**Parallel Session / 79**

## Neutron activation analysis (NAA) for the materials investigation: from high-temperature gas turbine to micro electronics

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Neutron activation analysis is a very sensitive method to determine main, minor and trace elements in materials. The FRM II offers a series of irradiation facilities with different neutron fluxes and properties for the multi-elements analysis. The presentation will introduce some projects to demonstrate the diverse applications of NAA.

Manufacturing of special alloys for the new generation of high-temperature gas turbines is a current research area. The concentration of components is determined by using NAA in some Co-Ta-alloy

samples. Due to the high density of such materials, the gamma-ray Gamma ray attenuation during the gamma-counting should be corrected. A new practical method using internal standards is developed for the calculation of the detector efficiency curve.

The micro electronic industry requires more and more high purity silicon materials. Trace elements with concentrations lower than 1 ppb (10E-9) can be determined using NAA after long time irradiations in high flux neutron field. Analysis of tail material of Si crystal after float-zoning process can give a new quality control method of semi-conductor starting materials.

**Parallel Session / 32**

## Water-processed hybrid solar cells

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*in situ* studies of particular fabrication steps

### Summary:

Particular environmentally friendly processing of hybrid solar cells with the solvent water is feasible with an active layer consisting of laserablated titania and a water-soluble polythiophene [1]. One way to optimize conversion efficiencies of these devices is the introduction of a vertical compositional gradient of the two components of the active layer. Dip-coating and spray-coating have been utilized as techniques which are suitable for the cost-effective preparation of hybrid photovoltaics. We followed the development of the morphology during spray deposition *in situ* with high spatial and temporal resolution. The mesoscale was probed with GISAXS and the crystallinity of the polymer and the inorganic component was probed with GIWAXS. The changes of the morphology and the influence on photovoltaic performance with the introduction of a compositional gradient are discussed. [1] Körstgens et al., *Nanoscale* 7, 2900 (2015).

**Parallel Session / 4**

## In-situ studies of thin-film composite reverse osmosis membranes with small-angle neutron scattering during the process of desalination

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Biofouling, RO Membranes, Small-Angle Scattering, in-operando wastewater desalination

**Summary:**

Formation of aggregates caused by the interaction of organic and inorganic molecules, in particular those involved in the formation of calcium phosphate minerals, has strong negative influence on membrane permeability in reverse osmosis (RO) wastewater desalination. Presently, RO is a major technology for water desalination and recovery. A better understanding of the origin of these aggregates is needed for economic reason as well as for scientific purpose as these phenomena are very much related to the broad field of biomineralization [1]. Small-angle neutron scattering (SANS) along with the technique of SANS contrast variation is a strong tool in this field as it is a non-destructive technique allowing quantitative analysis on a microscopic scale and the distinction between organic and inorganic components.

One of our goals is the realization of in-operando SANS experiments on RO desalination at close to realistic conditions. For this purpose we developed a cell for real-time SANS experiments simulating the process of RO-wastewater desalination up to 30 bar as described in Ref.[2].

The scattering from three different sources has to be distinguished, namely from feed, the fouling layer at the surface of the membrane, and from the membrane itself. It is shown that the scattering from RO membranes is very strong and dominating. Membrane performance was determined in parallel to SANS by measuring water permeability and rejection.

A short description of the in-operando cell as well as SANS data from various topics of this project will be presented. These are: (i) Formation and characterization of aggregates formed in a simulated secondary effluent after adding various organic molecules [3-5], (ii) characterization of RO thin-film composite (TFC) membranes using SANS contrast variation, and, (iii) results from desalination experiments performed at the classical and very-small angle scattering SANS instruments KWS1 and KWS3 of the FRM II (TUM in Garching).

1. A. Heiss, V. Pipich, W. Jahnen-Dechent, and D. Schwahn, *Biophysical Journal* 99, 3986 (2010).
2. D. Schwahn, H. Feilbach, Th. Starc, V. Pipich, R. Kasher, and Y. Oren, *Desalination* 405, 40 (2017)
3. V. Pipich, Y. Dahdal, H. Rapaport, R. Kasher, Y. Oren, and D. Schwahn, *Langmuir* 29, 7607 (2013).
4. Y. Dahdal, V. Pipich, H. Rapaport, Y. Oren, R. Kasher, and D. Schwahn, *Langmuir* 30, 15072 (2014).
5. Y. Dahdal, V. Pipich, H. Rapaport, Y. Oren, R. Kasher, and D. Schwahn, *Polymer* 85, 77 (2016).

**Poster / 30**

## Investigation of ZnO scattering layers for OLED applications

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Organic light emitting diodes (OLED) are reaching inner quantum efficiencies close to 100%, but the overall efficiency of conventional devices is limited to about 20% mainly by the photon extraction. One approach to overcome this issue is the implementation of an additional scattering layer into the device. A standard OLED is used to study the impact of such layer. This layer can either be created by a direct surface structuring or the introduction of an additional transparent layer. ZnO is a suitable choice for the latter due to its transmittivity in the entire visible spectrum, caused by its direct optical bandgap of 3.3eV. This layer is deposited on a glass substrate. The micro- and nano-structure of ZnO can be adjusted by combining a structure-giving diblock copolymer with sol-gel chemistry.

It is investigated how different structuring, which is analyzed by scattering techniques and electron microscopy, can influence the external quantum efficiency and the macroscopic properties of the OLEDs over the entire spectral range.

For the emissive layer mainly the well-studied Super Yellow (PDY-132) system is used, but, being a singlet emitter, one can not expect to reach top efficiencies.

Plenary Session / 98

## Testing the Standard Model of Particle Physics with Neutron Beta Decay

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Neutron Beta Decay is described accurately within the Standard Model of Particle Physics using the first CKM-matrix element,  $V_{ud}$ , and the ratio of vector and axial vector couplings,  $\lambda$ , as parameters. Angular correlations, spectra and the neutron lifetime are accessible experimentally, providing an excellent toolkit for investigating the structure of weak interaction and potential deviations from the predictions of the Standard Model.

In this talk I will present the world's most precise measurement of the Beta Asymmetry performed with the decay spectrometer PERKEO III carried out at the PF1B cold neutron beam facility at the Institut Laue-Langevin as one of the examples of recent measurements in this field.

Moreover an overview of the progression towards the next generation of instruments in the field of Neutron Beta Decay studies is discussed. This includes the instrument PERC which is currently under construction and is to be built up at the new MEPHISTO cold neutron beam facility at the FRM2.

Poster / 31

## Ingression of Moisture into Hybrid Perovskite Thin Films Probed with In-Situ GISANS

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Organometal halide perovskites mark a paradigm shift in photovoltaic research, as they combine high power conversion efficiencies with easy processing and cheap, abundant precursor materials making them a promising contender for other photovoltaic technologies. The commercial application of perovskite solar cells, however, is so far impeded by fundamental understanding lacking behind this fast progress in device efficiency. Though progress in device efficiencies has been remarkable, especially the sensitivity of the perovskite towards ambient moisture is a big issue which

basically renders them unsuitable for widespread use as toxic lead –contained e.g. in  $\text{CH}_3\text{NH}_3\text{PbI}_3$ , the most commonly used hybrid perovskite –could leak into the environment. Therefore, a lot of research focusses on improving the moisture stability of the perovskite, however, the process of the water uptake itself was so far not deeply addressed. Due to the high sensitivity of  $\text{CH}_3\text{NH}_3\text{PbI}_3$  to water, it tends to hydrolyze in the presence of moisture, leading to the degradation of the perovskite at a critical humidity of 55 %RH [1].

Using grazing-incidence small angle neutron scattering (GISANS) and introducing  $\text{D}_2\text{O}$  vapor, we probed the kinetics of water uptake and followed the structural evolution of a perovskite film synthesis with a common method [2]. We applied several humidities including humidities below and above the critical 55 %RH. As apparent from a shift in the Yoneda peak in the in-plane cuts of the 2D GISANS data the perovskite film is capable of up to 42 % water uptake, whereas the out-of-plane cuts indicate different degradation products depending on the humidity level. Furthermore, we gain insight into the reaction kinetics.

Based on this knowledge routes to stabilize perovskite films against moisture can be developed leading to higher long-term stability and less environmental hazards thus promoting fast market introduction of perovskite solar cells.

#### References:

[1] J. H. Noh, S. H. Im, J. H. Heo, T. N. Mandal, and S. I. Seok; Chemical Management for Colorful, Efficient, and Stable Inorganic–Organic Hybrid Nanostructured Solar Cells; *Nano Lett.*, 13, 1764–1769 (2013); DOI: 10.1021/nl400349b

[2] P. Docampo, F. C. Hanusch, S. D. Stranks, M. Döblinger, J. M. Feckl, M. Ehrensperger, N. K. Minar, M. B. Johnston, H. J. Snaith, and T. Bein; Solution Deposition–Conversion for Planar Heterojunction Mixed Halide Perovskite Solar Cells; *Adv. Energy Mater.*, 1400355 (2014); DOI: 10.1002/aenm.201400355

#### Poster / 33

## On the chemical origins of crystalline preferred orientations in hybrid organometallic lead halide perovskite thin films

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Solar cells based on organometallic lead halide perovskites have established themselves as a promising alternative to commercial thin film solar cells. The crystallographic versatility of the material allows the possibility of extensive chemical tuning, which manifests in the material as a spectra of properties that may be obtained. This entices research on hybrid perovskite structures combining different organic and inorganic groups into a crystalline framework. Preferential orientations of the crystalline hybrid perovskites (1) are reported and correlated to their morphological and chemical characteristics by grazing incidence wide angle x-ray scattering (GIWAXS). Remarkably, perovskite thin films prepared by the same methodologies displayed varying behaviors of preferred orientations, as their chemical composition was varied.

Moreover, the route and rate of crystallization (2) is known to radically influence crystalline preferred orientations as well, giving rise to information regarding kinetic and thermodynamic orientations. These results, for the first time propose the possibility of controlling crystallinity of spin-coated thin films by tuning the ingredients of and the treatment of the solution used for spin coating.

(1) Oesinghaus et al., *Adv. Mater. Interfaces* 2016, 3, 1600403

(2) Giesbrech et al., ACS Energy Lett. 2016, 1, 150-154

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## Morphology of Perovskite-based Hybrid Solar Cells

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Organometal halide perovskites have been shown to be great candidates for photovoltaics, owing to the strong absorption, and high mobility and diffusion length of photo-generated charge carriers. Subsequently, solar cells employing perovskite thin films have reached efficiencies of more than 20%, making them comparable with commercially available silicon solar cells. The performance of perovskite solar cells greatly depends on their crystal morphology. We fabricate and characterize different cells by varying processing parameters including film deposition methods, annealing temperature and solvent media. By means of X-ray scattering methods, we gain insight into the inner film morphology and thus are able to correlate morphology and photovoltaic performance, with the target to get better fundamental understanding. Especially, in-operando X-ray measurements performed on a photovoltaic device shed light on their degradation under operating conditions.

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## Morphological characterization of novel material systems for hybrid photovoltaics

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Organic materials have been found to offer various, promising advantages for photovoltaic (PV) devices like flexibility and the potential of low-cost/large scale production. Hybrid devices combine these advantages with the chemical/physical stability of inorganic materials and, thus, overcome the issue of limited lifetimes of purely organic cells. Poly(styrene-block-ethylene oxide) templated sol-gel chemistry is used to synthesize high surface-to-volume ratio, mesoporous titania thin films, which allows for precise structure control and an increased amount of interface. The n-type, electron conducting titania thin film serves as a basis for novel organic material studies. The studies aim to introduce new material combinations to the field of hybrid PV and to open up pathways for enhanced efficiency in terms of energy conversion and band alignment. Thin film spectral absorption characterization



is carried out via UV/Vis measurements. Furthermore, morphological characterization is realized via SEM, XRD and TOF-GISANS to extract the efficiency of backfilling and the crystal structure of the system.

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## Hybrid quantum dots: poly(3-hexylthiophene) solar cells

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Blends of semiconducting polymers and inorganic semiconductor nanocrystals, like quantum dots (QDs), have started to attract intensive interests because of their inexpensive costs and the ability of being solution processed. Both facts render them very promising candidates for next generation organic photovoltaics. Hybrid bulk heterojunction (BHJ) solar cells integrated with CuInSexS2-x (CISS) QDs and poly(3-hexylthiophene) (P3HT) are under investigation. CISS QDs are used as acceptor in our BHJ solar cell schematic, due to their strong optical absorption, tunable band-gap reaching to near infrared and long exciton lifetime, while P3HT is employed as donor material. The surface engineering of the QDs is investigated as a key factor to increase the exciton diffusion length and therefore improve the performance of solar cell devices. The QDs- P3HT active layers with 120 nm thickness are fabricated by blending using the spin-coating method. Different blend ratios are compared.

**Summary:**

Heavy metal free nano-crystals have been introduced to bulk heterojunction organic solar cells for the optimizations of the solar absorption behavior as well as the charge mobility.

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## Effect of incorporated inorganic nanoparticles on the performance of organic solar cells

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Organic solar cells have attracted increased attention due to their advantages in tunable characteristics, low-cost manufacturing processes and flexibility, which opens up a promising alternative for conventional photovoltaics. Recently the most widely investigated bulk heterojunction donor-acceptor system of P3HT:PCBM was doped with iron oxide nanoparticles, resulting in an increase of efficiency.[1] Based on this approach, we investigate the effect of doping P3HT:PCBM active layers with alternative inorganic nanoparticles. We study the influence of different inorganic nanoparticle concentrations on current density-voltage characteristics and the absorbance. These optoelectronic

properties are compared with structure information determined with scattering methods.

[1] D. M. González, V. Körstgens, Y. Yao, L. Song, G. Santoro, S. V. Roth, P. Müller-Buschbaum, *Adv. Energy Mater.* 2015, 5, 1401770.

Poster / 40

## Investigation of an n-type conducting polymer for potential use in all-polymer thermoelectric generators

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Thermoelectric generators are a promising approach in renewable energies, as they are able to convert waste heat into electricity. Possible applications are large scale applications like recovering the waste heat of a car engine as electricity as well as niche applications like using the heat emitted by human skin to drive a watch.[1]

In practice, a thermoelectric generator traditionally consists of a p- and an n-type semiconductor electrically connected as shown in Fig. 1.

In order to put the device into operation, a temperature gradient is applied along the legs. As a consequence, charge carriers, i.e., holes in the p-type and electrons in the n-type leg, respectively, diffuse from the hot to the cold side. This diffusion current causes a build-up of charge at the cold end that can be extracted by connecting a load. All in all, a thermoelectric generator is able to convert a temperature gradient into electric energy.

To build high efficiency thermoelectric devices, suitable thermoelectric materials are needed. Unfortunately, state-of-the-art thermoelectric materials have the drawback of using toxic or less abundant constituents, making it necessary to look for alternatives. One promising approach to overcome such challenges is to use conjugated polymers. They have the encouraging ability of easy and various types of scalable solvent processes like roll-to-roll printing. Although they are still less efficient than their inorganic counterparts, their potential flexibility and eco-friendliness make them a valuable alternative.

Various, especially p-type, conducting polymers have been investigated as thermoelectric materials. A very promising candidate among them is the hole-conducting PEDOT. Unfortunately, n-type polymers have rather been neglected which might stem from their low stability towards oxygen and moisture. Nonetheless, both types are needed for a thermoelectric device as explained before. Therefore, we also focus on the thermoelectric properties of the n-type polymer P(NDI2OD-T2). Its successful application to transistors [3] and solar cells [4] encourages an auspicious attempt in building an all-polymer thermoelectric generator. Both polymers which are investigated in our group are shown in Fig. 1 next to the leg where they are of potential use.

The main focus of this work is to enhance the so-called power factor where is the electrical conductivity and is the Seebeck coefficient. As already indicated by its name, the larger the power factor the larger the power output and subsequently the efficiency of the device.

Therefore, we successfully doped P(NDI2OD-T2) with an organic small molecule which can even be seen in a color change depicted in Fig. 2. The experiment resulted in a maximum power factor of

### References

- [1] G. J. Snyder, *The Electrochemical Society Interface* (2008)
- [2] R. Kroon et al., *Chem. Soc. Rev.* 45, 6147-6164 (2016)
- [3] H. Yan et al., *Nature* 457, 679-687 (2009)
- [4] J. R. Moore et al., *Adv. Energy Mater.* 1, 230-240 (2011)

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## In situ small angle X-ray scattering investigation of solid-state polymer electrolyte for lithium-ion batteries

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Many present problems regarding the safety of liquid electrolytes in lithium-ion batteries may potentially be overcome by the use of solid-state polymer electrolytes. Polystyrene-block-polyethylene oxide PS-*b*-PEO diblock copolymer (DBC) electrolyte have been recently investigated as a membrane for Li-ion battery. The performance of these DBC electrolytes strongly depends on its morphology, serving highly oriented PEO domains as pathways for lithium ions migration. Thus, in situ structural investigation of these Li-ion doped DBCs systems during cycling in an operating battery is essential, which can be done by neutron or X-ray small angle scattering. In situ small angle neutron scattering on a working pouch cell has been performed, which proved the structural stability of the polymer electrolyte. Also, capillary-based micro-battery cell allowing simultaneous electrochemical and structural evaluation by X-ray scattering has previously been reported [1].

Figure 1: Schematic of the in situ SAXS setup.

Figures 2 and 3 show 1d radial averages of the SAXS data acquired while cycling the battery for LFP/C (2) and LFP/Li (3) cells. While the system with the graphite anode shows a stable structure over big number of cycles, the LFP/Li system is less structured from the beginning of the measurements and loses the remaining ordering over cycling. The influence of the lithium metal on the polymer electrolyte and the interface between the two layers will be further investigated in this work in order to determine the applicability of lithium metal anodes.

[1] R.E. Johnsen, P. Norby, *J. Appl. Cryst.* (2013), 46, 1537.

[2] R. Bouchet, S. Maria, R. Mezziane et al., *Nature materials* (2013), 12, 452-7

The current in situ small-angle X-ray scattering (SAXS) study of the solid-state polymer electrolytes using a modified version of the micro-battery cell provides a deeper insight into the structural modification. Figure 1 shows the currently used setup used for the X-ray experiments. A battery cell is assembled inside a glass housing, consisting of a flat capillary tube. Lithium iron phosphate (LFP) and lithium/graphite (Li/C) are used as cathode and anode active materials for this system. Composite electrodes as well as the polymer electrolytes are prepared by solution casting onto copper current collectors [2].

Figures 2 and 3: 1d radial averages of the SAXS data acquired during the cycling of a LFP/C (left) LFP/Li cell (right).

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## Investigation of titania thin film morphologies via GISAXS and SEM for hybrid solar cells

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As the need for sustainable energy sources is steadily increasing, the concept of photovoltaics has attracted both scientific and economic interest. Whereas conventional semiconductor-based solar cells are already well researched and their efficiencies are promising, their energy need for the mere production and their lack of versatility remain a major drawback. Therefore, concepts are needed, which combine competitive efficiencies with the possibility for energy-inexpensive large-scale production. Hybrid solar cells, which combine the mechanical stability of inorganic semiconductors and the versatility of organic semiconductors, meet these criteria. Titania thin films as an inorganic material in combination with a conjugated polymer as an organic semiconductor are common for application in hybrid photovoltaics. Excitons are generated via light absorption in the p-type conducting polymer and split at the interface of the two compounds due to the band offset. Afterwards, the electrons are transported in the titania and the holes in the p-type polymer respectively.

Due to the restriction of the charge separation to the interfacial area, a nanoscale structure of the active layer is necessary in order to enhance the charge separation. Therefore, mesoporous titania structures, which serve as a matrix for infiltration with the polymer are a promising concept for

high-efficiency active layers. Challenges concerning this concept arise due to the difficulty of the infiltration with the polymer, since occlusion of the pores in the upper part of the layer can occur and prevent backfilling of pores in lower parts of the layers. Accordingly, ways to control the structure of mesoporous titania films are of major importance.

We focus on the tuning of the pore size of mesoporous. In our experiments, a solution composed of an amphiphilic block copolymer as a structure-directing agent and a precursor dissolved in an organic solvent is applied as a wet film. Immersion in an antisolvent after an evaporation step leads to a structure formation process in the composite film, so that the morphology depends both on the evaporation time and the immersion bath. By controlling the evaporation step, the porosity of the film can be tuned. After calcination, mesoporous titania films are obtained. The films are characterized concerning their suitability for photovoltaic application, which regards their morphology, crystallinity and thickness. Surface morphologies are experimentally investigated by scanning electron microscopy as well as atomic force microscopy. These methods are suited for the estimation of the porosities of the film and for showing the dependence of the morphology on the processing parameters. In addition to the surface morphology, also the inner morphology is investigated. Therefore, grazing incidence small angle X-ray scattering is applied as a non-destructive method to probe the deeper layers.

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## Germanium-based hybrid photovoltaics

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Electricity is needed in many situations of our daily life at many different locations around the globe. Solar energy has the major advantage that the conversion process light/energy is simply available during daylight. It does not have to be actively transported or stored and is free of political control. Therefore, a strong interest in solar energy conversion has manifested over the last decades with solar cells taking the role of converting solar energy to electricity.

Hybrid solar cells are a promising technique for future energy generation as they combine the advantages of organic and inorganic solar cells. Organic materials are solution processable. Thus, they enable large scale and cheap production with little energy demand. They also allow for thin film devices sparing scarce resources. Furthermore lightweight and flexible cells are suitable for new applications. On the other hand the usage of inorganic material provides high charge carrier mobility and avoids degradation, which enhances HPV lifetime stability.

Starting from an organic solar cell, the main objective is to incorporate an inorganic component into this structure in order to make a hybrid photovoltaic device. In this case, we use a wet chemical precursor for the germanium layer. First for this work, we focus on an inverted geometry system, which includes an additional compact titania blocking layer (figure 1). Therefore, the approach is to characterize and optimize every step of this organic system, especially the active layer which strongly influences the efficiency of the solar cell. Thus, its morphology needs to be optimized and a homogenous film is desirable. In order to achieve this, we investigate the different layers using several techniques such as an optical microscope (figure 2), UV-Vis (figure 3), Dektak, and a solar simulator. With these facilities, we are able to enhance our way of working, and thus in short term to integrate the germanium layer into it as the electron conductive film.

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## Structural investigation of two pH-responsive block copolymers using synchrotron-SAXS

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Multi-responsive polymers have gained a lot of attention, mainly due to the huge array of applications [1] they can be used for, such as sensors, drug delivery systems or tissue engineering. In this work, core-shell micelles with a pH-responsive shell, whose shell blocks undergo a phase transition from expanded to collapsed as a response to changes on the pH, are investigated. At higher concentration, network formation is found, and the phase transition results in strong changes of the mechanical properties [2,3]. Here, we focus on the structural changes.

Two block copolymers were investigated in this work PMMA-b-PDMAEMA-b-PMMA (PMMA and PDMAEMA are poly(methyl methacrylate) and poly[2-(dimethyl amino) ethyl methacrylate]) and PMMA-b-PDMAEMA-b-P2VP-b-PDMAEMA-b-PMMA (where P2VP stands for poly(2-vinylpyridine)). Both block copolymers have similar architectures, ABA and ABCBA, with small hydrophobic blocks A in the outer part of the chain and large pH-responsive blocks B and C in the inner part. While PDMAEMA is a weak polycation, P2VP is a strong one and becomes hydrophobic at high pH values.

To study structural changes under different conditions, solutions of the polymers were prepared in D<sub>2</sub>O at different concentrations (0.1-1 wt%) and pD values (1, 4 and 7). Synchrotron small-angle X-ray scattering experiments were carried out at the beamline D1 at CHESS to investigate the structure of the micelles.

#### References

- [1] C. Tsitsilianis, *Soft Matter*, 2010, 6, 2372.
- [2] F. Bossard, T. Aubry, G. Gotzamanis, C. Tsitsilianis, *Soft Matter*, 2006, 2, 510.
- [3] G. Gotzamanis, C. Tsitsilianis, S. C. Hadjiyannakou, C. S. Patrickios, *Macromolecules*, 2006, 39, 678.

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### Discussion: Future of MLZ and integration of HZB instruments

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#### Poster / 0

### C-SPEC- a cold time of flight spectrometer for the ESS

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The European Spallation Source (ESS), expected to be the world's most powerful neutron source, will begin operations in 2019. Among the endorsed instruments foreseen for day one instrumentation at ESS, is the cold time-of-flight spectrometer C-SPEC. C-SPEC is a joint proposal from the Technische Universität München, Germany, and the Laboratoire Léon Brillouin, Saclay, France. The high performance cold time-of-flight-spectrometer will serve multiple disciplines to address scientific questions from hard and soft matter research, life sciences, geosciences or magnetism. C-SPEC will address time dependent phenomena under realistic conditions. While current day spectroscopic experiments mainly probe the static state of a sample, neutron spectroscopy experiments that probe the time dependent behaviour, e.g. of electrolytes in an electric field, or laser excited light harvesting proteins, are still in an exploration stage, mainly due to the lack of flux at the instruments available today. C-SPEC benefits from the high brilliance of the ESS spallation source in addition to the use of a novel chopper implementation and as such will address scientific questions raised by probing time dependent phenomena.

The unique pulse structure of the ESS with its long pulse duration (2.86 ms) and a repetition rate of 14 Hz requires new concepts for the instrumentation to make optimum use of the available source time frame. With an instrument length of ~157 m, a wavelength range of  $\lambda \leq 1.8 \text{ \AA}$  can be probed within each ESS time period via rate-repetition mode. The energy resolution can be tuned in the range of  $\Delta E/E = 6 - 1\%$ , and C-SPEC will utilize cold neutrons in the range from  $\lambda = 2 - 20 \text{ \AA}$  with the focus on the cold part of the spectrum. The guide is optimised to enhance signal to noise and will be able to focus on samples ranging from several  $\text{mm}^2$  to several  $\text{cm}^2$  in area. The large detector area, with a radius of 3.5 m,  $5 - 140$  degrees and 3.5 m in height, typical on a chopper spectrometer will be designed with optimal energy and Q resolution in mind while maintaining the highest signal to noise ratio. C-SPEC is in the preliminary engineering phase and we will present the current design layout and the expected performance

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## The pretreatment of wood in ionic and complementary liquids

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The pretreatment of wood in ionic and complementary liquids is studied in and ex situ by small angle neutron scattering studies. We detect different stages of decomposition and connections to morphological stages. The general aim of the pretreatment is the accessibility of the cellulose to enzymatic scission of the chains such that valuable oligomers are obtained for further chemical reactions.

**Summary:**

We have learned that ionic liquids are by far more mild in the treatment of wood compared to classical acidic and alkaline liquors where the cellulose quality suffers from the pretreatment.

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## Investigating the organometal halide perovskite crystallization in mesoscopic hole-conductor-free perovskite solar cells

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Organometal halide perovskite based solar cells have emerged as the fastest-advancing photovoltaic technology to date, reaching certified solar cell efficiencies of up to 22.1%. Recently, the focus of research broadened beyond high efficiencies to key values like prolonged device lifetime and stability

that are required for industrial implementation. A novel perovskite cell architecture utilizing a mesoporous scaffold with embedded perovskite addresses these challenges and is furthermore adaptable for industrial scale production. However, little is known about the perovskite crystal formation in mesoscopic scaffolds.

In this project, we fabricate a mesoscopic scaffold comprised of a mesoporous triple-layer of titania, zirconia and carbon by screenprinting. We further investigate the influence of the processing additive 5-ammonium valeric acid iodide (5-AVAI) on the perovskite solution infiltration and perovskite crystallization. Hereby, our results grant us a better understanding of the perovskite crystallization processes in a mesoscopic scaffold and are of key importance for further developments.

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## Positron Annihilation Spectroscopy for investigation of defect evolution of $\text{Li}_{1-x}\text{Ni}_{1/3}\text{Mn}_{1/3}\text{Co}_{1/3}\text{O}_2$ Lithium Ion Battery Electrodes

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Understanding and controlling the aging behavior of lithium ion batteries is key for the successful application in various fields of interest. Especially when going from small handheld devices with short life times to electric vehicles or even energy in grid storage a limited lifetime and enhanced capacity losses have to be avoided. To achieve this, a fundamental understanding of the transport mechanisms and lithium trapping in the active materials is crucial. For example for the widely used  $\text{Li}_{1-x}\text{Ni}_{1/3}\text{Mn}_{1/3}\text{Co}_{1/3}\text{O}_2$  (NMC-111) cathode material it is established that during the first charge-discharge cycle Li-ions can be removed from the NMC-111 structure but cannot be completely re-intercalated back into the material under standard conditions, resulting in a capacity loss (CL) corresponding to a value of  $x \sim 0.08$ . The underlying process is poorly understood. Prior studies utilizing electrochemical methods and in situ X-ray diffraction (XRD), showed that a slowing down or freezing of the Li mobility or kinetic hindrance or barrier grows as the fully intercalated state is being approached, so that the initial structure with  $x = 0$  can only be recovered after an extended voltage hold at low potentials.

As such a kinetic limitation should be due to the type and concentration of atomistic defects in the material we applied Positron Annihilation Spectroscopy in combination with electrochemical methods and XRD to study the structure and evolution of vacancy type defects in NMC-111. The relation between positron annihilation and electronic structure is discussed in terms of structural dynamics during the lithiation process. Samples of NMC-111 electrodes with decreasing lithium content ( $x = 0 - 0.7$ ) covering the whole range of state of charge were electrochemically prepared for the non-destructive analysis using positron coincidence Doppler broadening spectroscopy (CDBS). The positron measurements allowed us to observe the evolution of the defect structure caused by the delithiation process in the NMC-111 electrodes. The combination of CDBS with X-ray diffraction for the characterization of the lattice structures enabled the analysis of the purported kinetic barrier effect in the first charge-discharge cycle and we discuss possible implications due to vacancy ordering. The usefulness of positrons to study such effects is not well known in the battery community as we also are the first group to report on the successful application of CDBS on NMC-111 electrodes yielding new insights in the important role of defects caused by the delithiation process and the kinetic barrier effect.

### Summary:

Positron Annihilation Spectroscopy is successfully established to investigate the defect evolution. New insights into the cause for the intrinsic NMC-111 1st cycle capacity loss are gained.

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## Neutron depth profiling for materials science application

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Neutron Depth Profiling (NDP) is a non-destructive, near-surface analytical technique to selectively study the distribution of several light elements with high lateral and depth resolution [1]. Upon capture of a neutron, the investigated elements emit charged particles, which carry the depth information of the parent nuclei and are detected via surface barrier detectors. NDP offers a wide range of application for several branches of materials science, as polymer, metal alloy and microelectronic materials [2]. We focus on the construction and testing of a NDP beamline at the Forschungs-Neutronenquelle Heinz Maier-Leibnitz (MLZ) at the Prompt gamma-ray activation analysis facility (PGAA). Here we utilize a high cold neutron beam flux up to  $6 \cdot 10^{10}$  n cm<sup>-2</sup> s<sup>-1</sup> [3], which enables novel NDP characterization pathways for materials science.

[1] Y. He et al., Journal of Power Sources 2015, 287, 226-230.

[2] R. G. Downing et al., J. Res. Natl. Inst. Stand. Technol. 1993, 98, 109.

[3] L. Canella et al., Nucl. Instr. Meth. Phys. Res. A 2011, 636(1), 108-113.

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## Studying soft-matter and biological systems over a wide length scale from nm to microns and with high intensity and high resolution at the versatile SANS diffractometer KWS-2

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The small-angle neutron diffractometer KWS-2, operated by the Jülich Centre of Neutron Science (JCNS) at Heinz Maier-Leibnitz Zentrum (MLZ), is dedicated to the investigation of mesoscopic multi-scale structures and structural changes due to rapid kinetic processes in soft condensed matter and biophysical systems. Following demands from the user community, it was recently considerably upgraded, with the aim of boosting its performance with respect to the intensity on the sample (using lenses and large sample area while maintaining the pinhole resolution), the counting rate capabilities (up to 5 MHz for 10% dead time with a new <sup>3</sup>He tubes detector supplied by GE Reuter-Stokes), the instrumental resolution (wavelength resolution between 2% and 20% using a double-disc chopper with variable slit opening and TOF data acquisition), and the minimum and maximum scattering variable;  $Q_{\min} = 0.0002$  1/Å (using lenses and a secondary high-resolution detector) and  $Q_{\max} = 1$  1/Å (using  $\lambda = 3$  Å), respectively. All these new options, and the new user-friendly control software, have significantly increased the maneuverability of the instrument. Consequently,



KWS-2 is a highly versatile tool which can address a broad range of structural studies by offering multiple working modes that can be selected and used in a direct and user-friendly manner.

The concept, the various operation modes and the performance of KWS-2 will be presented in detail. This will be supported by example results obtained in research activities carried out at the instrument on soft-matter and biological systems.

[1] A. Radulescu *et al.*, *J. Vis. Exp.*, 2016, **118**, e54639, doi:10.3791/54639

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## Coarsening and precipitation kinetics of TaC precipitates in Co-Re alloys

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There is a need to supplement Ni-base superalloys in future gas turbines for gas entry temperatures > 1500 °C to improve their efficiency. Co-Re-Cr based alloys are a promising candidate, since they have the required high melting point as well as the required strength. Measurements by means of small-angle neutron scattering (SANS) and neutron diffraction (ND) were an important part of their development in the past several years. These methods allow the investigation of the complex interplay between the different phases that are present in nano- and mesoscopic scale in-situ at high temperatures (up to 1500 °C). Especially with SANS, it was possible to observe the size distribution of fine Tantalum mono-carbide precipitates (<30 nm) and their evolution within the matrix of a Co-Re-Cr-Ta-C alloy. In addition, ND shows that the Co-Re alloy matrix undergoes an allotropic transformation hcp ↔ fcc at temperatures > 1200 °C, similar to pure Co (at 400 °C). This transformation is very sensitive to the Cr and Re content since they stabilize the hcp-Co phase. The fine TaC precipitates can imbed semi-coherently in the hcp-Co matrix and are therefore very sensitive to the Co matrix phase [1].

In this contribution, the influence of Co-Re matrix transformation on the fine TaC precipitate morphology is presented. Alloys with a Ta content of 1.2 at.% and varying C/Ta ratios from 0.5-1 were studied in order to investigate the stability of TaC phase in form of fine precipitates in detail. The coarsening kinetics at high temperature, as well as the formation and dissolution of TaC phase at temperatures > 1200 °C, was determined. Moreover, the influence of Chromium addition to the alloy matrix is discussed.

References

[1] L. Karge, R. Gilles, D. Mukherji, P. Strunz, P. Beran, M. Hofmann, J. Gavilano, U. Keiderling, O. Dolotko, A. Kriele, A. Neubert, J. Rösler, W. Petry, The influence of C/Ta ratio on TaC precipitates in Co-Re base alloys investigated by small-angle neutron scattering, *Acta Materialia* (2017).

Poster / 28

## Development of a new testing machine (load and pressure) for high-temperature alloys

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A great effort has been focused on the development of a new alloy that can operate over 700 °C and can be processed by normal industrial wrought techniques, mainly for aircraft engines and gas turbine applications. VDM Alloy 780, a Ni-based superalloy (NiCoTiAlNbCrMoNiFe), is a promising candidate for this high-temperature application that require e.g. good mechanical properties. This superalloy is based on the  $\gamma$   $\gamma'$ -system and the austenitic matrix ( $\gamma$ -phase) is strengthened by inter-metallic precipitates of Ni<sub>3</sub>Al ( $\gamma'$ , fcc L1<sub>2</sub> structure) and Ni<sub>3</sub>Nb ( $\gamma''$ , bct DO<sub>22</sub> structure).

For studying the forming process of the alloy a certain sample environment is required. To perform experiments at high temperatures and under load/pressure a new testing machine is developed. In this work we present an overview of the testing machine with its application. In addition first structural studies on VDM 780 superalloy were performed by XRD and ND. Three samples with the same composition but one with standard heat treatment and two with different additional heat treatments were investigated. The mutual project of TU München, TU Braunschweig and VDM Metals is founded by BMBF (FKZ 05K16W02).

**Summary:**

A new Ni-based superalloy called VDM 780 based on the  $\gamma$   $\gamma'$ -system is under optimization. For this purpose it is necessary to study the microstructure under various conditions as high temperature or deformation. Therefore several experiments like X-ray diffraction (XRD) and neutron diffraction (ND) were performed. Furthermore a testing machine (high temperature, load/pressure) is developed.

**Poster / 5**

## Effect of membrane active drugs on the structure of lipid bilayers.

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phospholipid-based bilayers are widely used as model systems for studying the more complicated biological cell membranes, providing information about their structure and interactions. In particular, we are interested in understanding the effect of drugs on phospholipid-based membranes, i.e. the action mechanism, and the eventual toxicity when administered at high concentrations. This knowledge can in principle support a chemical design of more efficient variants having lower side effects. In the present study, we have investigated the effect of some active principles, namely benzocaine and propranolol on bilayers composed of L- $\alpha$ -phosphatidylcholine (SoyPC) by means of Neutron Reflectivity (NR) and Small Angle Neutron Scattering (SANS). Benzocaine is a commercial drug that serves as topical pain reliever, used for instance in cough drops. It is also found as main component in many anesthetic ointments such as products for oral ulcers. Propranolol is a beta-blocker, affecting the heart and blood circulation: it is used for treating tremors, angina, hypertension and other heart or circulatory conditions. We generally found a variation of the structural parameters of the membranes with incorporated drug molecules, with a destabilization found at high drug concentrations, through the formation of ruptures inside the double layers, randomly distributed over the space. Propranolol has a bigger perturbative effect on the membranes, due to the structure of his hydrophobic part.

## Diskussion: Sample environment

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### Poster E13

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## Near surface dynamics in thin adsorbed layers of ethylene glycol (EG) based thermoresponsive microgel particles

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Scanning the dynamic profile across thin polymer coatings opens a new field for a better understanding and the design of novel surface functionalisation. Surface functionalisation via formation of stimuli-responsive surface structures using colloidal structures is an active field of research.

Here, we used ethylene glycol (EG) based thermoresponsive microgel particles as building blocks and studied their adsorption at silicon surfaces.<sup>1)</sup> They are investigated with respect to potential biomedical applications aiming on a systematic combination of the intrinsic biocompatibility of PEG with the physico-chemical properties of microgels to overcome the biomedical drawbacks of other systems. Scattering techniques (DLS, SANS) were used to systematically characterize particle size and inner structure depending on the comonomer content<sup>2)</sup> and the reaction time of the precipitation polymerization<sup>3)</sup>. The cooperative and inner dynamics of the dispersed microgel particles was characterized by neutron spin echo spectroscopy in transmission geometry (NSE).

To access the inner properties of the adsorbed microgel particles we used the newly established method of neutron spin echo spectroscopy under grazing incidence (GINSES)<sup>4)</sup>. The reported GINSES experiment shows technically, that the dynamic profile within layers of colloidal objects of less than 200 nm height can be scanned perpendicular to the substrate surface.

The scientific impact is that the slowing down of the dynamics towards the substrate might have a strong effect on the swelling/deswelling ratio, the swelling kinetics and eventually even on the VPTT.

This is of fundamental interest with respect to application of adsorbed gels e.g. in catalysis, for sensors or for implants.

1) S. Wellert, D. Kesal, S. Schön, R. von Klitzing, K. Gawlitza, *Langmuir*, 2015, 31 (7), 2202–2210

2) K. Gawlitza, A. Radulescu, R. von Klitzing, S. Wellert, *Polymer*, 2014, 55 (26), 6717–6724

3) S. Wellert, A. Radulescu, A. Carl, R. von Klitzing, K. Gawlitza, *Macromolecules*, 2015, 48 (14), 4901–4909

4) K. Gawlitza, O. Ivanova, A. Radulescu, O. Holderer, R. von Klitzing, S. Wellert, *Macromolecules*, 2015, 48 (16), 5807–5815

Parallel Session / 83

### News from Poli

Author: Vladimir Hutanu<sup>None</sup>

Solving complex magnetic structures like direct distinguishing between cycloidal, helical and amplitude modulated spin arrangements; interplay between the crystal and magnetic chirality; short range magnetic/nuclear correlations in frustrated systems; local spin anisotropy (susceptibility tensor approach) at the unit cell level; magnetic domains distribution and their dynamics in complex antiferromagnets are only few examples of the actual applications of the single crystal diffraction with polarized neutrons and polarization analysis in addition to the classical spin densities mapping and separation of nuclear-magnetic and nuclear-spin-incoherent scattering contributions in different types of materials (multiferroics, superconductors, magnetic shape memory alloys, giant-magnetoresistance oxides, molecular magnets, etc.). Dedicated instrument Polarization Investigator POLI have been developed, built and commissioned in the last years at MLZ in cooperation between JCNS and RWTH Aachen. 2014 first neutron beam on the dedicated beam-port SR 9a in front of the hot neutron source of FRM II reactor was obtained. 2015 POLI enters into user operation with Spherical Neutron Polarimetry technique using third generation Cryopad [1-5]. POLI is the first instrument worldwide routinely using  $^3\text{He}$  spin filters both to produce and to analyze neutron polarization. This results in the enhanced flux of the polarized short wavelength neutrons and increased in the comparison to other instrument of this type resolution [6]. 2016 new polarized diffraction setup for Flipping –Ratio measurements in magnetic field using 2.2 T HTS magnet was implemented on POLI [7]. Dedicated for polarised neutron diffraction of hot neutrons 8 T magnet with recondensing cryostat, asymmetric field, active shielding and large vertical and horizontal access was developed and is under production at Oxford Instruments Company. First factory tests are successfully pass in April 2017. Until the end of 2017 new magnet is planned to be implemented on POLI. Also implementation of the new supermirror polarizers developed in cooperation with NOB (Neutron Optics Berlin GmbH), optimized for short wavelength neutrons and largely divergent beam from the focused monochromator is planned to finish in 2017 on POLI. Available on POLI polarized neutrons with very short wavelength (0.5 Å) are rather unique feature, and they are interesting not only for the solid state physics and magnetism community but also for fundamental nuclear physics for study of the parity violation in the resonance decay process in the U and La nuclei. First feasibly experiments of this type, using dedicated setup on POLI have been successfully performed in 2016. The preliminary results show the confirmation of the expected effect. Continuation with more detailed studies are planned in 2017. [8]

[1] V. Hutanu, W. Lubertetter, E. Bourgeat-Lami, M. Meven, A. Sazonov, A. Steffen, G. Heger, G. Roth, and E. Lelièvre-Berna, “Implementation of a new Cryopad on the diffractometer POLI at MLZ”, *Review of Scientific Instruments* 87, 105108 (2016)

[2] V. Hutanu, A. P. Sazonov, M. Meven, G. Roth, A. Gukasov, H. Murakawa, Y. Tokura, D. Szaller, S. Bordács, I. Kézsmárki, V. K. Guduru, L. C. J. M. Peters, U. Zeitler, J. Romhányi, and B. Náfrádi, “Evolution of two-dimensional antiferromagnetism with temperature and magnetic field in multiferroic  $\text{Ba}_2\text{CoGe}_2\text{O}_7$ ”, *Phys. Rev. B* 89, 064403 (2014)

[3] V. Hutanu, A. Sazonov, G. Roth, I.-H. Oh, M. Baum, J. Stein, M. Braden, H. Murakawa, Y. Tokura, S. Bordács, I. Kezsmarki and B. Nafradi, “Spherical neutron polarimetry in multiferroics under external stimuli”, *Acta Cryst. A* 70, C151 (2014)

[4] J. Stein, M. Baum, S. Holbein, V. Hutanu, A.C. Komarek and M. Braden „Control of multiferroic domains by external electric fields in  $\text{TbMnO}_3$ ”, *J. Phys.: Condens. Matter* 27, 446001 (2015)

[5] D. Fobes, E. Bauer, J. Thompson, A. Sazonov, V. Hutanu, S. Zhang, F. Ronning, M. Janoschek, “Low temperature magnetic structure of  $\text{CeRhIn}_5$  by neutron diffraction on absorption-optimized samples” *J. Phys.: Condens. Matter*, 29 17LT01 (2017)

[6] V. Hutanu “POLI: Polarised hot neutron diffractometer” *Journal of large-scale research facilities*, 1, A16. <http://dx.doi.org/10.17815/jlsrf-1-22> (2015)

[7] H. Thoma, “Setup for polarized neutron diffraction on POLI diffractometer at MLZ”, Bachelor thesis TU München University 2016.

[8] Yu. Kopatch, V. Novitsky, G. Ahmadov, A. Gagarsky, D. Berikov, G. Danilyan, V. Hutanu, J. Klenke, S. Massalovich, “Measurement of T-odd effects in the resonance neutron induced fission of  $^{235}\text{U}$  on a hot source of polarized neutrons”, Presentation on ISINN25 Dubna, Russia, 2017

**Parallel Session / 6****Opportunities of the thin film laboratory at MLZ****Author:** Sabine Pütter<sup>1</sup>**Co-authors:** Amir Syed Mohd <sup>1</sup>; Thomas Brückel <sup>2</sup><sup>1</sup> *Jülich Centre for Neutron Science JCNS, Outstation at MLZ, Forschungszentrum Jülich GmbH*<sup>2</sup> *Forschungszentrum Jülich GmbH***Corresponding Author:** s.puetter@fz-juelich.de

To solve today's challenges in energy conversion and information technology, fundamental understanding of thin films and nanostructures is required [1,2,3]. Prerequisite, however, is the fabrication of thin films. Molecular Beam Epitaxy (MBE) is a very versatile method to grow high quality and high purity epitaxial films with low intrinsic defect concentrations and atomic-layer control.

At the JCNS thin film laboratory at the MLZ, we run an oxide MBE system for the growth of various samples, i.e. "classical" magnetic thin films, transition metal oxide thin films and films for soft matter studies, like Gold layers.

However, thin film growth is a research topic on its own which requires investigation to finally obtain thin films with optimum properties. In the presentation we will give examples for high quality metal and complex oxide thin film systems like e.g. SrCoO<sub>x</sub>, La<sub>1-x</sub>SrMnO<sub>3</sub>, FeN<sub>4</sub> or Cu/Fe multilayers with focus on stoichiometry, morphology and thickness precision and give detailed information about the possibilities in sample preparation for users.

To enable quasi in-situ neutron scattering studies on freshly produced samples by subsequent transfer of the sample from the MBE laboratory to the neutron instrument MARIA we have developed a small versatile transfer chamber [4].

The use of the MBE setup and the transfer chamber is open for users and collaborators. Users who apply for beam time at neutron instruments like MARIA are welcome to prepare their samples on-site with our technical support.

[1] R. Ramesh and N. A. Spaldin, *Nature Mater.* 6, 21 (2007)

[2] J. Mannhart and D. G. Schlom, *Science* 327, 1607 (2010)

[3] S. Pütter et al., *Appl. Phys. Lett.* 110, 012403 (2017)

[4] A. Syed Mohd et al., *Rev. Sci. Instrum.* 87, 123909 (2016)

**Summary:**

The JCNS thin film laboratory offers thin film fabrication for all neutron users. Simply apply within the framework of the MLZ proposal system!

**Parallel Session / 13****Simultaneous SANS/FTIR to investigate the conformation of polyethylene glycol dimethyl ethers inside a co-crystalline matrix of syndiotactic polystyrene****Author:** Maria Maddalena Schiavone<sup>1</sup>**Co-authors:** Aurel Radulescu <sup>1</sup>; Fumitoshi Kaneko <sup>2</sup>; Juergen Allgaier <sup>3</sup>; Koichi Ute <sup>4</sup>; Naoki Seto <sup>2</sup>; Shuma Sato <sup>2</sup>; Tobias Schrader <sup>1</sup>

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The development of combined techniques for measuring of the samples is generally desirable, because it allows following two or even more physical parameters on the same sample at the same time. In this regard, complementary time-resolved in-situ Fourier-transform infrared spectroscopy (FTIR) applied to small-angle neutron scattering (SANS) is useful for the investigation of structural changes in samples of interest, especially for monitoring the sample condition during the SANS study and for getting complementary structural information. Using this simultaneous measurement method (SANS/FTIR), we have recently investigated the distribution and the conformation of guest molecules (small oligomers, polyethylene glycol dimethyl ethers) inside the co-crystals of syndiotactic polystyrene when varying the temperature. In particular, we found that at low temperature close to the ambient one the guest molecules are distributed in both the crystalline and amorphous regions, while they are predominantly included in the amorphous region in the high-temperature case. Moreover, the 2-D SANS profiles and the FTIR spectra suggest that the small oligomers stored in the crystalline region adopt a stretched form perpendicular to the lamellae plane, while the oligomers residing in the amorphous region form agglomerates with a dense core and loose arms. In the last part of the contribution, the newly developed optical system will be presented together with the new variable temperature cell holder, that allowed to extend the IR measurement system combined with the SANS experiment to different kinds of specimen.

**Parallel Session / 15**

## **Structural characterization of new VDM-780 Ni-based superalloy by means of X-ray diffraction and Neutron diffraction**

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Ni-based superalloys based on the gamma/gamma' system are widely used for high temperature applications, as parts for jet engines, due to their good mechanical properties at high temperatures. In these materials, the austenitic matrix (gamma phase) is strengthened by intermetallic precipitates of Ni3Al (gamma', fcc L12 structure) and Ni3Nb (gamma'', bct DO22 structure) and it has been also observed the existence of co-precipitates of both phases with different morphologies (plate, needle, cube or disc shape). Other phases that can also be formed are Ni3Nb-based (delta, orthorhombic DOa structure) and Ni3Ti-based (eta, hexagonal DO24 structure). The existence of the different phases and the quantity and shape of the different precipitates and co-precipitates depend on composition, heat treatment and processing conditions. Especially, it is crucial to control the evolution of the different phases at high temperature in order to tailor the mechanical properties at high temperatures. In this work we present the first structural studies on VDM-780 superalloy. By means of neutron diffraction (ND) we have determined the different phases present in this material as prepared and the differences induced by two different aging conditions performed for setting up different microstructures. First measurements performed by X-ray diffraction (XRD) have shown, apart from the gamma matrix, the presence of the gamma' and delta (or eta) phases, depending on the temperature history. But XRD patterns do not allow to distinguish between the orthorhombic delta phase and the hexagonal eta phase. Both phases are usually present at the grain boundaries and the correct identification of them is crucial for the high temperature applications, as a small amount of delta phase is essential for a good workability of the alloy.

Neutrons are essential for the identification of the different phases as present important advantages compared to XRD. Due to the structural factors we expect higher number of reflections (as the one

of the eta phase at 35°) and with higher intensity, more evident at higher angles. Furthermore, we can choose higher wavelength of 2.4 Å with high penetration in the sample, while by measuring with XRD we have to select Mo (0.709 Å) in order to obtain some information from the interior of the material and not only from the surface. Last but not least neutrons allow to study a real bulk volume of the order of ~ 0.5 cm<sup>3</sup>.

**Parallel Session / 23**

## **Annealing of Diblock Copolymer Thin Films using Solvent Vapor Mixtures**

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**Co-authors:** Anatoly V. Berezkin <sup>1</sup>; Christine Papadakis <sup>1</sup>; Detlef-M. Smilgies <sup>2</sup>; Dorthe Posselt <sup>3</sup>

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Block copolymers self-assemble into nanostructures. Solvent vapor annealing (SVA) is an efficient method to improve the long-range order or to alter the morphology in block copolymer thin films.

In the present work, SVA is carried out on thin films from a polystyrene-*b*-poly(dimethyl siloxane) (PS-*b*-PDMS) diblock copolymer. For annealing, vapor mixtures of toluene and n-heptane were used, which are weakly selective for PS and highly selective for PDMS, respectively. The morphological changes were investigated by in-situ, real-time grazing-incidence small-angle X-ray scattering (GISAXS). Varying the vapor composition during the annealing cycle results in a lamellar morphology and cylinders with different orientations. Using the scattering contrast, the distribution of the two solvents in the microphase separated thin film can be determined. This information can be transferred to a phase diagram and be related to the observed morphologies during annealing.

The results show that solvent exchange during SVA gives control over the morphology, and that the scattering contrast can be used to track the distribution of two solvents in a phase separated thin film experimentally.

**Parallel Session / 84**

## **Polarized GISANS from lateral correlations of the spin misalignment**

**Author:** Emmanuel Kentzinger<sup>1</sup>

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In the past, we have simulated off-specular scattering of polarized neutrons from laterally patterned magnetic multilayers, based on the formalism developed by Boris Toperverg [1]. We would like to present how we used this theory so far [2].

[1] E. Kentzinger, U. Rücker, B. Toperverg, *Physica B* 335, 82 (2003)

[2] E. Kentzinger, U. Rücker, B. Toperverg, F. Ott and T. Brückel, *PRB* 77, 104435 (2008)

**Parallel Session / 94****HEIDI, instrument status and surprising phase transitions****Author:** Martin Meven<sup>None</sup>

The single crystal diffractometer HEIDI is jointly operated by RWTH Aachen, Institut für Kristallographie and the Jülich Centre for Neutron Science (JCNS). Using the hot source of FRM II the instrument covers a range of wavelengths between 1.17 Å down to 0.56 Å to study chemical and magnetic structures with high resolution (and large Q range respectively) using unpolarized neutrons. The talk will give an overview of the instrument including the current status of the BMBF funded project to optimize measurements on single crystal samples in the sub-millimeter range and first experimental results using the high temperature mirror furnace with gas handling option. In addition, some very recent and surprising experimental results concerning the temperature T and time t dependent order-disorder of H bonds in a small molecule and the not so obvious T dependent behaviour of incommensurate superstructure reflections in a multiferroic compound are presented.

**Parallel Session / 11****Archaeometrical studies using PGAA and INAA****Author:** Christian Stieghorst<sup>1</sup>**Co-author:** Zsolt Revay<sup>1</sup> TUM / FRM II**Corresponding Author:** christian.stieghorst@frm2.tum.de

PGAA and INAA are ideally suited for a panoramic analysis of the elemental composition in various materials. A bundle of advantages make these two methods attractive for archaeometry and cultural heritage, for instance low-destructiveness, straightforward sample preparation and good detection limits for many elements. Due to the fact that PGAA and INAA are complementary for several elements, a combination of both methods makes sense for certain applications. We have the opportunity to perform additional INAA measurements subsequently after the PGAA irradiation in a separate low background chamber. At our instrument, archaeometrical and cultural heritage applications include provenance analysis of archaeological findings, conservation-restoration research and reverse engineering of ancient aqueduct systems. New instrument developments provide additional variety and flexibility in this field. The presentation will give an overview about the current projects and the new possibilities at the PGAA facility.

**Parallel Session / 17****In-situ neutron reflectivity investigations of D<sub>2</sub>O-H<sub>2</sub>O exchange kinetics in thermoresponsive PNIPAM based block copolymer thin films****Author:** Lucas Kreuzer<sup>1</sup>**Co-authors:** André Laschewsky<sup>2</sup>; Christine Papadakis<sup>3</sup>; Jean-Francois Moulin<sup>4</sup>; Kun Wang<sup>5</sup>; Nuri Hohn<sup>5</sup>; Peter Müller-Buschbaum<sup>5</sup>; Tobias Widmann<sup>5</sup><sup>1</sup> TU München, Physik-Department, Fachgebiet Physik weicher Materie/ Lehrstuhl für Funktionelle Materialien, James-Frank-Str. 1, 85748 Garching<sup>2</sup> Universität Potsdam, Institut für Chemie<sup>3</sup> Technische Universität München, E13



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Responsive polymers, especially in thin film morphology, are of great interest for a wide variety of applications where a strong change of volume is desired even for small changes of an external stimulus such as temperature. In this context the most prominent representative is poly(N isopropylacrylamide) (PNIPAM). We study a new block copolymer which comprises a PNIPAM block and a poly(sulfobetaine) (PSB) block. Thin films are prepared by spin coating on silicon substrates. We have followed the swelling of such films in water vapor atmosphere and found signature of H<sub>2</sub>O - D<sub>2</sub>O exchange in FT-IR data. We use neutron reflectivity to study the swelling behavior and the H<sub>2</sub>O - D<sub>2</sub>O exchange of PNIPAM-b-PSB films in more detail. In-situ neutron reflectometry enables to follow the kinetics and determine the underlying fundamental processes.

**Parallel Session / 21**

## **Diffusion kinetics of H<sub>2</sub>O and D<sub>2</sub>O in cross-linked PNIPAM microgel thin films followed with in-situ neutron reflectivity**

**Author:** Tobias Widmann<sup>1</sup>

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Strong volume shifts of polymer thin films due to small modifications of an external stimulus like temperature are desired for a number of applications such as thermoresponsive nanoswitches or drug delivery in medicine. In this context the polymer which received most attention so far is poly(N-isopropylacrylamide), PNIPAM. The volume shift arises due to the collapse transition of the polymer at a lower critical solution temperature (LCST) which manifests in a swelling or deswelling of the polymer with water from its surroundings. To further our understanding of the kinetics of water uptake, release and exchange and the induced changes of the polymer properties, microgel thin films from a PNIPAM homopolymer with varying amounts of N,N'-Methylenebisacrylamide cross-linkers are prepared. In-situ neutron reflectometry in time of flight (TOF) mode is used to investigate the uptake and exchange kinetics of H<sub>2</sub>O with D<sub>2</sub>O and vice-versa for these films at temperatures below the LCST of PNIPAM.

**Parallel Session / 51**

## **Investigation of ordering and disordering of $\beta/\beta_0$ -phase in $\gamma$ -TiAl alloys by neutron diffraction**

**Author:** Victoria Kononikhina<sup>1</sup>

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$\gamma$ -TiAl alloys are attractive materials for structural high temperature applications due to their high specific tensile and creep strength. Nevertheless, their wider application is still hampered by the difficulties involved with TiAl processing and by the limited understanding how ductility and damage tolerance of the material during service is influenced by microstructure and phase constituents. For both aspects the body centered cubic  $\beta$  phase and its ordered low temperature  $\beta_0$  variant are of importance.  $\beta$  phase improves hot workability of the  $\gamma$ -TiAl alloys, while the ordered  $\beta_0$  phase is said to embrittle the material at service temperature and to reduce the creep strength. A better knowledge about the ordering and disordering process of  $\beta/\beta_0$  phase will widen the possibilities for a better microstructural control.

Neutron and synchrotron radiation are widely used for performing in-situ measurements during heating and cooling in  $\gamma$ -TiAl alloys. While synchrotron radiation is well suited for relatively fast measurements of the phase constitution over wide temperature ranges, the neutron measurements have an advantage for the investigation of the  $\beta/\beta_0$  phase ordering/disordering transformation. This is due to the fact that the scattering length of Ti and Al are almost equal in modulus but of opposite sign. This difference causes a high intensity of the ordered  $\beta_0$  super-lattice reflections by neutrons in comparison to the fundamental reflections of ordered and disordered phase. In-situ neutron measurements on this order/disorder transition using the materials science diffractometer STRESS-SPEC at FRM II in Garching, Germany have been performed in the current study. Three binary and 5 ternary  $\gamma$ -TiAl alloys with nominal composition Ti-(39, 42, 45 at %)Al and Ti-42Al-2X, (X=Fe, Cr, Mo, Nb, Ta) were investigated. For the heat treatments a vacuum high temperature furnace was used. The samples were stepwise heated in a temperature range from 1100°C up to 1440°C. A heating ramp of 20 °C/min was used. Diffraction patterns were extracted using the program STeCa and quantitative phase analysis was performed in MAUD software. As a result three samples, with 2 at.% of Fe, Mo and Cr, show a superlattice  $\beta_0$ -(100) peak in the three phase field  $\beta_0+\alpha_2+\gamma$ . Five samples including all binary Ti-Al based compositions show no  $\beta_0$  phase at all. At temperatures above 1300 °C no ordered  $\beta_0$  phase appeared even in the high temperature two phase region  $\beta+\alpha$ . Mo additions shift the  $\beta_0\leftrightarrow\beta$  transformation to higher temperatures. In the talk more results and details of neutron measurements will be shown.

**Parallel Session / 90**

## **Lithium Distribution inside Li-Ion-Batteries, effect of fatigue/aging**

**Author:** Martin Muehlbauer<sup>None</sup>

Lithium-ion batteries are part of our everyday life powering innumerable devices. Especially lately the number of applications related to electromobility and energy storage is increasing. Besides higher energy/power density and rate capability this calls for further improvements the life span of Li-ion cells. There are still some processes inside lithium-ion batteries that are not understood completely. Therefore, single cells or even integrated batteries have to be investigated under real operating conditions. Neutrons offer a capability to conduct in operando investigations on standard size Li-ion cells making it possible to follow structural changes, phase transitions or cation exchange reactions even under different environmental conditions [1,2]. The homogeneity of the lithiation states inside different Li-ion cells has been determined by spatially resolved neutron diffraction [3]. Recent studies have shown that the observed inhomogeneity of the lithium concentration is dependent on fatigue and aging [4].

**Keywords:** Li-ion batteries, fatigue, neutron, diffraction

### **References**

- [1] A. Senyshyn, M.J. Mühlbauer, O. Dolotko, H. Ehrenberg., Journal of Power Sources 282 235-240 (2015).
- [2] O. Dolotko, A. Senyshyn, M.J. Mühlbauer, K. Nikolowski, H. Ehrenberg, Journal of Power Sources, 245 197-203 (2014).

[3] A. Senyshyn, M.J. Mühlbauer, O. Dolotko, M. Hofmann, H. Ehrenberg, *Nature Scientific Reports*, 5, 18380 (2015), doi: 10.1038/srep18380.

[4] M.J. Mühlbauer, O. Dolotko, M. Hofmann, H. Ehrenberg, A. Senyshyn, *Journal of Power Sources*, 348 145-149 (2017).

## Parallel Session / 12

# Interfacial properties of NiO/Fe/FePt and Fe/NiO/FePt trilayers probed by x-ray and neutron reflectivity

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Different combinations of ferromagnetic (FM) layers and antiferromagnetic (AFM) layers give rise to many exciting effects such as exchange bias [1] and exchange spring [2, 3]. It is well known that these effects are mainly governed by the proximity of FM/FM or FM/AFM or AFM/AFM interfaces. Moreover, different combinations of FM and AFM materials in the form of trilayers allow the co-existence of (a) the exchange spring and exchange bias effect together and (b) simultaneous in-plane and out of plane exchange bias. In this context, we have deposited epitaxial NiO/Fe/FePt and Fe/NiO/FePt trilayers using molecular beam epitaxy (MBE) method and have studied growth, structure and the interface magnetism.

In order to study the interfacial properties of NiO/Fe/FePt and Fe/NiO/FePt trilayers, ex-situ x-ray reflectivity (XRR) and polarised neutron reflectivity (PNR) measurements have been performed. XRR and PNR results indicate that growth of NiO on Fe forms a complex structure of Fe-O at the interface as a result exchange coupling is suppressed between Fe and NiO. On the other hand deposition of Fe layer on NiO layer results in reduced magnetic moment in Fe layer and shows significantly high spin flip reflectivity in PNR measurement. These observations may be attributed to interlayer coupling between Fe and FePt layer. In summary, it was found that interfacial proximity of oxide AFM is chemically reactive. The obtained results are very helpful in tailoring the coupled FM and oxide AFM systems.

1. J. Nogues et al., *J. Magn. Magn. Mater.* 192, 203 (1999).
2. R. Skomski et al., *Phys. Rev. B* 48, 15812 (1993).
3. T. Jungwirth et al, *Nat. Nanotech.* 11, 231 (2016).

## Summary:

Different combinations of ferromagnetic (FM) layers and antiferromagnetic (AFM) layers give rise to many exciting effects such as exchange bias [1] and exchange spring [2, 3]. It is well known that these effects are mainly governed by the proximity of FM/FM or FM/AFM or AFM/AFM interfaces. In this context we have studied the interfacial properties of NiO/Fe/FePt and Fe/NiO/FePt trilayers using x-ray and polarised neutron reflectivity.

**Parallel Session / 9****Structure visualization for microgel polymer systems adsorbed on a solid substrate****Author:** Tetyana Kyrey<sup>1</sup>**Co-authors:** Judith Witte<sup>2</sup>; Marina Ganeva<sup>3</sup>; Olaf Holderer<sup>3</sup>; Stefan Wellert<sup>2</sup><sup>1</sup> JCNS at MLZ, Forschungszentrum Jülich GmbH, Stranski-Laboratorium, TU Berlin, 10623 Berlin<sup>2</sup> Stranski-Laboratorium, TU Berlin, 10623 Berlin<sup>3</sup> JCNS at MLZ, Forschungszentrum Jülich GmbH**Corresponding Author:** t.kyrey@tu-berlin.de

Nanostructures and nanoparticles are on the top of technique and biomedical application. A special class of such systems is the polymers adsorbed on a substrate. Confinement at the surface changes their physical and chemical properties with respect to a bulk system that open a new possibility for the usage in long-time biomedical applications also at body temperature. Formation of stimuli responsive surface structures using microgel particles as colloidal building blocks is an active field of research.

A variety of experimental methods such as static and dynamic light scattering, neutron scattering, nuclear magnetic resonance, etc.[1-3] were used for the characterization of the microgel bulk phase morphology, the internal network structure and the dynamics. The more complicated task is the investigation of systems adsorbed on a surface. Methods such as atomic force microscopy, grazing incidence small-angle neutron/X-ray scattering (GISANS/GISAXS) can reveal characteristic parameters of the studied systems. But the data analysis in this case is not a trivial task. Use of modern computer methods opens a new opportunity for visualization of the samples and their structures.

In our research we use the BornAgain[4] software package (actively developing at JCNS) to simulate and decode structure of poly(ethylene glycol)(PEG)-based microgel particles adsorbed on a Si substrate. The characteristic parameters of the system obtained from GISANS data are used for system simulation in BornAgain and at the same time the simulation results provide better understanding of the experimental results. This closed circle of simultaneous analysis of the real and virtual data makes it possible to obtain a model of the system and visualize the structure of the microgel particles.

1. Clara-Rahola, J.; Fernández-Nieves, A.; Sierra-Martín, B.; South, A. B.; Lyon, A. L.; Kohlbrecher, J.; Fernández-Barbero, A. Structural properties of thermoresponsive poly(N-isopropylacrylamide)-poly-(ethyleneglycol) microgels. *J. Chem. Phys.* 2012, 136, 214903.
2. Crowther, H. M.; Saunders, B. R.; Mears, S. J.; Cosgrove, T.; Vincent, B.; King, S. M.; Yu, G.-E. Poly(NIPAM) microgel particle deswelling: a light scattering and small-angle neutron scattering study. *Colloids Surf., A* 1999, 152, 327–333.
3. Sierra-Martín, B.; Romero-Cano, M. S.; Cosgrove, T.; Vincent, B.; Fernández-Barbero, A. Solvent relaxation of swelling PNIPAM microgels by NMR. *Colloids Surf., A* 2005, 270–271, 296–300.
4. Burle, J., Durniak, C., Fisher, J. M., Ganeva, M., Pospelov, G., Van Herck, W., Wuttke, J., BornAgain - Software for simulating and fitting X-ray and neutron small-angle scattering at grazing incidence, version 1.7.1, <http://www.bornagainproject.org> (2013-2017)

**Parallel Session / 7****Inner dynamics in adsorbed microgels****Author:** Judith Witte<sup>1</sup>**Co-authors:** Olaf Holderer ; Stefan Wellert<sup>1</sup>; Tetyana Kyrey<sup>2</sup>

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The physical properties of stimuli-responsive microgels and polymer brushes still attract great interest in basic research and lead to a lively discussion of potential technical applications. Prominent examples are systems, which undergo a temperature induced phase transition as the sample temperature changes.

Microgel particles can be easily organized as ultra-thin films at solid surfaces, e.g. silicon single crystal surfaces. This leads to changes in the swelling behavior and shifts the LCST with respect to the bulk phase. These findings raise the question how the interactions with the solid surface affect the inner structure and dynamics of the adsorbed microgel particles. Here, we focus on neutron spin echo spectroscopy (NSE) experiments in transmission and reflection geometry. Up to now, only few publications report NSE experiments on the inner dynamics in microgels. NSE provides access to the dynamics in the ns to ms time range on nanoscopic length scales. The microgel layers were for the first time studied by NSE under grazing incidence (GINSES) which uses evanescently scattered neutrons and therefore probes the near-surface dynamics in the adsorbed microgel films.

In particular, we discuss the inner dynamics in different types of microgels in bulk and in thin films adsorbed onto silicon surfaces.

**Evening talk / 65**

## Dust from „recent“ Supernovae, just around the corner

**Author:** Thomas Faestermann<sup>1</sup>

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Stars with a mass larger than about ten times that of our Sun usually end in Supernova-explosions. Most of the material synthesized in earlier burning stages or during the explosion is expelled and travelling through space. If such an explosion happens close to the solar system also radionuclides will be deposited on Earth and other Solar system bodies. At the MLL tandem accelerator in Garching we are using the most sensitive technique for the detection of long-lived radionuclides, accelerator mass spectrometry, to determine minute quantities of the long-lived radioisotope <sup>60</sup>Fe (T<sub>1/2</sub> = 2.6 Myr). Already in 1999 we found an indication of an increased <sup>60</sup>Fe content in a deep-ocean crust. Five years later we reported a clear enhancement for a time period around 2 Myr ago in another slow-growing (3mm/Myr) crust. To obtain this <sup>60</sup>Fe signal with good time resolution we searched also in 1000 times faster growing sediments. Last year we could publish our finding in two sediment cores that the <sup>60</sup>Fe signal started about 2.7 Myr ago and lasted for about 1 Myr. Here we had made use of the fact that so-called magnetotactic bacteria live in sediments who build little magnets in their body from iron-oxide dissolved in the ocean water. By selectively leaching such magnetite from fossilized bacteria, the signal is not washed out by large grain iron-oxide dust, brought into the ocean by erosion. A few months earlier last year a competing group in Canberra, Australia, has also reported the <sup>60</sup>Fe peak in different sediments with about the same timing. In order to obtain a reliable estimate for the total fluence of <sup>60</sup>Fe that had reached the solar system, we searched also in Lunar samples provided by NASA, since on the moon there is no redistribution through atmosphere and ocean currents. Also here we find <sup>60</sup>Fe in samples down to about 20 cm depth. That is about the depth down to which the lunar surface is reworked by micrometeorites on a time scale of about 3 Myr.

In the meantime astrophysicists have even an idea in which group of young stars, about 300 light years from the sun, a number of Supernova explosions must have happened between 3 and 2 Myr ago which are thought to be the cause for the increase in <sup>60</sup>Fe concentrations. It is interesting to note that the geologists start a new epoch, the Pleistocene, exactly 2.588 Myr ago, in which the ice ages started and, in the development of the hominins, the genus homo appeared. However, we do not claim a causal connection.

**Parallel Session / 39**

## Self-Assembly of Diblock Polythiophene Polyelectrolytes for Organic Photovoltaic Devices

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The performance of organic photovoltaic devices (OPVs) depends critically on simultaneous control of the optoelectronic properties and nanoscale morphology of conjugated polyelectrolytes (CPEs).[1] Recently, self-assembly strategies have emerged as an elegant approach for the design and fabrication of reproducible nanoscale aggregates from CPE building blocks.[2] The challenge, however, is to determine the key structure-property relationships in these novel materials and demonstrate how structural order tailoring can be harnessed to deliver highly efficient OPVs.

Here we will demonstrate the solvent-mediated[3] (methanol, water and methanol/water mixtures), surfactant-mediated[4] (SDS, d25-SDS and PFOS) self-assembly of a series of amphiphilic diblock copolymers each containing a hydrophobic poly(3-hexylthiophene) (P3HT) block and a hydrophilic cationic P3HT block bearing different terminal ionic groups. Their optical properties and aggregate structures were studied in solution, and in subsequently prepared thin films, using photoluminescence, scattering and microscopic techniques. In particular, small-angle neutron scattering (SANS) was used to elucidate the nanoscale morphology and solvent content of the CPE and CPE-surfactant structures in solution. A variety of well-defined, solution-phase structures (*e.g.* rods, lamellar sheets) can be generated through careful modulation of the solvent polarity and surfactant charge ratio. In addition, direct comparison between the diblock copolymers and their analogous homopolymers has revealed the significance of the hydrophobic P3HT block in controlling aggregate morphology. Solvent- and surfactant-mediated self-assembly of all-conjugated block CPEs may therefore provide a simple inexpensive route for obtaining nanostructured active interfaces suitable for OPV devices.

### References

1. R. Noriega, J. Rivnay, K. Vandewal, F. P. V. Koch, N. Stingelin, P. Smith, M. F. Toney and A. Salleo, *Nat. Mater.*, 2013, **12**, 1038.
2. R. C. Evans, *J. Mater. Chem. C*, 2013, **1**, 4190.
3. M. Chevrier, J. E. Houston, J. Kesters, N. Van den Brande, A. E. Terry, S. Richeter, A. Mehdi, O. Coulembier, P. Dubois, R. Lazzaroni, B. Van Mele, W. Maes, R. C. Evans and S. Clément, *J. Mater. Chem. A*, 2015, **3**, 23905.
4. A. Thomas, J. E. Houston, N. Van den Brande, J. De Winter, M. Chevrier, R. K. Heenan, A. E. Terry, S. Richeter, A. Mehdi, B. Van Mele, P. Dubois, R. Lazzaroni, P. Gerbaux, R. C. Evans and S. Clément, *Polym. Chem.*, 2014, **5**, 3352.

Parallel Session / 96

## Diffraction Based Determination of Single Crystalline Elastic Constants on Polycrystalline Alloys

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The single crystalline elastic constants are essential for technical materials. For most of the engineering-alloys the fabrication of single-crystalline specimen is either difficult or even impossible and therefore the derivation of these constants is complicated.

Different diffraction techniques allow the investigation of poly-crystalline and multi-phase materials due to its outstanding possibility to visualize the different strains of all phases averaged over all orientations. This allows a type of reversal of the classical stress analysis with the single crystalline elastic constants as result.

As proof of principle the results of one- and two-phase steels are presented. Additionally the single crystalline elastic constants for different single- and multi-phase Ti alloys are discussed.

Parallel Session / 95

## Mapping of spin and lattice excitations in the magnetocaloric compound MnFe<sub>4</sub>Si<sub>3</sub>

Author: Kirill Nemkovskiy<sup>None</sup>

One way for saving energy in daily life is using the magnetocaloric effect (MCE), i.e. the change of magnetic entropy and adiabatic temperature following a change in an applied magnetic field. The ferromagnetic compound MnFe<sub>4</sub>Si<sub>3</sub> is a promising candidate for applications. It has a magnetic phase transition in the range of 300 K and shows a moderate MCE of 2.9 J/kg K at a reasonable magnetic field change from 0 T to 2 T. In order to understand the fundamental driving forces of the MCE in this material a study of magnetism, lattice dynamics and their interaction is necessary. We present the results of mapping of the lattice and magnetic excitations below and above ordering temperature. The measurements have been performed at the time-of-flight spectrometer 4SEASONS at J-PARC at 7.5K and 360K. The collected data are complementary to the information on phonon and magnon dispersion obtained from triple-axis spectrometer. In particular they give us further insight in the excitation spectrum and provide more details for the map of the paramagnetic scattering above  $T_C$ .

Parallel Session / 2

## Combining the strengths of Neutrons and Molecular dynamics for the study of bio-membranes

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Neutron reflectometry is one of the most powerful methods for investigating the structure of model lipid membranes. These model systems are more easily prepared and experimentally controlled than natural lipid membranes, which are an important integral part of animal and plant cells. In the present work we combine measurements of supported lipid membranes (SLBs) at the MARIA neutron reflectometer and coarse-grained molecular dynamics simulations using the MARTINI force field, for the precise characterization of SLBs at the sub-nanometer scale. The proposed methodology delivers more precise results and should pave the way for studying membranes of a more complex nature, having in mind experiments where membranes interact with bio-molecules, e.g. proteins, small peptides, and nanoparticles that are candidates for drug delivery applications.

Parallel Session / 97

## Discussion: Future of neutron structure determination

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Diffraction methods as tools for structure determination undergo a permanent development during the last century. Being perfectly parameterized technique and equipped by a powerful mathematical

and crystallographic apparatus, the diffraction methods provide unique information about the crystal and magnetic order and disorder on the atomic scale, as well about microstructure (both averaged in time and space). Diffractometry is considered nowadays as a routine analytical technique, but is this really true?

In the frame of the current session it is proposed to discuss the challenges which the neutron-based methods of structure determination may face in the future, especially taking into account rapid development of photon and electron scattering techniques.

**Parallel Session / 92**

## UGe2

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**Parallel Session / 19**

## Printed nanostructured polymer films embedded with magnetic nanoparticles

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Nanostructured polymer films containing magnetic nanoparticles (NPs) are promising materials due to their potential applications in the areas of high-density storage and magnetic sensors. Owing to the advantages, like large-scale production and energy saving, printing techniques were employed to fabricate hybrid films composed of maghemite NPs and PS-*b*-PMMA diblock copolymer (DBC). External magnetic fields were applied during the printing process to guide the NPs within the polymer matrix. The mesoscopic structure of PS-coated maghemite NPs within the DBC films was investigated as a function of the NP concentration using optical microscopy, AFM, SEM and GISAXS. The PS-coated NPs were selectively dispersed in the PS domains of the lamella-structured hybrid films. At high NP concentrations, the coalescence of NPs into large micro-sized metal-oxide wires was observed. The superparamagnetic behavior of the hybrid film was proved using a superconducting quantum interference device magnetometer.

### Summary:

By employing printing technique, thin magnetic films were successfully prepared based on diblock copolymer and magnetic  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub> particles. Via joint utilization of external magnetic field and printing technique, homo-geneous hybrid films with highly oriented magnetic nanostructures were prepared. These obtained magnetic films were investigated in both real space and reciprocal space. At macroscale, NPs self-assembled into highly oriented wires in polymer matrices with controlled widths and separation distances, which endows the hybrid films with magnetic anisotropy. At nanoscale, NPs grafted with PS chains were selectively incorporated and dispersed inside PS domains at low NP concentrations. As concentration increased, NPs assembled into nanosized cluster without losing the superpara-magnetic



property. Due to the high PS weight fraction in the diblock copolymer and microphase separation, a high density of magnetic nanostructures containing dispersed single magnetic NPs or nanosized NP clusters were achieved.

**Parallel Session / 34**

## **Flexible nanoporous titania/silica hybrid electrodes for lithium-ion batteries**

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Stable and safe lithium-ion batteries with high capacity are a current research area of great importance due to its applications in electric vehicles and flexible portable electric devices. Using the sol-gel method, TiO<sub>2</sub>/SiO<sub>2</sub> nanostructured hybrid electrodes were prepared using polystyrene-block-polyethylene oxide (PS-b-PEO) diblock copolymer as a guiding template. The current study showed the possibility to fine tune the TiO<sub>2</sub>/SiO<sub>2</sub> nanoporous electrode morphologies, especially both pore size and pore-to-pore distance. An experimental method to achieve extremely flexible with additional very high flexural endurance freestanding nanoporous hybrid thin film electrodes is described. Thin film of gold metal current collector was further deposited on the TiO<sub>2</sub>/SiO<sub>2</sub> nanoporous hybrid thin film. In situ grazing incidence small angle X-ray scattering (GISAXS) was employed to investigate the nanoscale structure of the metal contact film during metal deposition in a real-time mode. The GISAXS 2D patterns showed distorted powder-like Debye-Scherrer (DS) elliptic half rings which are attributed to the intrinsic hexagonally ordered nanopores arrangement in the TiO<sub>2</sub>/SiO<sub>2</sub> hybrid electrodes. The real time GISAXS study proves a preferential deposition of gold in the near surface pores, forming vertically oriented gold metal nanorods. From the current results, a possible future implementation of these free-standing anodes in flexible lithium-ion battery applications is potentially foreseen.

**Parallel Session / 93**

**TBD**

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**Parallel Session / 14**

## **Aging in Li-ion cells examined with neutron diffraction, electrochemical analysis and physico-chemical modeling**

**Author:** Neelima Paul<sup>None</sup>

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Aging in 18650-type NMC/C cells, produced under commercial conditions, has been experimentally characterized by *in situ* neutron diffraction and electrochemical analysis. The comparison of discharge capacity of an uncycled cell with that of a cell which has undergone 1000 cycles under ambient conditions, shows a capacity fade of 21% on cycling. Neutron diffraction of the uncycled and cycled cell, in their charged state, shows a reduction in the weight fraction of the LiC6 phase as well as an increase in the weight fraction of the LiC12 phase on aging, from which a cyclable lithium loss corresponding to a capacity loss of 23% can be extracted. In spite of this large capacity loss, both the anode and cathode materials are scrutinized to be structural stable and no evidence of active material loss is observed in the evaluation of these neutron diffractograms. Thus, other aging mechanisms could be excluded from these measurements, within the experimental accuracy of the method. A physico-chemical aging model, which attributes capacity fade solely to loss of cyclable lithium in the growth of a continuous solid electrolyte interface (SEI) film on the anode surface, is developed to reconsider aging contributions. This model is first validated by reproducing the obtained experimental aging and voltage profiles which confirms cyclable lithium loss into SEI layer growth as the sole aging mechanism. It also predicts a reduction or shift in  $x = 0:18$  for anode stoichiometry  $\text{Li}_x\text{C}_6$  ( $0 < x < 1$ ), for the cycled cell. This is in good agreement with the anode stoichiometry shift of  $x = 0:20$  for the cycled cell as obtained from neutron diffraction experiments.

Parallel Session / 42

## Morphological investigations on thermoelectric thin films based on a PEDOT:PSS/Si-NP nano composite using tender x-ray scattering

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Parallel Session / 62

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Parallel Session / 67

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Parallel Session / 1

## **Novel Reflection High-energy Positron Diffractometer at NEPO-MUC**

**Authors:** Christoph Hugenschmidt<sup>1</sup>; Matthias Dodenhöft<sup>1</sup>

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The precise knowledge of the surface structure is essential to understand e.g. chemical reactions, optimize catalytic techniques or develop nanoelectronic devices. It has been shown that Total Reflection High-energy Positron Diffraction (TRHEPD) is a powerful tool to determine the positions of adatoms and topmost layers of reconstructed surfaces with unprecedented accuracy. In contrast to the application of high-energy electrons in RHEED, positrons exhibit the phenomenon of total reflection at surfaces due to their positive scattering potential. For this reason, TRHEPD shows outstanding surface sensitivity and thus provides information, which cannot be obtained with other techniques such as RHEED or SXRD.

In order to enable TRHEPD experiments, we intend to set up a new positron diffractometer coupled to the high-intensity positron beam NEPOMUC. Beside the identification of surface structures, this setup will also enable us to investigate surface related phenomena such as phase transitions, reconstruction or surface melting. This project is supported by the BMBF (funding number 05K16WO7).

**Parallel Session / 58**

**TBD**

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**Parallel Session / 60**

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**Parallel Session / 61**

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**Parallel Session / 8**

## **Comparison of heavy ion and in-pile irradiation induced IDL growth in UMo/Al fuels**

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Heavy ion irradiation (out-of-pile irradiation) has been used to simulate uranium fission damage in monolithic U-Mo/Al layer systems on account of its time, simplified handling and cost savings compared to in-pile irradiation. After irradiation an amorphous layer (IDL) resulting from the inter-diffusion effect is generated in the bilayer system, which has a similar structure as the one produced during in-pile irradiation. By studying of the IDL behaviour in U-Mo/Al fuels with different analytical methods, a comparison with in-pile irradiation regarding IDL growth is presented and the reliability of this technique is verified.

**Plenary Session / 77**

## **The Nobel Prize in Physics 2016 : Neutrons and Topology**

**Author:** Sebastian Muehlbauer<sup>None</sup>

The Nobel Prize in Physics 2016 was awarded with one half to David J. Thouless, and the other half to F. Duncan M. Haldane and J. Michael Kosterlitz “for theoretical discoveries of topological phase transitions and topological phases of matter”.

In my talk I will explain the theoretical concepts awarded with the Nobel Prize and their experimental realizations with a strong focus on the neutron scattering world: Typical examples include (i) low dimensional quantum magnets where a magnetic field induced long range order transition of a gapped 1D spin chain can be described akin to a Bose Einstein Condensation of magnons. (ii) Vortex states in 2D spin systems (Kosterlitz-Thouless transition). (iii) The particle properties of Skyrmions.

**Plenary Session / 64**

## **Structure in Geosciences**

**Author:** Nicolas Walte<sup>None</sup>

Most material of the Earth is situated in its deep interior and therefore subject to pressure and temperature conditions that are conventionally considered extreme. In addition, this material is largely inaccessible to direct observation; hence, knowledge of the interior structure of the Earth stems from a combination of geophysical probing methods such as the travel times of seismic waves and experimental investigations that simulate the conditions in the deep Earth. The past decades have shown that the distinctly layered structure of the mantle can be linked to phase transitions that the major constituents undergo at various depths. The talk will trace the structural changes of a few key mineral phases from crust to core, explain how their crystallography controls the evolution and current shape of the Earth, and highlight the role of neutron research for understanding global processes such as transport and storage of water in the Earth's mantle.

66

## **Departure**

72

## **Overview fundamental physics**